

# **Protocols for Verifying the Performance of Hydrocarbon Sensors**

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## **Protocols for the ACT Demonstration of In Situ Hydrocarbon Sensor**

### **1. Background on ACT Technology Evaluations**

Instrument performance verification is necessary to effectively evaluate existing technologies and to encourage the development and adoption of promising new technologies that support coastal science, resource management and the long-term development of an Integrated Ocean Observing System. The Alliance for Coastal Technologies (ACT) has therefore been established to provide an unbiased, third party testbed for evaluating coastal sensors and sensor platforms.

The following protocols describe how ACT will examine the environmental performance characteristics of commercially available in situ or flow-through hydrocarbon sensors through the evaluation of objective and quality assured data. The goal of ACT's evaluation program is to provide technology users with an independent and credible assessment of instrument performance in a variety of environments and applications. Therefore, the data and information on performance characteristics will focus on the types of information that users most need. ACT surveyed the broader community to define the data and operational parameters that are valuable in guiding instrument purchase and deployment decisions.

It is important to note that *ACT does not certify technologies* or guarantee that a technology will always, or under circumstances other than those used in testing, operate at the levels verified. ACT does not seek to determine regulatory compliance; does not rank technologies or compare performance among specific instruments tested; does not label or list technologies as acceptable or unacceptable; and does not seek to determine "best available technology" in any form. ACT will avoid all potential pathways to picking "winners and losers." Therefore, although the following protocols will apply to all instruments evaluated, no direct comparisons will be made between instruments from different manufacturers and instrument-specific Performance Verification Statements will be released to the public for each instrument type as a final report. Finally, we emphasize that these protocols were developed with the direct assistance of participating manufacturers and an external Technical Advisory Committee and have been agreed upon in signed contracts with ACT.

### **2. Introduction to Technology**

As oil remains one of the world's most important energy sources, permissible and unintended release of hydrocarbons into the environment becomes inevitable as oil is explored, extracted, refined, transported, and consumed. Although aquatic and terrestrial environments are susceptible to contamination by spills, the Alliance for Coastal Technologies will focus on aquatic sensors for the detection and monitoring of hydrocarbons in coastal freshwater, estuarine, and marine settings. Hydrocarbon sensors provide the means to detect and monitor hydrocarbons before, during, and after an oil spill. In April 8-10, 2008, in Seward, Alaska, the Alliance for Coastal Technologies conducted a workshop entitled, Hydrocarbon Sensors for Oil Spill Prevention and Response (available at: [www.act-info.us](http://www.act-info.us); Ref. No. [UCMECS]CBL 08-095, Alliance for Coastal Technologies Indexing No. ACT-08-01). In that report Appendix C summarizes in table format current in-situ and laboratory hydrocarbon sensors. Based on

summaries from that workshop and recent enhanced focus on the need to more effectively monitor oil spills and remediation efforts, ACT Partner Institutions and Stakeholder Council have chosen to conduct a performance verification of commercially available, hydrocarbon sensors. There are a number of challenges in assessing hydrocarbon concentrations in coastal aquatic systems that point to the value of sustained in situ observations. This ACT Technology Evaluation will examine individual sensor performance both in the laboratory and across different field conditions in moored and vertically profiled applications.

### **3. Objectives and Focus of Hydrocarbon Sensor Performance Verification**

The fundamental objectives of this Performance Verification are to: (1) highlight the potential capabilities of hydrocarbon sensors by demonstrating their utility in a range of coastal environments, (2) verify manufacturer claims on the performance characteristics of commercially available hydrocarbon sensors when tested in a controlled laboratory setting, and (3) verify performance characteristics of commercially available hydrocarbon sensors when applied in real world applications in a diverse range of coastal environments.

ACT has performed a customer needs and use assessments and held a technology workshop on hydrocarbon sensors. As part of these reviews, scientists, resource managers, and other users of these technologies were asked about their current use or application of these instruments, their perceptions of limitations or problems with the technology, and the most important criteria they use when selecting a sensor or instrument package. The results of these assessments were used to identify the main applications and key parameters that ACT will evaluate in this Technology Verification.

