Environmental Monitoring Equipment and *in situ* Systems

OCN 633

Fall 2013

Need for monitoring tools

- *in situ* measuring devices allow unattended and/or real-time measurements to be made
- Temporal data provide a better indication of conditions than individual samples
- It is not always possible to manually collect data at “key times”

Advantages

- Data are gathered under ambient conditions
- *In situ* data acquisition is useful for exploratory or diagnostic studies
- Allows you to decide if you wish to collect samples for laboratory work
- Real time data acquisition allows altering research strategy (adaptive sampling), if necessary
- Becoming more and more important with “ocean observing”

Disadvantages

1. Cannot always make additional "bottle" measurements
2. Requires additional sample collection strategy if laboratory measurements and/or archiving are desired
3. Some important types of measurements cannot be made in the field

Compromise Approach

1. Combine *in situ* spot measurements with automated time-series data acquisition
2. Conduct manual and automatic sampling for laboratory analyses
3. Use newer *in situ* samplers that allow to make measurement and collect samples (for subsequent retrieval and analysis)

“Real Time” Devices

- instruments that produce continuous (or at least high frequency discrete) measurements.
- “sampling” frequency varies from multiple hertz to every few minutes to hours, depending on device
- devices can be single parameter or multi-parameter
- most are based on physical properties, but some instruments conduct “chemistry in a box”

CTD

- Conductivity, temperature, depth
- Electrical conductivity of solution measured through a “Wheatstone bridge” approach
- Temperature measured with a thermistor
- Depth measured with a pressure sensor


Instrument Design

- Sea Bird Electronics is main supplier for rigorous oceanographic CTD applications
- Workhorse of physical oceanographers Capable of high frequency sampling
- Designed for infrequent calibration and generally trouble free
- SBE also have a DO sensor (membrane based)
- Often combined with Wet Labs sensors for fluorescence (chl-a) and turbidity.

Sea Bird Electronics 911 http://www.seabird.com/

- Accurate and stable modular Conductivity and Temperature sensors
- Paroscientific Digiquartz® pressure sensor
- *TC-Ducted Flow* and pump-controlled time responses to minimize salinity spiking
- 24 Hz all-channel scan rate
- Depth capability 6800 meters (aluminum) or 10500 meters (titanium)
- Built-in interface for dual C & T sensors (sensors optional)
- 8 A/D channels and high power capability for auxiliary sensors
- Modem channel for real-time water sampler control (without data interruption)
- Built-in NMEA 0183 interface to merge real-time GPS data with the CTD data
- Optional Serial Data Uplink allows 9600 baud data pass-thru on shared CTD telemetry channel
- Optional SBE 17*plus* V2 SEARAM module for *in-situ* recording and programmable Carousel bottle firing
- Windows software included

SBE Advantages/Disadvantages

- Highly robust
- Can go to great depth
- Calibration done at factory and stable
- High frequency sampling
- Can observe data in real time and log
- Great graphical interface
- Powered by ship power (if desired)

- Costly!!!!
- Need individual sensors (other than CTD) for each application
- Usually need “cage” to house instruments
- Need conducting cable
- Need to send to factory for calibration

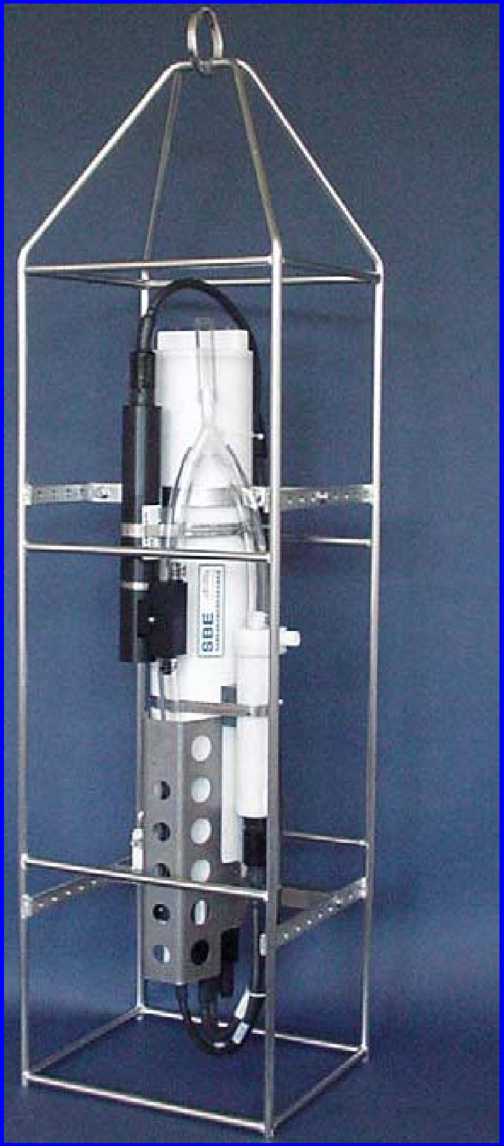
Other SBE CTD Instruments

- SBE 37 SMP Microcat, deep water (left) and shallow (middle) water versions
- SBE 49 FastCAT (right)

