Standardizing Eureka's Turner Fluorometers

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Background

Over the years, Eureka integrated many of Turner Design's fluorometric sensors into its multiparameter instruments because Turner is the world leader in designing and manufacturing miniature fluorometers for aqueous field applications. The integrated sensors include blue-green algae (both phycocyanin and phycoerythrin), CDOM/fDOM, chlorophyll a, crude oil, rhodamine, fluorescein, optical brighteners, refined fuels, and tryptophan.

Note that fluorometers do not measure their analytes directly in, for instance, weight per unit volume. They measure prescribed situations of fluorescence, and then infer analyte concentrations from that fluorescence. Calibration defines that inference.

Calibration can be difficult because of the relatively exotic fluorometer analytes. It's easy to obtain a calibration standard for temperature or conductivity because those parameters are well-defined and can be measured directly. It's not so easy to obtain a calibration standard for analytes like chlorophyll and refined fuels because those parameters often come in different forms, or combinations of forms, and cannot be measured directly. For instance, "crude oil" can be composed of many different combinations of different hydrocarbons, with each combination giving a slightly different fluorometric response for the same weight concentrations. The hydrocarbons typical in River A may not be the same hydrocarbons typical in River B.

Traditional Calibration Methods

There are four calibration methods commonly used for fluorometers. Each has its own pros and cons.

Purchased Standards – Standards for many of the sensors can be purchased from various vendors. However, these standards may be of an inconvenient value and/or perishable and/or quite expensive. And purchased standards cannot always mimic the constituents of the waters

to be monitored. A single chlorophyll standard, for instance, cannot represent all the different combinations of algae species.

Secondary Standards - Calibrations for some of the sensors can be made with secondary calibration standards ("cal cubes"). However, because of the variations among natural waters, the cal cube is only an approximate standard, and each cal cube produces different readings for each individual sensor of the same type. Cal cubes are also rather expensive.

Substitute Standards – Because the fluorescence response of some of the analytes overlap, you can calibrate a few of the sensors with different analytes. For instance, a chlorophyll sensor has a minor response to rhodamine, meaning that a carefully prepared rhodamine solution can be used to calibrate a chlorophyll sensor. But this technique cannot account for different water compositions of the analyte of interest and may not provide optimum calibration values.

Laboratory Analyses – A grabbed sample can be analyzed for the analyte of interest, and the value determined can be used to calibrate the sensor either through the usual calibration routine, or by correcting data in a spreadsheet. The latter means that you can correct historical data if you believe that the laboratory sample resembles the waters of the historical data. However, lab analyses depend on proper sample handling, can be expensive and time consuming, and may be valid only for water samples of similar composition to the grabbed sample.

Nonetheless, laboratory analyses are usually the best calibration method when accuracy, as opposed to consistency, is required.

A New Calibration Method

Because of the problems mentioned above, Eureka recommends a new calibration procedure for all Manta-based fluorometers (aside from the dyes rhodamine and fluorescein, which can be calibrated specifically with known concentrations of those analytes). More accurately, this is a method for standardizing your fluorometer so that it always reads the same number in the same solution.

To calibrate with this method, clean and dry the sensor (that is, the optical window on the tip of the sensor) and point it into the air, away from direct light. Slowly move a target material, such as a Post-It Note, toward the surface of the sensor. The sensor's reading will increase until it reaches the "saturation" point, which is the highest reading available from the sensor (see photos below). With the target material placed so that the sensor is saturated, calibrate the sensor, in the customary way, to Turner's recommended upper-range limit.

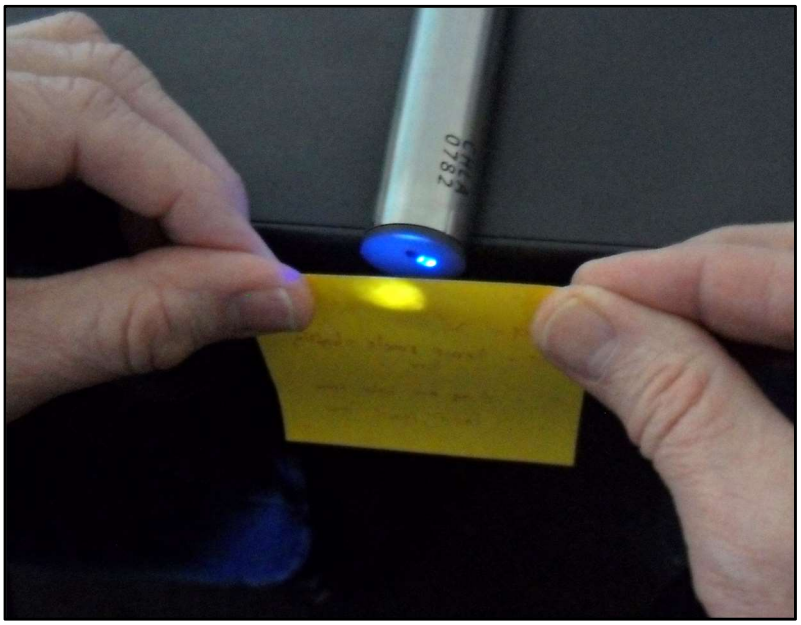
(Why Post-It Notes? Because they contain wide mixtures of organic dyes that fluoresce to a wide range of incident lights. Plus, they are cheap, repeatable, and readily available worldwide.)