Over ninety percent of colleagues surveyed in ACT's Customer Needs and Use Assessment Survey use or plan to use hydrocarbon sensors in estuarine and near-shore environments. Slightly more than half (52%) and 39%, respectively, of respondents indicated that in situ hydrocarbon sensors were commonly deployed on remote platforms and used in profiling applications, typically down to at least 100 meters depth with more than 50% of respondents wishing to profile to depths greater than 100 m. Therefore, the present performance verification will focus on both moored and profiling applications. It was also clear from the user survey that range (i.e., detection limits), reliability, accuracy, and precision are the most important parameters guiding instrument selection decisions. Given that the majority of instruments submitted to the verification utilize fluorometry, and that in situ fluorometry is a relative measurement with no absolute "true value" reference, accuracy cannot be measured directly. As an alternative to the direct measurement of accuracy, this Performance Verification will determine response linearity, or stability of the response/calibration factor, to a defined reference (see below). Protocols were developed with the aid of manufacturers and the Technical Advisory Committee (listed below) to evaluate these specific areas. Complete needs and use assessment reports can be found at [www.act-us.info/customer\\_needs.php](http://www.act-us.info/customer_needs.php).

### 3.1. Definition of Test Parameters

Because of the inherent limitations of making quantitative estimates of hydrocarbon concentrations in situ and the inability to control various factors that can impact hydrocarbon composition and optical properties during field tests, response linearity, precision and range will be determined in the laboratory only. Field tests will focus on reliability/stability and the ability of the instrument to detect variation of hydrocarbon loads in natural waters.

- **Response Factor** – Stability of a predetermined response or calibration factor, computed as: (fluorometer measurement in sample solution – fluorometer measurement in blank solution) / [challenge compound] over a range of challenge concentrations.
- **Precision** – Precision is a measure of the repeatability of a measurement. Instrument precision will be determined by calculating the coefficient of variation (STD/Mean x 100) of 30 replicate fluorometer measurements at a minimum of 3 different challenge compound concentrations at a fixed temperature in the laboratory.
- **Range** – Range or detection limits is a measure of the minimum and maximum concentration of a particular challenge compound that an instrument can resolve from ambient background or saturation of instrument signal, respectively (dependent on precision, challenge compound and detector capacity). Response factors, detection range and measurement precision will be determined in darkened tanks for a minimum of three challenge compounds using separate addition series trials in UV treated deionized lab water.
- **Reliability** – Reliability is the ability to maintain integrity or stability of the instrument and data collection over time. Reliability of instruments will be determined in two ways. In both laboratory and field tests, comparisons will be made of the percent of data recovered versus percent of data expected. In field tests, instrument stability will be determined by pre- and post-measures of blanks and reference dye to quantify drift during deployment periods. Comments on the physical condition of the instruments (e.g., physical damage, flooding, corrosion, battery failure, etc...) will also be recorded.

### 4. Summary of Verification Approach

Testing protocols are based on a synthesis of standard procedures for calibrating and testing hydrocarbon sensors provided by the participating manufacturers, and protocols recommended by ACT personnel and an external Technical Advisory Committee. The protocols were refined through direct discussions between all parties during an ACT Hydrocarbon Performance Verification Protocol Workshop held on February 3-4, 2011 at Moss Landing Marine Laboratory (MLML). Participants at this workshop included ACT Headquarters Staff, ACT Partner Institution Technical Coordinators, an ACT Quality Assurance Manager, an external Technical Advisory Committee, and representatives from the participating manufacturers.

The goal of this Verification is to test the same model instrument in laboratory and field tests covering a range of coastal environments, to the extent that the submitted test instrument is appropriate for each of the testing applications or sites. Where the test instrument specifications are not appropriate for a given environment or application, we will accept a separate instrument

package as long as it has been pre-approved and meets all of the original conditions defined in the request for testing. It is also preferred to evaluate instruments incorporated in stand-alone packages, which include features such as data logging, data transformation/conversion equations, independent power supplies, and biofouling prevention. In some cases, however, submitted test instruments may only be tested in one type of field application (if they are designed and sold for one particular use) and some independent sensors will be incorporated into other associated equipment (e.g., datalogger, CTD) owned and operated by ACT Partner Institutions.