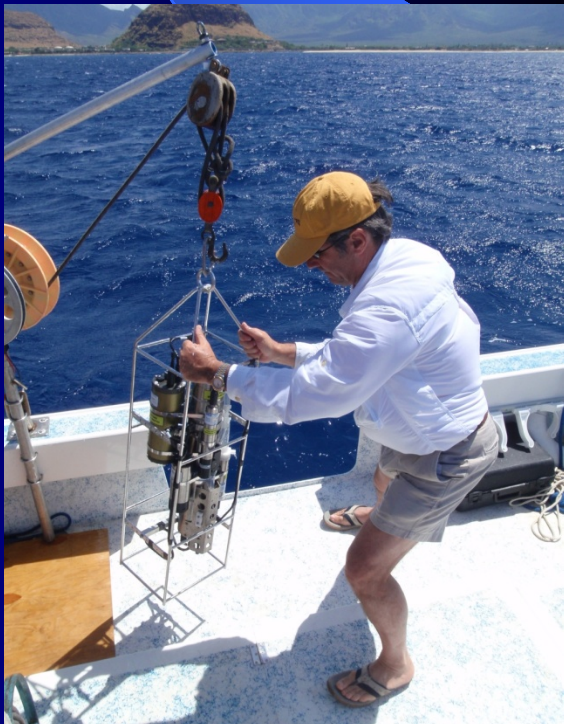
Other SBE CTD Instruments

- SBE 16 system
- Has C, T, D
- Pumped system
- Also DO 43
- Includes WETLabs FLNTUS (chl-a and turbidity
- On HIOOS buoy

Other SBE CTD Instruments



- SBE 19 system
- Similar to SBE 16 but is in cage for profiling applications
- Depth capability to 5000 m (ours only to 2000m)
- Will be used on field trip



SBE Deck Box Unit

- Allow real time viewing of data during deployment
- Require use of coaxial/conducting cable on a winch
- Excellent to use with rosette system as allow selection of depth at which to trigger bottles

YSI Multiparameter Sondes

- Useful for monitoring of pipe discharges, streams and rivers, lakes, estuaries, and to a more limited extent, the ocean
- Most multiparameter sondes do not measure depth (designed for shallow water or pipe settings)
- Some (e.g., YSI 6600) include a pressure sensor and are suitable for profiling down to ~200 m.
- Biofouling and settling onto sensors is addressed by cleaning the probes with sponges and brushes

Advantages/Disadvantages of YSI devices

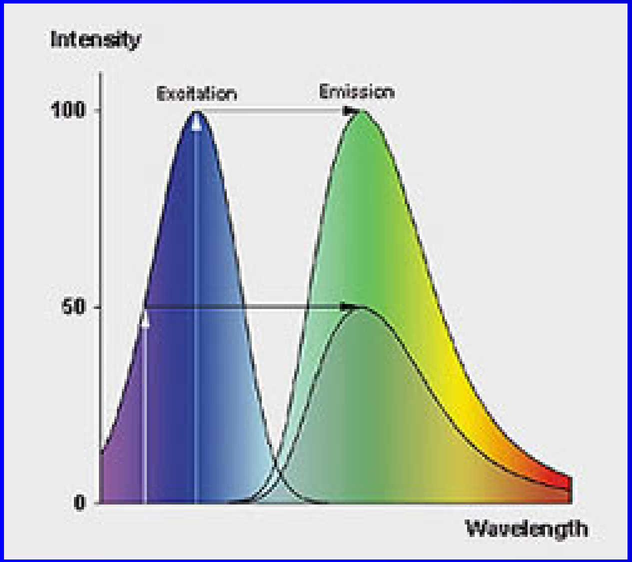
- Less costly than SBE
- Combine many probes in one device
- Small and easy to handle
- Ease of operation
- Powered by batteries

- Need to calibrate each probe individually
- Calibration is not stable over long periods
- Systems not as robust as SBE devices
- Sampling frequency lower than SBE
- Restricted to shallow depth
- Deployment period limited by battery/memory

WET Labs Sensors

- Typically mated with SBE CTD systems
  - Fluorescence (measure of Chlorophyll-a)
  - Turbidity (particles)
- Principles of operation are simple

