

A NEW IN-SITU MEASUREMENT AND ANALYSIS SYSTEM FOR EXCITATION-EMISSION FLUORESCENCE IN NATURAL WATERS



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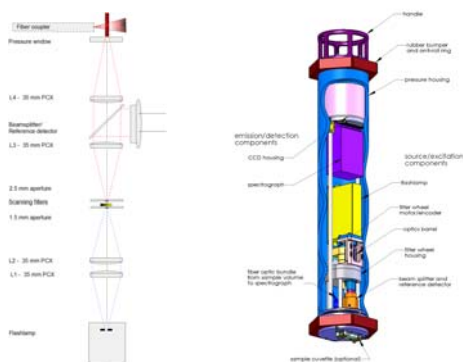
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A newly designed eXcitation-eMission Fluorometer (XMF) couples a high spectral resolution scanning pulsed spectral source with a focusing spherical grating CCD spectrograph, to produce real-time underwater excitation-emission images. This meter employs a configurable source spectrometer that can produce up to twenty four separate excitation pulses per second encompassing a range from 220 nm to 670 nm. The emission spectrometer generates a complete spectrum for each excitation pulse that extends from approximately 250 to 700 nm. The excitation and emission ranges provide capabilities to provide concurrent complex signatures of hydrocarbons, CDOM species, and other biogenic compounds. Coupled with a parallel factor analysis data reduction package adapted for the meter, the raw data can be deconvolved into specific biogeochemical parameters.

DESCRIPTION



The cut-away view of the instrument shows primary components. Source optics entail a scanning filter spectrometer light focused at the output aperture of the instrument. The light source consists of a Xenon flashlamp. The flashlamp resides in a steel shielded canister with its own power supply. A broadband silicon photodiode detector serves as a beam reference for pulse-to-pulse excitation signal normalization. A fiber input co-located with the output light couples the broadband fluorescence emission signal to a holographic spherical grating spectrograph. The spectrograph output is captured by a CCD camera developed by WET Labs. Data generated from the camera goes to a CF-2 host processor for secondary processing and storage or transmission.



Configured instrument without the pressure can. The current embodiment is designed to operate in-situ with open volume measurements or in the lab with use of a flow cell.



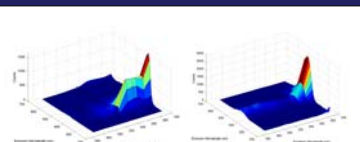
A scanning filter spectrometer disperses the excitation beam from the flashlamp. The wheel holds three separate variable filters spanning from 220 nm through the visible spectrum. In operation the user may select excitation from 1 to n wavelengths depending upon their application.



The CCD assembly encompasses the CCD, CCD controller, amplifier, and digitizer into single integrated instrument controller. This results in an order of magnitude reduction in packaging size with equal performance when compared to currently available commercial alternatives.

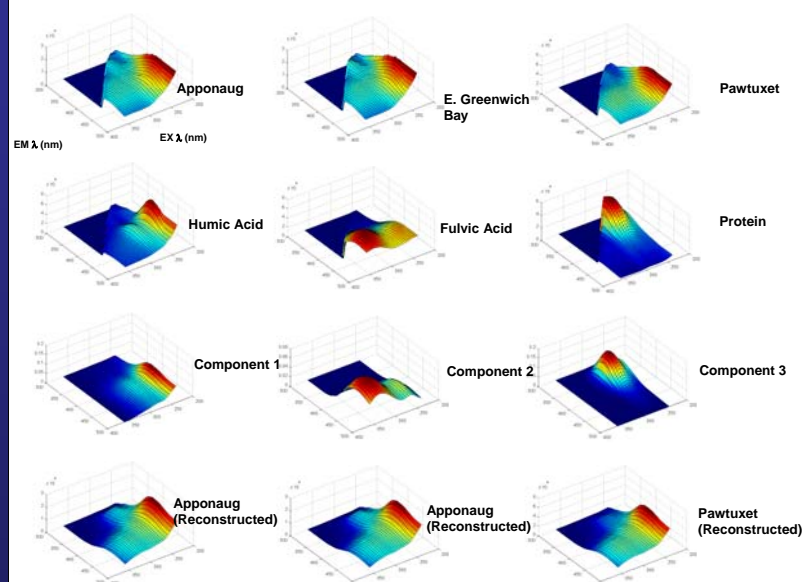
PRELIMINARY SPECIFICATIONS

Optical	Specification	Comments
Source	Flashlamp	
Arc size	1.5 mm	
Flash rate	28 Hz Max	
Duration	<1µsec	
Excitation		
Range	220-700 nm	250-700 operational
Dispersion	Discrete 10 nm	
Bandwidth	13-20 nm	
Scan Rate	24 wavelengths/sec	Selectable scan
Receiver		
Effective Dispersion	10 nm	
Range	250- 750 nm	
Dynamic Range	>80 dB	
Electrical		
Input Voltage	12-18 VDC	
Power	15 watts	
Interface	RS-422	
Data Rate	~20 Kbits/sec	
Resolution	16 bit	
Acquisition Rate	24 scans/sec	User selectable
Internal Memory	>350 MB	
Max sample storage	350,000	with binning
Mechanical		
Depth	500 m	
Dimensions	5in dia X 26 in length	
Housing	6061 Al	



Uncorrected spectra for diesel in water (left) and quinine sulfate (right). Data were accumulated with an excitation scan spanning from 250 nm to 370 nm. Both source and receiver operate at approximately 10 nm resolution.

PARAFAC ANALYSIS



Integral to the project is the implementation of a method for the canonical decomposition of the data stream. We have adapted a parallel factor analysis routine (PARAFAC) to separate component fluorescence signatures embedded in excitation-emission matrices (EEMs) of complex chemical mixtures. In this example the PARAFAC model is initialized with a 3-D array consisting of EEMs of unconcentrated samples from various locations in Narragansett Bay. The model deconvolves these natural mixture EEMs into individual EEM components and assigns relative concentrations for each component. Original component fluorescence signatures are not needed by the model but they improve the accuracy of the deconvolution. Further efforts will incorporate the analysis package with the instruments software package for near real-time analysis.

STATUS

The XMF sensor development is near completion. Full characterization and initial sea trials will be undertaken in November 2004. Currently development efforts iterate between bench testing for performance and implementing required modifications. Current efforts focus upon:

- Reconfiguration of receiver optics—Remount of the receiver pick-up fiber to eliminate secondary window reflections.
- Long term filter spectrometer evaluation—Tests to determine the UV source filters' stability are ongoing.
- Optical power optimization—This is part of an ongoing effort to enhance meter sensitivity. While the current configuration shows comparable sensitivity with the WET Labs' SAFIRE at wavelengths below 270 nm and above 370, optical output in the 300-370 range limits EEM fidelity with lower component concentrations.
- Software completion—While both real-time and post analysis software components of the software are currently operable, completion efforts are still required.