We propose to schedule the various laboratory and field tests in such a manner that only one instrument package of each particular model, or a single instrument for a site-specific model, will be needed for the Performance Verification. All instruments should be delivered to MLML by May 11, 2011 to be available for training and confirmation of factory calibration settings. An initial laboratory test, using one of each model instrument package submitted will follow the training workshop and take place during the week of May 18 – 20, 2011. ACT will be responsible for shipping the instruments from MLML to the respective field test sites following the training and laboratory testing.

A consensus was reached that the testing protocols will incorporate or require:

- ACT PI's, along with experts from the external Technical Advisory Committee will oversee the set-up, training, and use of the Lab instrument during the evaluation.
- a lab test will be conducted at Moss Landing Marine Lab to examine response factors, precision, range and reliability using a suite of certified reference materials with well established fluorescence and absorbance properties.
- a tank test will be conducted at the Belford Institute of Oceanography in Dartmouth, Nova Scotia to evaluate performance against two types of crude oil with and without added dispersant.
- field tests will include a freshwater and estuarine environment for moored applications of approximately 1 month duration as well as a vertical profiling application for those instruments that are designed to sample at appropriate rates and with appropriate sensor response times. (NB – funding reductions have made it necessary to drop the freshwater moored field test).
- standard, approved laboratory analytical methods (GCFID, EPA SW846-8015B and GCMS, EPA SW846-8270D or equivalent) to provide best possible measure of the “true” total hydrocarbon concentrations from field and laboratory samples, which will serve as performance standards against which instrument estimations will be compared.
- standard, approved laboratory analytical methods to provide best possible measure of the optical properties of the field and laboratory reference samples which will serve as performance standards against which instrument estimations will be compared. These include Excitation –Emission Matrix Spectrofluorometry (EEMS, following Coble et al 1998) and UV-VIS spectrophotometry using calibrated research grade instrumentation to enable interpretation of instrument performance variation with respect to challenge compound and environmental water quality.

- all samples designated for hydrocarbon analysis will be processed by a contract lab following their established SOP's. Optical analyses will be conducted on a single instrument suite owned by Moss Landing Marine Laboratory, and maintained and operated by trained ACT technical staff. Haphazard split samples will be shipped to an independent lab (e.g. P. Coble USF) to enable instrument inter-calibration.
- all samples will be collected in approved, standardized bottles, along with field blanks.
- all samples and blanks will be collected, stored, and shipped according to approved Standard Operating Procedures that will be finalized and practiced at the Training Workshop prior to the beginning of the evaluation. The Manufacturers and the Chief Scientist will verify that all staff are trained in both instrument and sample collection SOP's.
- the QA manager will conduct technical audits at the lab test and field site tests to verify compliance with these SOP's during the test.

All ACT personnel involved in this Verification will be properly trained on use of instruments by each manufacturer's representative and on standardized water sampling, storage and shipping methods. All laboratory analyses will be conducted by trained ACT staff using approved standardized methods. ACT will conduct a QA audit of the laboratory during the Verification to assure that all components of established SOPs are being thoroughly followed. Company participants are welcome to visit any of the test sites at any time during the Verification. Additional agreements for the protocols include:

- if requested, an evaluation of the test instrument's factory calibration can be performed using manufacturer's recommended challenge compound. This check will be performed during the training session at MLML by ACT staff and monitored by the manufacturer representative to ensure proper handling and expected performance.
- any post-corrections of data based on improper calibration or drift are the responsibility of the companies.
- post-corrected data can be included in the companies' response page that is included within each report.
- all instrument test data will be reported over time, position, or depth as directly downloaded from the test instruments.
- for those instruments that derive engineering units, values will be reported in the default units reported by the instrument, as well as original voltages or relative fluorescence units.
- reports will include means, standard deviations, and number of replicates of laboratory determined hydrocarbon values for corresponding reference samples at the same time, position, or depth of instrument measurements.
- reports will include an independently determined temperature record collected within the water column over corresponding time, position, or depth, recorded with an RBR TR-1060 Temperature Recorder which has a stated accuracy of 0.002 °C and a resolution of < 0.00005 °C.
- the TR-1060 temperature sensors will be used for laboratory tests and field tests.