Fluorometers

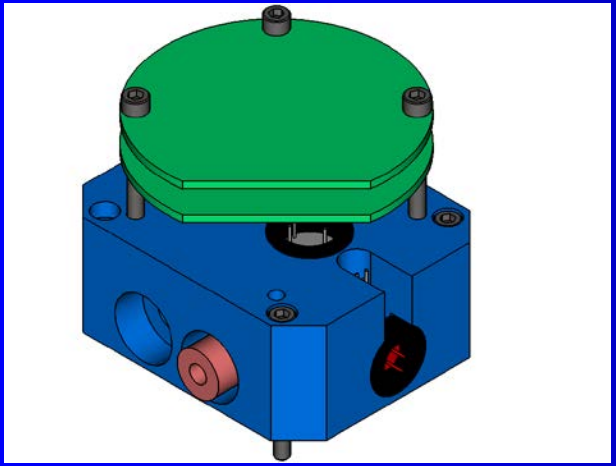


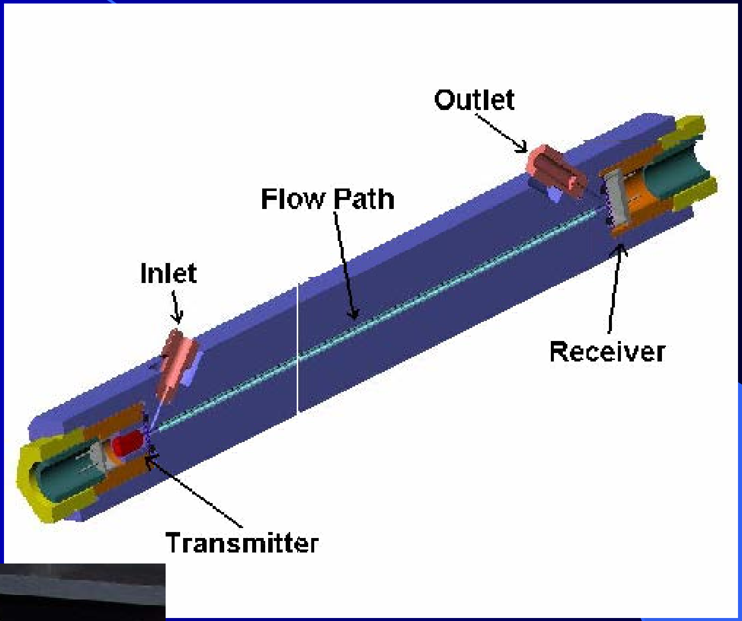
- Use specific or broadband excitation sources to excite water volume
- Fluorometers are emission detectors to determine the fluorescent response of a substance or an environment
- Fluorescence response is proportional to the concentration of the material of interest
- Non-destructively measures the concentration of material.

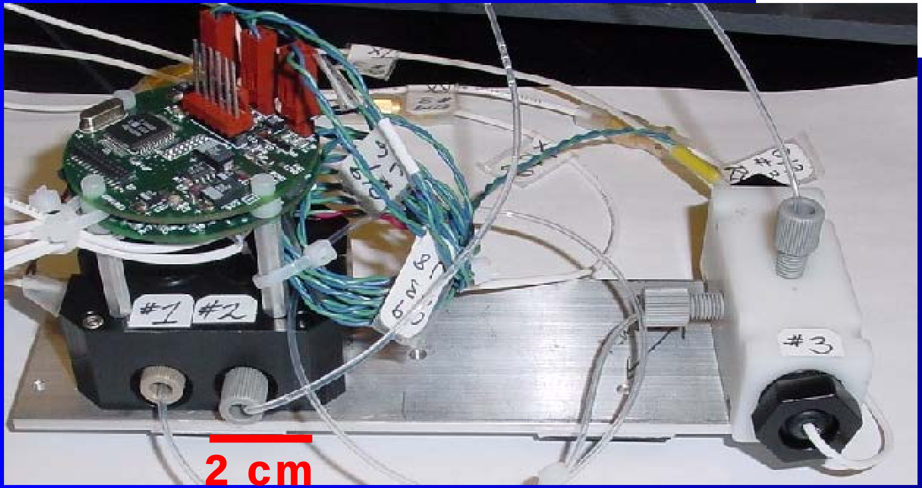
- WET Labs has pioneered the use of LED in fluorometers.
- Use of wavelength-specific LED and their relatively low power consumption allows for high S/N ratios and extremely low LOD
- Chlorophyll, CDOM, Rhodamine, and Phycoerythrin fluorescence

WET Labs
ChemStar

Sensitive Absorbance and Fluorescence Detectors







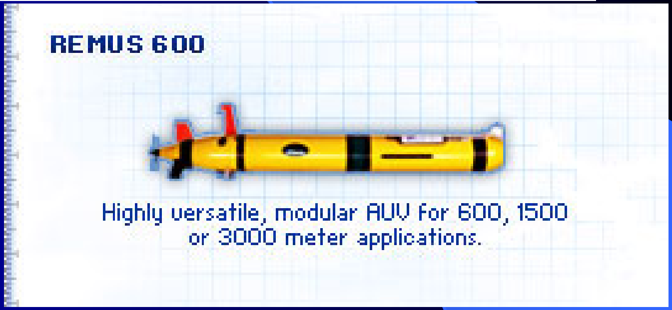
Turbidity Sensors

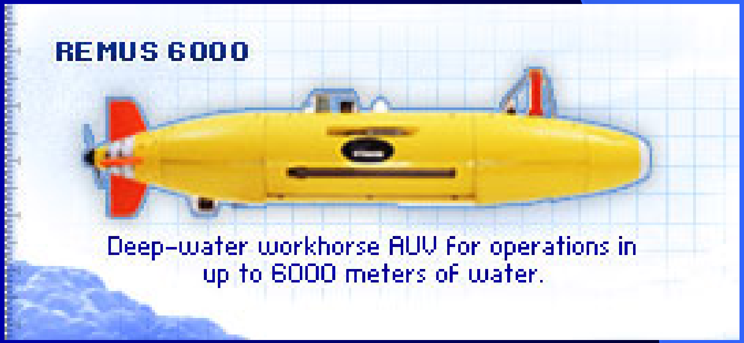
- Based on scattering of light from a reference beam
- Various modes allow total turbidity determination or individual particle size classes

- WET Labs *ECO* FLNTU
- Dual wavelength
- Single angle sensor
- Measures Chl-a and turbidity simultaneously
- *ECO* BB2F combination meter measures optical backscattering at 117 degrees at both 470 and 700 nm **and** chlorophyll fluorescence within the same volume.

