

SWEPT FREQUENCY FLUOROMETER

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims benefit to provisional patent application serial no. 63/027,587 (911-023.9-1-1/N-YSI-0045US01), filed 20 May 2020; 63/028,013 (911-023.010-1-1/N-YSI-0046US02), filed 21 May 2020, and 63/028,723 (911-023.011-1-1/N-YSI-0047US02), filed 22 May 2020, which are all incorporated by reference in its entirety.

BACKGROUND OF THE INVENTION

1. Field of Invention

10 This invention relates to a fluorometer for identifying species in a liquid, including where the liquid contains overlapping species.

2. Description of Related Art

In general, traditional fluorescence sensing techniques suffer from spectrally broad features often yielding ambiguous identification of the water species, especially when the fluorescence signatures of multiple species overlap.

In particular, traditional (single channel) fluorometers typically consist of a single excitation light source (at specified optical wavelength) used to optically excite the water parameter of interest and re-emit optical light (at a longer optical wavelength) specific to the water parameter of interest. Such sensors often utilize lock-in detection which selectively measures sinusoidal signals at a fixed (in-band) frequency, and reject signals that possess other frequencies (out-of-band frequencies).

There is a need in the art for a better fluorometer, e.g., for identifying species in a liquid that contains overlapping species.

SUMMARY OF THE INVENTION

In summary, the sensor according to the present invention differs from traditional fluorometers in that the lock-in frequency for this sensor is to be “swept”,
5 i.e., gradually increased from some initial modulation frequency, f_i , to some final modulation frequency, f_f . Every fluorescence species possesses its own distinct fluorescence “lifetime” (FLT) in which an excited fluorophore (excited by the excitation optical wavelength) remains in an excited state for a finite amount of time e.g., the lifetime [sec.], before returning to the ground state accompanied by
10 subsequent emission. As the signal’s modulation frequency is swept through the characteristic frequency of the species, $f = (1/\text{lifetime})$ [Hz], the phase of the signal undergoes an overall relative phase shift of 90 degrees in addition to a decrease in signal amplitude. The midpoint of the relative phase transition (45 degrees) precisely corresponds to the characteristic/lifetime frequency of the fluorescence
15 species. In short, if there is uncertainty in the identity of overlapping fluorescence species, then knowledge of the lifetime can further delineate between the two species.

In effect, fluorescence lifetime (through swept excitation frequency) promises another dimension of information, adding depth to the “fingerprint” of the water body.

20 The fluorometer according to the present invention will measure: $E_x/E_m +$ Fluorescence lifetime for providing an enhanced detection technique.

Moreover, one key to this invention pertains specifically to the opto-mechanical configuration which utilizes a wide linear array along the length of the quasi-collimated light.

The design herein is compatible with non-intensity-based determinations of turbidity.

By way of example, the present invention has applications in environmental water quality monitoring

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Specific Embodiments

By way of example, and according to some embodiments, the present invention may include, or take the form of, apparatus featuring a signal processor or processing module configured to:

10 receive signaling containing information about reflected light off one or more fluorescence species-of-interest in a liquid sample that is swept with light having a variable frequency range, the information including a characteristic optical frequency corresponding to a fluorescence species-of-interest in the liquid, and a characteristic/lifetime optical frequency
15 corresponding to a distinct fluorescence lifetime in which the fluorescence species-of-interest remains in an excited state; and

 provide corresponding signaling containing information about an identity of the fluorescence species-of-interest detected and distinguished from overlapping fluorescence species in the liquid using the
20 characteristic/lifetime optical frequency, based upon the signaling received.

The apparatus may include one or more of the following additional features:

The apparatus may include a light sensor configured to sense the light across the variable frequency range, and provide the signaling received by the signal processor or processing module.

The light sensor may be a linear sensor array configured to sense the light across the variable frequency range along the length of a light source providing the light.

The apparatus may include a light source configured to sweep excitation light
5 having an excitation optical wavelength across the variable frequency range to excite the one or more fluorescence species-of-interest.

The light source may be a swept-frequency light source, including a quasi-collimated light source.

The variable frequency range may include a lock-in frequency that is swept by
10 gradually increasing the excitation light from an initial modulation frequency f_i to a final modulation frequency f_f .

The variable frequency range may include a mid-point frequency that corresponds to the characteristic/lifetime optical frequency.

The apparatus may include, or take the form of, a swept frequency
15 fluorometer.

A Swept Frequency Fluorometer

By way of further example, and according to some embodiments, the present invention may take the form of a swept frequency fluorometer featuring a light
20 source, a light sensor and a signal processor or processing module.