## 4.1. Laboratory Tests

### 4.1.1. Performance against surrogate standards and challenge environmental variables

Laboratory tests of response factor, precision, range, and reliability will be conducted at MLML. The goal of the laboratory tests is to assess performance of the hydrocarbon detection systems submitted for evaluation. These systems range from fluorescence-based (spanning a range of excitation-emission pairs), to absorbance based detection. Consequently no single challenge compound will encompass the range of detection windows to be tested. Ideally, to facilitate testing challenge compounds should be directly water soluble or be compatible with a water soluble carrier. The compounds to be utilized in laboratory characterizations of instrument performance are listed in Table 1 and cover the range of optical detection windows utilized by participating hydrocarbon sensors.

**Table 1.** Proposed challenge compounds for laboratory evaluations of hydrocarbon sensors.

| <i>Compound</i>             | <i>Ex</i> | <i>Em</i> | <i>Carrier</i>                        | <i>Stock (ppm)</i> |
|-----------------------------|-----------|-----------|---------------------------------------|--------------------|
| Carbazole                   | 270       | 342, 358  | methanol                              | 5000               |
| Naphthalene Disulfonic Acid | 270       | 380       | 0.05 M H <sub>2</sub> SO <sub>4</sub> | 5000               |
| Quinine Sulfate             | 350       | 450       | 0.05 M H <sub>2</sub> SO <sub>4</sub> | 5000               |
| Basic Blue 3                | 250, 320  | 430       | water                                 | 5000               |
| Diesel Fuel SPEX CRM        | 250-300   | 350-500   | methanol                              | 5000               |

Basic Blue 3 (BB3, C.I. 51004, CAS 33203-82-6, M.W. 359.9) meets these specifications as a fluorometric reference standard and, critically, has been employed as a wide wavelength range (220 -700nm) quantum counter for correction of fluorescence emission spectra (Kopf and Heinze 1984 *Anal. Chem.* 56, 1931). ACT has successfully utilized BB3 in its Performance Verifications of Chlorophyll Fluorometers (Ref. ACT PV05-01). Naphthalene Disulfonic Acid and Quinine Sulfate, being acid soluble, are also readily amenable to aqueous testing. Carbozole and Diesel fuel can be utilized at low concentrations by dilution into water, but upper test concentrations (if analyte solubility maintained) will be limited to a maximum of 1 ppm to minimize methanol exposure hazards.

Laboratory challenges will be performed in insulated 500 L, black acrylic tanks in a dark room using filtered deionized water as the background medium. Test tanks have been preconditioned by several years of use with deionized and seawater exposures and cleanings. Temperature will be maintained at  $15 \pm 0.5$  °C with Nestlab recirculating chillers and copper heat exchange tubing. Water will be continuously circulated with submersible pumps (ca 10 L/min) placed at opposite ends of the tank. Temperature will be monitored at opposite ends of the tank at sensor detector level by two calibrated RBR 1060 recording thermistors. After immersion and equilibration of instruments to tank temperatures (a minimum of 30 minutes), challenge experiments will begin.

*Response Linearity* – After instruments are allowed to acclimate to each challenge condition, instrument response to those conditions will be reported as the mean and standard deviation of 10 instrument readings at a sampling rate of at least 1/minute. The mean and S.D. of instrument reads will be compared to the mean and S.D. of 5 water samples collected at 2-minute intervals during the recording interval. These will be characterized by absorbance spectroscopy and EEMS. Test baths filled with DI water (to provide a baseline or zero response factor), held in the dark, and at least six challenge concentrations will be tested over the range of 0-100 ppm (e.g. 0, 0.01, 0.05, 0.1, 0.5, 1.0, 10 and 100 µg / mL) by additions of known amounts of challenge compound.