REMUS AUV

- Made by Hydroid
- http://www.hydroidinc.com/
- Can be equipped with CTD, ADCP and other sensors (e.g., nutrients)
- Different sizes (37 to 884 kg)
- For coastal to deep ocean
- Applications
- Programmable, remotely operated





Other Optical Instrument Manufacturers

- Turner Designs: http://turnerdesigns.com

  Make fluorometers and other multiprobe sensors (esp. C3 and C6 submersible multi sensor platforms)

- Satlantic: http://satlantic.com

  Make: radiometers, fluorometers, data loggers, nutrient sensor (ISUS), other monitoring systems

Turner C3

- Incorporates up to three optical sensors ranging from the ultraviolet to the infrared spectrum.
- Internal memory storage capacity and external submersible Li^+ battery
- Equipped with temperature sensor and a depth rating of 600 meters
- Optional depth sensor and mechanical wiper
- Mateable to CTD profilers and other platforms
- The C-Soft Windows based software used for calibration, datalogging set up & file management

Turner C6

- Integrates up to six Cyclops-7 fluorescence and turbidity sensors
- Individual automatic gain control, calibration, digital data reporting and datalogging for each sensor
- T and P sensors and a depth rating of 600 meters
- Uses C-Soft Windows based user interface for calibration, datalogging set up and file downloading
- Existing Cyclops-7 sensors can be integrated into the C6 Multi-Sensor Platform

Turner Cyclops-7 Sensors

- **Chlorophyll-*a***
- **Turbidity**
- **Blue Green Algae (phycocyanin or phycoerythrin)**
- **CDOM**
- **Blue Green Algae**
- **Optical Brighteners**
- **Rhodamine WT**
- **Crude Oil**

- **Compact (4.3 in)**
- **Low power consumption (<300 mW)**
- **Fast sampling rate**
- **Relatively low cost fluorometers**
- **Integrate with C6**

Turner "Phytoflash" Active Fluorometer

- Submersible Active Fluorometer to determine the quantum efficiency of phytoplankton (in oligotrophic and mesotrophic environments)
- Solid-state instrument capable of variable fluorescence measurements on natural concentrations of phytoplankton
- Red PhytoFlash version specific to cyanobacteria
- Real time *in situ* measurement of phytoplankton photosynthetic parameters
- Can operate in three modes
  - Integrated with a CTD
  - Self-contained with internal datalogging
  - Laboratory mode

Satlantic Radiometers

- Hyperspectral OCR radiometers (irradiance and radiance in 350-800 nm range, sampling rate up to 3 Hz)

- OCR 500 series (stand alone systems)

- PAR sensors (400-700 nm range)

- ECO PAR sensor (made jointly with WET Labs… measures PAR in 350-800 nm range)

Satlantic ISUS V3

- Originally developed by Ken Johnson and Luke Colletti (MBARI) in 2002
- Real time, reagent free sensor designed to overcome challenges associated with reagent-based nitrate analysis in aquatic environments
- Uses UV absorption to measure NO_3^- concentration in real-time
- 1000 m depth range
- Detection limit ~2 μM

Satlantic SeaFET

- Sensor for pH based on ion sensitive FET developed by Todd Martz (SIO) and Ken Johnson (MBARI)
- Uses two electrodes to measure pH: A reference electrode with a liquid junction (internal reference) and a solid state reference electrode without a liquid junction (external reference).
- Stable system but factory calibrations are not very good so need to calibrate with “bottle samples”
- Todd Martz has now developed a SeaPHOX detector that measures both pH and DO (we will have one here soon)

Alliance for Coastal Technology

- http://www.act-us.info/
- ACT is a partnership of research institutions, resource managers, and private sector companies dedicated to fostering the development and adoption of effective and reliable sensors and platforms for use in coastal, freshwater and ocean environments.
- Hawaii ACT run by Dan Schar at HIMB
- Will be doing pH sensor evaluation at our CRIMP-2 buoy in Kaneohe Bay

“CHEMISTRY IN A BOX”

- Systems that depend on reaction chemistry
- Typically pump a water sample into a reactor
- Mix in reagents to allow reaction with analyte (e.g., color development)
- Pumps, valves, and other microfluidic devices used to move various streams
- Measure signal intensity as abs. or fluor.