The light source may be configured to provide excitation light on a liquid sample having one or more fluorescence species-of-interest, the excitation light having a variable frequency range with an initial frequency f_i and a final frequency of f_f .

The light sensor may be configured to sense reflected light off the one or more fluorescence species-of-interest in the liquid sample and provide signaling containing information about the reflected light off the one or more fluorescence species-of-interest in the liquid sample that is swept with the excitation light having
5 the variable frequency range, the information including a characteristic optical frequency corresponding to a fluorescence species-of-interest in the liquid, and a characteristic/lifetime optical frequency corresponding to a distinct fluorescence lifetime in which the fluorescence species-of-interest remains in an excited state.

The signal processor or processing module may be configured to:
10 receive the signaling, and
provide corresponding signaling containing information about an identity of the fluorescence species-of-interest detected and distinguished from overlapping fluorescence species in the liquid using the characteristic/lifetime optical frequency, based upon the signaling received
15 The swept frequency fluorometer may also include one or more of the features set forth above.

The Method

By way of still further example, and according to some embodiments, the
20 present invention may include a method featuring:
receiving, with a signal processor or processing module, signaling containing information about reflected light off one or more fluorescence species-of-interest in a liquid sample that is swept with light having a variable frequency range, the information including a characteristic optical frequency corresponding to a
25 fluorescence species-of-interest in the liquid, and a characteristic/lifetime optical

frequency corresponding to a distinct fluorescence lifetime in which the fluorescence species-of-interest remains in an excited state; and

providing, with the signal processor or processing module, corresponding signaling containing information about an identity of the fluorescence species-of-interest detected and distinguished from overlapping fluorescence species in the liquid using the characteristic/lifetime optical frequency, based upon the signaling received.

The method may also include one or more of the features set forth above.

10 Computer-readable Storage Medium

By way of still further example, and according to some embodiments of the present invention, the present invention may also take the form of a computer-readable storage medium having computer-executable components for performing the steps of the aforementioned method. The computer-readable storage medium may also include one or more of the features set forth above.

BRIEF DESCRIPTION OF THE DRAWING

The drawing, which are not necessarily drawn to scale, includes Figures 1 - 5, as follows:

20 Figure 1 is a graph of excitation, emission and fluorescence lifetime, and provides a concept plot of the fluorometer according to the present invention, in which three different, but overlapping species can be measured within the same Ex/Em band pass region. Traditional fluorometers do not have the ability to distinguish between the three species, but with the rendering of fluorescence lifetime, a distinction can be made according to the present invention.

Figure 2 includes Figures 2A and 2B and is an Excitation Emission Matrix (EEM) plot of two overlapping species (TrisBipy Ru (II) and Pt Porphyrin). For clarity, the plots are stacked (not overlaid). The axes and scale are the same in both frames.

5 Figure 3 is a graph or plot of relative phase angle (Deg.) vs. swept modulation excitation frequency (Hz) of the respective species (TrisBipy Ru (II) and Pt Porphyrin), e.g., showing how the phase responses are completely distinguishable though their respective EEM signatures occupy the same region of the EEM chart, causing ambiguity.

10 Figure 4 is a block diagram of a swept frequency fluorometer, e.g., having a light source, a light sensor and a signal processor or processing module for performing signal processing functionality, according to some embodiments of the present invention.

 Figure 5 is a diagram of the light sensor in the form of a linear sensor array,
15 e.g., having rows and columns of optical elements, according to some embodiments of the present invention.

 To reduce clutter in the drawing, each Figure in the drawing does not necessarily include every reference label for every element shown therein.

20 DETAILED DESCRIPTION OF BEST MODE OF THE INVENTION

 Figure 4 shows apparatus 10, including a swept frequency fluorometer, according to the present invention, e.g., having a light source 20 such as quasi-collimated light source, a light sensor 30 such as a linear sensor array, and a signal processor or processing module 40.

25 The light source 20 may be configured to provide light on a liquid sample having one or more fluorescence species-of-interest, the light having a variable

frequency range with an initial frequency f_i and a final frequency f_f . According to some embodiments, the light source 20 may be configured to respond to a light source control signal, e.g., provided by the signal processor or processing module 40 and provide the light having the variable frequency range.

5 The light sensor 30 may be configured to sense reflected light off the fluorescence species-of-interest in the liquid sample and provide signaling containing information about the reflected light off the one or more fluorescence species-of-interest in the liquid sample that is swept with the light having the variable frequency range, the information including a characteristic optical frequency corresponding to a
10 fluorescence species-of-interest in the liquid, and a characteristic/lifetime optical frequency corresponding to a distinct fluorescence lifetime in which the fluorescence species-of-interest remains in an excited state. According to some embodiments, the light sensor 30 may be configured to respond to a light sensor control signal, e.g., provided by the signal processor or processing module 40 and sense the
15 reflected light.