*Precision* – Precision tests will be conducted simultaneously by monitoring the variance of instrument fluorescence signal over 30 consecutive measurements at a maximum of 1 minute intervals in a selected subset of controlled bath conditions in the test matrix described above.

*Detection Range* – The experimental matrix above will enable determination of the linear detection ranges at each test temperature. Limit of detection will be computed as: Mean + 3 S.D. of blank readings; and, upper detection range will be determined as either the challenge compound concentration causing saturation of instrument output or a greater than 20% decline in response factor. Only tests conducted in dark conditions will be used to determine detection limits of the instruments.

*Turbidity and CDOM Interference* – Sensitivity to ambient water quality will be assessed by exposing the test instruments to varying turbidity and artificial CDOM levels. Instruments will be placed in a bath at 15 °C, and baseline readings determined as above. BB3 will be used as reference challenge at 0.1 ppm. After equilibration and monitoring instrument response to dye challenge, as described above, turbidity in the tank will be incrementally raised above background by addition of SDVB beads (GFS Chemicals) targeting measurement of instrument response at 5, 50, 100, 200 NTU particle loads. Subsequently dye challenge concentration will be increased to ca 1 ppm to assess turbidity effects on response linearity. Effects of chromophoric dissolved organic matter (CDOM) will be similarly assessed by standard additions of humic acid from a 100 ppm stock. Turbidity test conditions will be quantified by a benchtop turbidity sensor in NTU (e.g. Hach 1100AN); CDOM will be determined by absorbance spectroscopy on filtered samples (see below) and EEMS.

*Temperature* – The thermal environment can affect all aspects of the sensor measurement system and, to a greater extent, the optical properties of the challenge solutions. Therefore, our analysis will restrict tests to a single challenge compound BB3 for which we have previously characterized the temperature dependence of fluorescence ( $-1.56\% \pm 0.06\% / ^\circ\text{C}$ ) to provide a reference for comparison. In addition to the 15 °C tests, additional BB3 concentration challenges will be performed in tanks held at 5 and 25 °C. The response factor for each instrument should change at the same level as the dye thermal response if the sensing system has minimal thermal dependence in its detection performance.

#### **4.2. Performance against crude oil challenge compounds and dispersants in a Wave Tank Test**

A test application of instrument response against crude oil compounds, with and without addition of dispersant, will take place in a simulated water column using the DFO/US EPA Wave Tank Facility located at the Bedford Institute of Oceanography, Dartmouth, Nova Scotia, Canada. Reference samples will be collected from the tank to allow real-time characterization of the sample water with three-dimensional Excitation/Emission spectroscopy (EEMS). A goal of this test is to determine how reliably instruments reproduce the sensitivity and range of response to variable concentrations of two different types of crude oil that would be predicted based on manufacturer's specifications of excitation and emission sources/sensors and the actual EEMS spectra of the samples. A complete three-dimensional EEMS will be obtained for every type of oil and oil/dispersant combination at the time of each experiment, which will allow for interpretation of sensor response that may result from "bleed through" or scatter that leads to sensitivities that are unexpected, based on manufacturer's reported wavelength ranges.

We will conduct experiments to examine instrument performance against two types of crude oil, Louisiana Sweet Crude (LSC) and Marine Diesel (IMO-B). Tests will be run under two conditions including the pure oil compounds and with compounds at oil to dispersant ratio of 20:1. During each experimental configuration, the concentration of oil will be diluted from an initial concentration of approximately 10 ppm down to extinction, with measurements made at several points during the time course of dilution. Experiments will be run on fresh (unweathered) mixtures of oil and dispersant only.

The test materials will be created experimentally at the Bedford Institute of Oceanography (Department of Fisheries and Oceans, Halifax, Nova Scotia) using Louisiana Sweet Crude source oil and Corexit 9500 dispersant. Preparation of the experimental material will permit generation of sufficient material to support simulated in-situ deployment of test instruments in the wave tank.