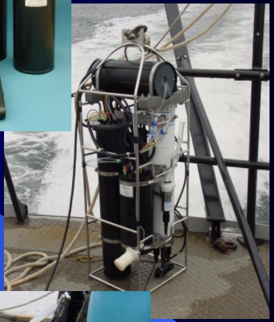
Advantages/Disadvantages

- *In situ* measurement of potentially ephemeral parameters
- Allow time series analysis under ambient conditions
- Multiple parameters analyzed simultaneously

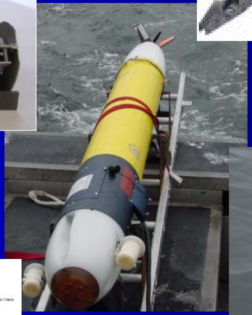
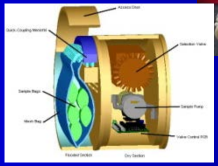
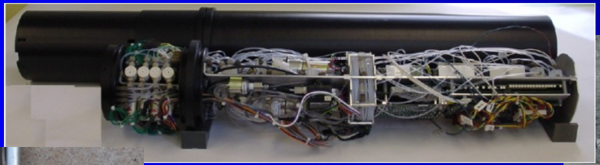
- Complex instruments
- High Maintenance
- Not “idiot proof”
- Operation requires sound knowledge of instrument AND underlying chemistry
- Need to frequently replace reagents

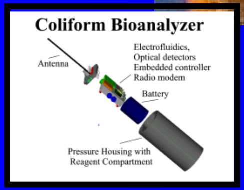
SubChem Systems Submersible Analyzer Technologies

1. SubChemPak Profiling Analyzer
2. Autonomous Profiling Nutrient Analyzer
3. SubChem Analyzer Payload for REMUS
4. Sample Collection Module for REMUS
5. WET Labs Cycle - Nutrient Analyzer
6. SubBio Analyzer



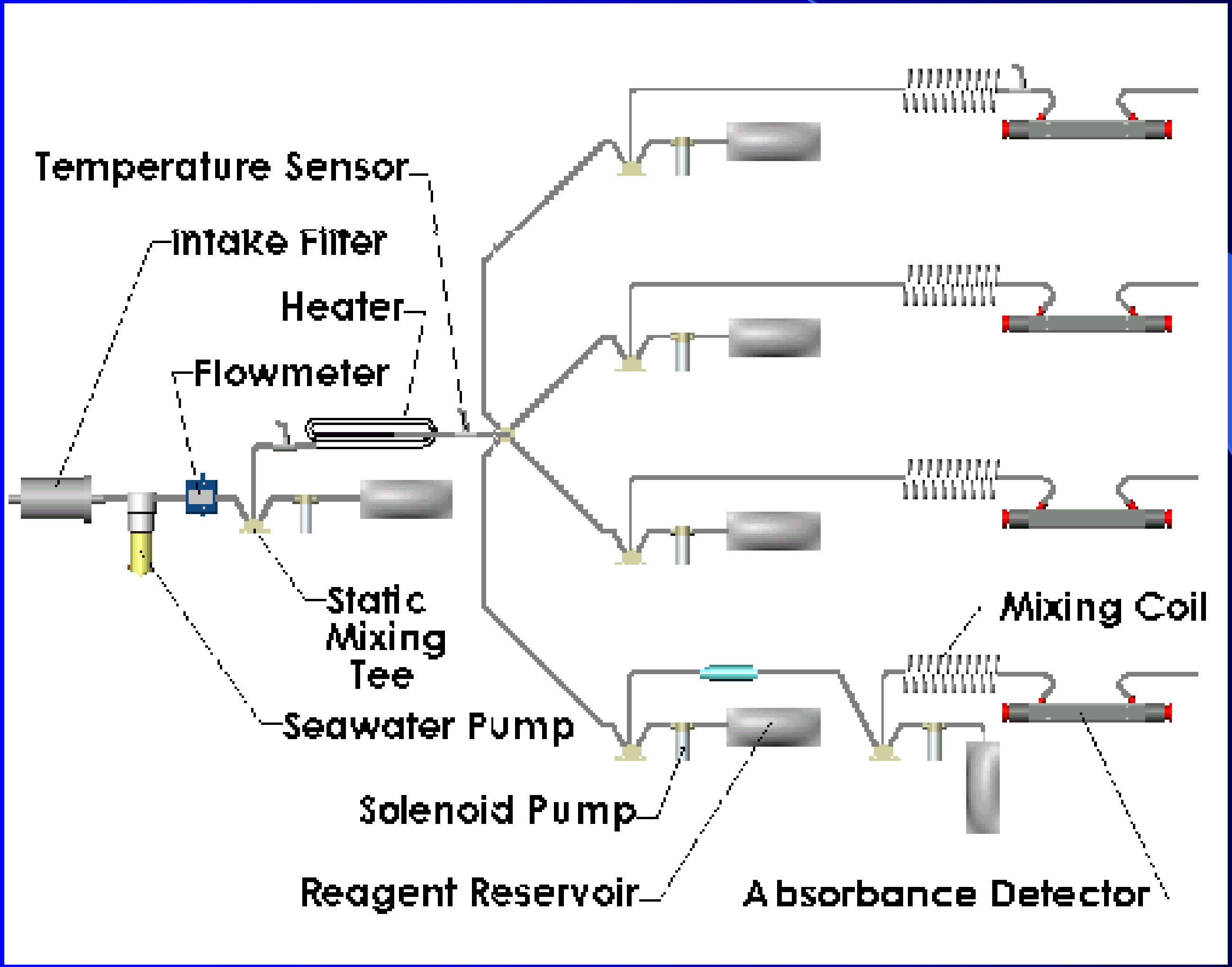
SubChemPak Analyzer

- Real time results
- Fast response
- High resolution profiles
- Multi-chemical capability
- Trace concentrations
- *In situ* calibration
- Accurate determinations