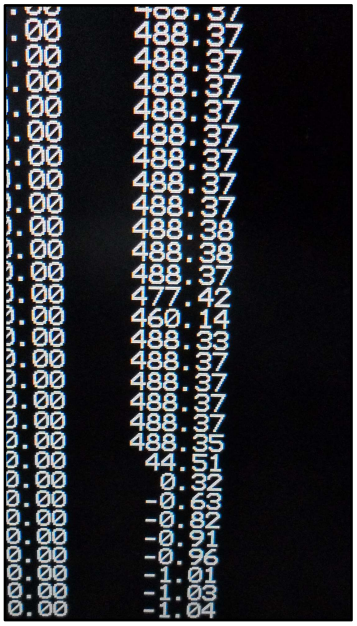
You may find it easier to fix the location of the target, and slowly move the Manta or Trimeter closer to the target.

For instance, suppose that moving the target toward a chlorophyll sensor causes the reading to increase until it hits 493, and will not increase further. You would enter the Manta's calibration routine and set the chlorophyll sensor value to the maximum reading which, for chlorophyll, is 500 µg/L (see chart below). Note that Eureka sets each fluorometer in this fashion before shipment, so the saturation point for your first calibration should be close to 500.

This method does not necessarily provide *accurate* chlorophyll readings, but it does provide *consistent* chlorophyll readings. A consistently calibrated sensor provides two advantages. First, a chlorophyll reading of, say, 30 µg/L means that there is twice as much chlorophyll as would be indicated by a reading of 15 µg/L. Second, the readings will always be the same when the sensor is deployed in the same measurement situation.

The sensor's zero point can be set in water that is free from the analyte, but Eureka prefers the open-space technique: clean and dry the sensor, point it away from direct light, and calibrate the Manta to zero in the customary method.





How to Use the New Calibration Method

The consistency of this calibration technique means that if you perform a laboratory analysis for chlorophyll, you can use that analysis to adjust the data collected with any sensor that has been calibrated once, or multiple times, with this method.

For instance, suppose that a chlorophyll sensor calibrated with this method is used for field readings over a period of three months. Later, if a laboratory analysis indicates that the sensor reads, say, 11.2 µg/L when it should be reading 9.4, then you can safely adjust the data taken with that sensor by a factor of 9.4/11.2, or 94%.

The same applies to any other chlorophyll sensor that is calibrated with the new method, except that each sensor will likely have a slightly different correction factor. For instance, a second sensor might read 8.7 in the situation described above, meaning that its correction factor is 9.4/8.7, or 108%. Knowing both correction factors means that both sensors are providing data based on the same situation and are roughly as accurate as the laboratory analysis – provided the waters monitored have a relatively consistent combination of chlorophyll-producing biota.

APPENDIX: Fluorometer Upper Ranges and Example Target Materials

Sensor	Units	Range	Example Target Material
chlorophyll a	µg/l	0.03 – 500	hot pink Post-It Note
fresh B/G algae (phycocyanin)	cells/ml	0 - 400,000	hot pink Post-It Note
salt B/G algae (phycoerythrin)	cells/ml	0 – 750	hot pink Post-It Note
CDOM/FDOM	ppb	0-5000	hot pink or blue Post-It Note
rhodamine	ppb	0 – 1000	orange Post-It Note
fluorescein	ppb	0 – 500	not yet determined
crude oil	ppb	0 – 2700	hot pink or blue Post-It Note
refined fuel	ppb	0 - 10,000	clean motor oil
optical brighteners	ppb	0 - 15,000	clean, white shirt
tryptophan	ppb	0 - >20,000	not yet determined

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