A LISST will also be deployed to confirm degree of physical dispersion. Reference samples collected from the wave tank will be collected for analysis on fixed wavelength and scanning fluorimeters to confirm degree of chemical dispersion. The latter analysis will also generate EEM signatures for the various oil mixes being used. We expect to conduct 8 individual experimental "runs" of the wave tank during the tank test, which would include duplicate runs for each of two oil compounds at each of two dispersant ratios. For each experiment, the initial conditions will include oil at concentrations in the 10 ppm range; to achieve dilution during the experiment, the tank will be run in "flow through" mode with filtered seawater used to dilute the oil to extinction. To evaluate the concentration of oil during the experiment, water from the effluent will be sampled and analyzed for hydrocarbons at five time points during the dilution series for each experimental run. Satisfactory analysis will require each of these samples to be collected in triplicate; two points at the beginning of the experiment can be analyzed by Gas Chromatography with a flame graphite detector (GCFID); once concentrations are lower (the last three time points), the samples will be analyzed by Gas Chromatography with a mass spectrometer (GCMS).

### 4.3. Field Tests

#### 4.3.1. Vertical Profiling

The vertical profiling application will be conducted at two test sites in the northern Gulf of Mexico onboard the R/V *Acadiana* (Louisiana Universities Marine Consortium). One site is adjacent to an oil installation in the Mississippi Canyon (the MC-20 block, 28° 56'N, 88° 58'W) at 160m depth and the other is located at a shipwrecking site leaking oil off Terrebone Bay (position TBD). Prior to the profiling cast, an exploratory profiling will be done to determine the best location of detecting oil within each of the sites. To avoid contamination between casts, the CTD rosette will be cleaned with a dilute, non-fluorescent, surfactant solution between profiles. The actual test will consist of 2 or 3 profiling casts with hydrocarbon sensors at each site and 1 profiling cast conducted at a control station adjacent to, but outside, any observed oil plume. The profiling test will compare simultaneous instrument measurements and discrete reference water samples collected at five discrete depths throughout the water column. Sampling depths will be spaced to provide one reference sample in the surface mixed-layer, and two each within regions of maximum and minimum oil concentrations in order to capture the maximum range in detectable hydrocarbon concentrations. One of the five discrete depths will be sampled in replicate with two independent water collection bottles. Exact sampling depths will be determined on the basis of the CTD profile in real-time during the downcast of the rosette system. The rosette and test instrument assembly will be lowered and raised at a standard rate of approximately 0.25 m/sec and the data collected by test instruments will be presented for both down- and up-casts. Test instruments will be mounted to an ECO Water Sampler rosette (SBE55) so that all instruments and water sample bottles are located at the same depth and as close as physically possible to each other. A standard and calibrated CTD package will be attached to the rosette and programmed to provide an independent record of conductivity, temperature, depth and time during each instrument sampling event. The tested instruments that are not a “stand-alone” package will be connected to a common WET Labs DH4 data logger powered with an external battery package. All hydrocarbon sensor profiling data will be synchronized by each timestamp to the CTD profiling data.

*Reference Water Samples* - Reference hydrocarbon samples will be collected only during the CTD up-cast. At each of the selected depths, the rosette will be paused for 2 minutes to ensure that all test instruments have stabilized prior to water sampling at that specific depth. After the 2 minute delay, each water sample bottle will be fired at the determined depth and the CTD timestamp will be synchronized to the hydrocarbon test instruments. The reference water samples will be matched up with the hydrocarbon sensor data by averaging the instrument readings for 10 seconds before and after the specific time the water bottle was fired. Bottle numbers, depth, and CTD profile number will be recorded in a field data log. Water samples will be collected immediately upon retrieving the rosette on deck, following the same procedures as defined for the mooring test.