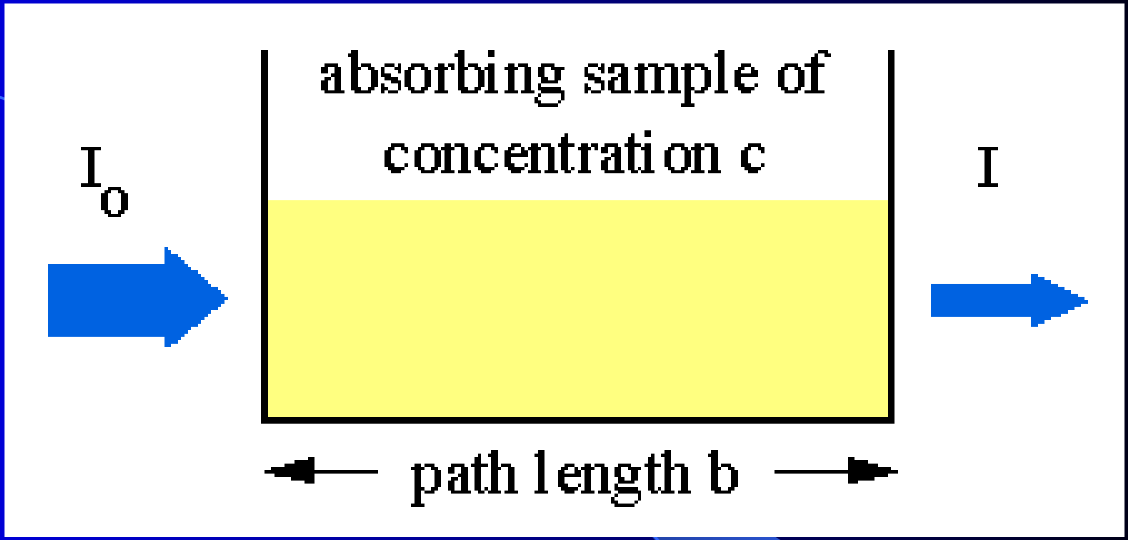
2000

SubChem Systems APNA

Continuous Flow Electro-fluidics



Spectrophotometry



Absorbance = – log T = log (1/T) = - log (I/Io)

<u>Primary equation for spectrophotometric analysis</u>

A= abc

A = Absorbance (no units),

B = optical cell path length (meters)

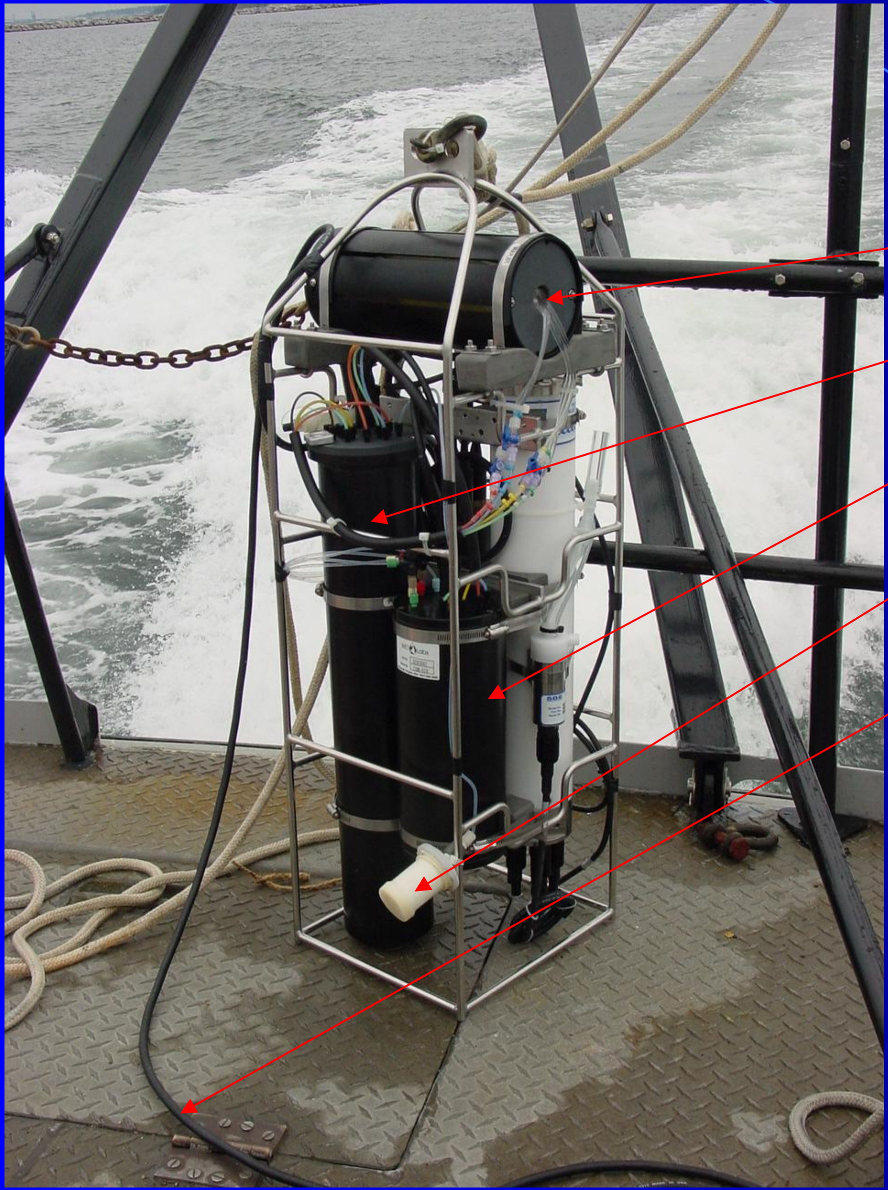
C = concentration (molar)