 The signal processor or processing module 40 may be configured to
 receive the signaling; and
 provide corresponding signaling containing information about an
 identity of the fluorescence species-of-interest detected and distinguished
20 from overlapping fluorescence species in the liquid using the
 characteristic/lifetime optical frequency, based upon the signaling received.

According to some embodiments, the signal processor or processing module 40 may be configured to provide the light source control signal and/or the light sensor control signal, e.g., to the light source 20 and/or light sensor 30.

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The Light Source 20

By way of example, the light source 20 may be configured to provide the light, including quasi-collimated light, along a corresponding length of the linear sensor array 30, e.g., as shown in Figure 5, through a liquid sample arranged in relation to the light source 20 and the linear sensor array 30 so as to reflect the light off the one or more fluorescence species-of-interest in the liquid sample being monitored or tested onto the linear sensor array 30.

As a person skilled in the art would appreciate, quasi-collimated light sources are known in the art, and the scope of the invention is not intended to be limited to any particular type or kind thereof either now known or later developed in the future.

The Linear Sensor Array 30

By way of example, the linear sensor array 30 may include, e.g., a linear photodiode array, a linear charge-coupled device (CCD) array, or a linear CMOS array. In particular, the linear sensor array 30 may include a two-dimensional array of rows and columns of optical elements (r1, c1; r1, c2; r1, c3; r1, c4; r1, c5; r1, c6; r1, c7; r1, c8; ...; r1, cn; r2, c1; r2, c2; r2, c3; r2, c4; r2, c5; r2, c6; r2, c7; r2, c8; ...; r2, cn; r3, c1; r3, c2; r3, c3; r3, c4; r3, c5; r3, c6; r3, c7; r3, c8; ...; r3, cn; ...; rn, c1; rn, c2; rn, c3; rn, c4; rn, c5; rn, c6; rn, c7; rn, c8; ...; rn, cn) like that shown in Figure 5, e.g., that are individually addressable. Linear sensor arrays are known in the art, and the scope of the invention is not intended to be limited to any particular type or kind thereof either now known or later developed in the future.

By way of example, linear sensors arrays are disclosed in the following US Patent nos. 9,020,202; 8,022,349; 7,956,341; 7,040,538; 5,252,818; and 4,193,057, which are all hereby incorporated by reference.

The Signal Processor or Processing Module 40

By way of example, the signal processor or processing module 40 may be configured to determine the one or more fluorescence species-of-interest based upon the frequencies so determined, and then determine the concentration of turbidity of the liquid, based upon the same. Techniques for processing signaling containing information about sensed optical frequencies, e.g., in relation to the concentration of turbidity in the liquid, are known in the art, and the scope of the invention is not intended to be limited to any particular type or kind thereof either now known or later developed in the future.

Implementation of Signal Processing Functionality

By way of example, the functionality of the signal processor or processing module 40 may be implemented using hardware, software, firmware, or a combination thereof. In a typical software implementation, the signal processor 40 would include one or more microprocessor-based architectures having, e. g., at least one signal processor or microprocessor. One skilled in the art would be able to program with suitable program code such a microcontroller-based, or microprocessor-based, implementation to perform the signal processing functionality disclosed herein without undue experimentation.

The scope of the invention is not intended to be limited to any particular implementation using technology either now known or later developed in the future. The scope of the invention is intended to include implementing the functionality of the signal processor(s) as stand-alone processor, signal processor, or signal

processor module, as well as separate processor or processor modules, as well as some combination thereof.

By way of example, the apparatus 10 may also include, e.g., other signal processor circuits or components generally indicated 50, including random access
5 memory or memory module (RAM) and/or read only memory (ROM), input/output devices and control, and data and address buses connecting the same, and/or at least one input processor and at least one output processor, e.g., which would be appreciated by one skilled in the art.

By way of further example, the signal processor may include, or take the form
10 of, some combination of a signal processor and at least one memory including a computer program code, where the signal processor and at least one memory are configured to cause the system to implement the functionality of the present invention, e.g., to respond to signaling received and to determine the corresponding signaling, based upon the signaling received.

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The Scope of the Invention

While the invention has been described with reference to an exemplary embodiment, it will be understood by those skilled in the art that various changes may be made, and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment(s) disclosed herein as the best mode contemplated for carrying out this invention.

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