### ***4.3.2 Moored Deployment***

A moored application test will be conducted by the Chesapeake Biological Lab ACT Partner Institution within Winans Cove, Baltimore Harbor, MD. The port of Baltimore is highly industrialized, especially in the area surrounding Winans Cove. Runoff from industry and nearby Interstate 95 directly impacts the test area, especially during rains. The instruments will be deployed on a pontoon buoy at the end of a US Government pier. The pier is behind a locked gate, guarded and only accessible to authorized personnel. A weather station will provide continuous weather monitoring on the deployment site. Baltimore Harbor has been well studied and water quality data for the months of August through October is readily available from the Maryland Department of Natural Resources and Maritime Environmental Resource Center. The average temperature for those months is 72.3°F (range: 57-85°F), salinity is 9.9 ppt (range: 1.7-15.6 ppt), chlorophyll is 12.4 µg/L (range: 0-165 µg/L), turbidity is 4.07 NTU (range: 0-101.2 NTU) and TSS is 6.37 mg/L (range: 1.69-20.4 mg/L).

The field mooring test will follow after the profiling test during the month of August. The moored test will run for a duration of four continuous weeks. Prior to deployment, ACT will clean and service the instruments according to the written protocols of the companies. ACT will provide the companies with a copy of the instrument recorded data to confirm that the instruments are still operating properly and suitable for use at the next site. We will provide 3-4 weeks in-between the field tests in order to allow for the data check and, if necessary, shipment of a replacement unit. Alternatively, companies can simply provide 2 sets of instruments to ACT and one would be shipped to each new test site. Instruments will only be removed from the water after the test period is complete, or in the event of an obvious problem or environmental condition that could jeopardize the safety of the instruments.

*Instrument Setup* - Prior to deployment, all instruments will be set up at the field site by a trained ACT staff member following established SOP's that will be developed in collaboration with the manufacturers at the Instrument Training workshop to be conducted in May 18-20, 2011 in Moss Landing, CA. In the event that any initial calibration is required, the manufacturers can either supply their own certified standards for calibration or submit a purchasing requirement list to ACT at least 4 weeks in advance of any initial testing. Instruments will be programmed to record data based on a time interval that will allow for a 30 day deployment. Intervals will be selected such that there is a common 30 minute interval achieved by all instruments. This schedule will allow us to coordinate our reference sampling for all instruments. Internal clocks will be set to local time and synchronized against the time standard provided by [www.time.gov](http://www.time.gov). In high flow coastal environments, clock drift could lead to significant bias. We will examine and record any clock drift in the final reports.

*Instrument Deployment* - A photograph of each individual instrument and the entire instrument rack will be taken just prior to deployment and just after recovery to provide a qualitative estimate of biofouling during the field tests. All instruments will be exposed to an internally defined reference solution (e.g. BB3) made up of ambient field site water both before and after deployment as an estimate of calibration drift over time. Salinity, chlorophyll, CDOM, and turbidity will also be determined on the ambient water used for the dye standard. The post-deployment reading will be taken after the instruments are cleaned according to manufacturer specifications. Instruments are to be set-up as self-recording but should a manufacturer choose,

they may add a real-time telemetry component to the test instrument. The manufacturer will be responsible for adding this additional component including all required hardware and software. ACT can facilitate providing server space or web portal access. Manufacturers will train ACT on the protocols on data down-loading and processing during the Instrument Training workshop. A copy of all instruments test data will be given to the companies after each test application and its receipt verified in writing before clearing any memory or data files. If possible, all original data will be left on the instrument for the entire verification when it is returned to the company.

*Deployment Rack* – We will work with the instrument manufacturer to design an appropriate deployment rack for their analyzer. The goal will be to arrange all test instruments in a manner so that we can collect a single representative field sample that is no more than 1 m apart from any of the individual sampling inlets. We will conduct an initial test of the sensor mounting configuration to ensure that there is no interference among instruments. The test will be conducted during the training workshop and will involve the direct participation of the manufacturer representatives. The deployment frames will be arranged so that all of the instruments remain at a fixed depth of 1 m below the water surface (using a float system or fixed dock in environments not affected by tidal changes or strong wave action). A calibrated CTD package will also be attached to the mooring at each test locale and programmed to provide an independent record of temperature at the same depth and the highest required frequency to match any of the test instruments.