a = absorptivity (units = l/(mole-1 m-1))

Choice of Optical Cell Path Length and Analytical Ranges

Analyte	1cm Cell	15 cm	Wavelength
Nitrite	0 - 60.0 mM	0 - 10 mM	540 nm
Nitrate	0 - 60.0 mM	0 - 10 mM	540 nm
Phosphate	0 - 60.0 mM	0 - 5 mM	880 nm
Silicate	0 - 60.0 mM	0 - 10 mM	820 nm
Iron (II)	0 - 60.0 mM	0 - 5 mM	560 nm
Ammonium	Fluorescence	0 - 20 mM	Ex 370, Em 480

SubChem Pak Profiling System



Reagent Reservoir

Reagent Delivery Module

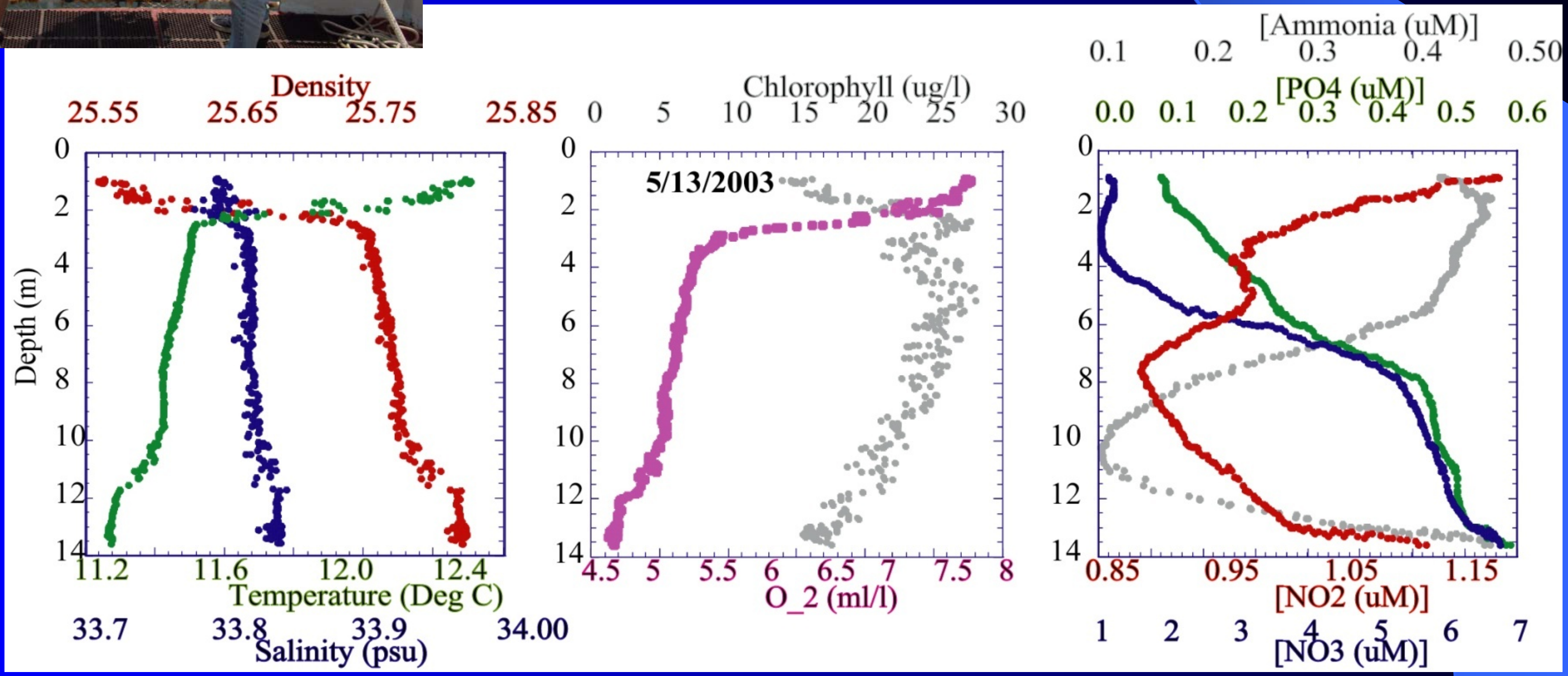
ChemStar Detector

Inlet Filter

Deck Box and Sea Cable

Vertical Profiling Systems

SubChemPak Analyzer
Z-Profiler System



Santa Barbara - May 2003

Autonomous Profiling Nutrient Analyzer (APNA) on the URI IOPC Profiler

2005

ORCAS IOPC Profiler

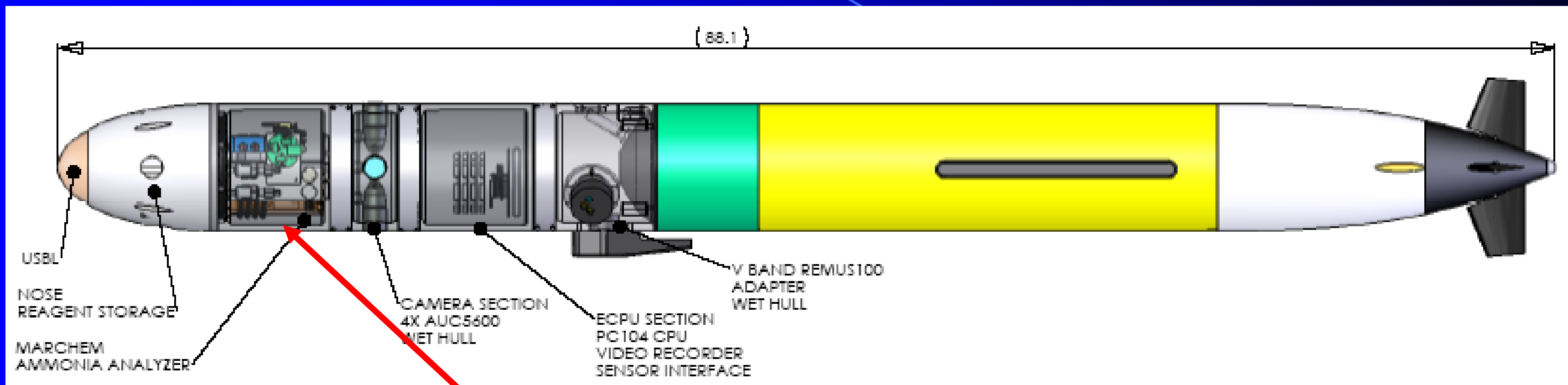
- Multi-channel chemical analyzer
- Autonomous or cabled profiling
- NO3, NO2, PO4, Si, NH3
- 2-4 week duration
- Nutrient data telemetry

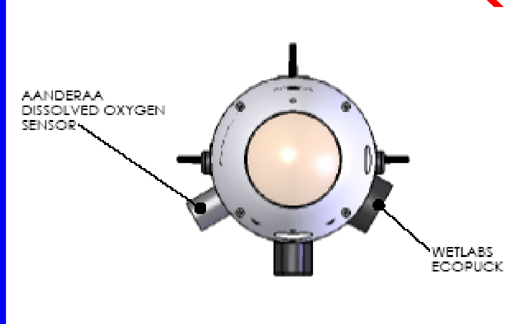
APNA Components

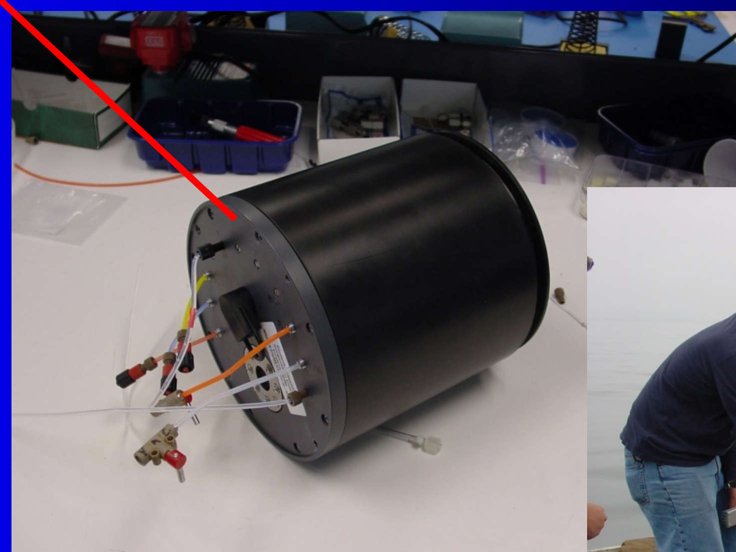
The APNA is comprised of several components:

- Autonomous Profiling Nutrient Analyzer (APNA) - submersible multi-channel reagent delivery module with multiple ChemStar electro-optical detectors.
- A submersible flooded, reservoir for reagents and standards.
- The LabView Graphical Interface (MS Windows) operating on a host computer.
- A Pelican Case for storage and shipping.
- A Deckbox with test cable for power and communications

MARCHEM Ammonia Analyzer on URI's REMUS Vehicle







Continuous underway surveying of ammonia, oxygen, chlorophyll, CDOM, CTD, and optical scattering.