*Reference Water Sampling Schedule* – The sampling frequency will be structured to examine changes in water quality and hydrocarbon concentrations over daily and weekly time scales. Due to holding time constraints for hydrocarbon analyses, and logistics of shipping, we will conduct multiple time-point sampling over three consecutive days during each week over the month duration, and then ship those samples in batches to the contract lab for analysis. Specifically, on each of the sampling days we will collect duplicate reference samples spaced at one-hour intervals. The duplicate samples will help to identify fine-scale variability within the environment being measured by the test instruments. This sampling schedule will result in at least 48 potential reference samples (each collected in duplicate) against which we can compare instrument response, and should be sufficient to capture event based scales of variation and provide a continuous check on instrument performance throughout the deployment. The specific timing of when water samples will be collected will be left up to the individual sites, but with the goal of capturing maximum variations in water quality. All sampling times will be recorded on logsheets and entered into a database for final data comparisons.

*Reference Water Sample Collection* – During moored deployments two standard 4L Van Dorn trace metal compatible water sampler will be used at the field test site to collect duplicate water samples for reference measurements. These samples will be used to examine instrument performance and stability over time. Water sample collections will be timed to correspond directly with the instrument readings. The water samplers will be lowered to the same depth and as close as physically possible to the sampling inlets and should be no more than 1 m from any of instrument sampling inlets. The water samplers will be soaked at sampling depth for 1 minute prior to sampling. If water is not flowing the samplers should be moved to ensure that it is being flushed with the ambient water. The water samplers will be triggered to match the programmed sampling times of each instrument. Sample processing for hydrocarbon analysis will be done according to the SOP's of the contract lab (TestAmerica) using designated sample bottles cleaned and provided by the lab. For EEMS analysis, four 20 mL glass scintillation vials will be

rinsed and filled directly from the spigot to overflowing and immediately capped. Finally, a 1 L amber polycarbonate bottle will be rinsed and filled for processing additional sub-samples for CDOM, turbidity, and chlorophyll back at the lab (as described below). Processed samples will be stored in cold (ca 4 °C with ice packs) in dark conditions. These conditions will be maintained during transport from the field and during weekly shipping to MLML and the contract lab for analysis. Once per week, Type I lab water will be loaded into the clean Van Dorn sampler, taken to the sampling locale and a corresponding set of field blank sample bottles filled to provide monitoring for potential environmental contamination. All personnel handling sampling gear and sample bottles will wear powder free polypropylene or nitrile gloves to minimize the risk of inadvertent sample contamination.

*Cleaning sampling apparatus* – All sample glassware for hydrocarbon analyses is provided by the contract lab and cleaned according to their SOP's. All sample glassware provided by ACT for EEMS analysis will be detergent cleaned (ISOClean), DI rinsed, 10% HCl cleaned MilliQ rinsed, air dried and baked at 450 °C for 4h to remove organics. Cleaned glassware will be sealed until use. Plastic sample ware will be detergent and acid washed with a final MilliQ rinsed before storage. The water samplers will be rinsed with DI between every sample taken, wiped with a methanol saturated lens tissue, re-rinsed with DI water, and stored closed. The samplers will also be soaked in the environment for 1 minute prior to collecting a new sample. At the end of each sampling day, the samplers will be acid washed, DI rinsed and allowed to air dry until next deployment.

*Sample Shipping* – Samples for hydrocarbon will be shipped to TestAmerica once per week according to their specified SOP's, specifically allowing for samples to be processed within the required 7 day holding time. Samples for EEMS, CDOM, and turbidity will be shipped unpreserved at 4 °C to MLML for analysis once per week during the deployment. One of the four replicates from each sampling timepoint will be reserved on site as a replacement in the event of loss or damage during shipping. It may also serve as an additional analytical replicate should the variance of the initial 3 replicates be too high. All samples will be recorded onto Chain of Custody forms, and include a description of the condition in which the samples were shipped and received. A copy of the form will be sent with the samples and the receiving laboratory will confirm receipt and condition of samples within 24 hours of their arrival by signing and faxing a copy of the form to the test site. Original copies of these forms will be maintained on site.

#### **4.4. Analysis of Reference Samples**

##### ***4.4.1. Hydrocarbon concentrations***

Diesel range hydrocarbons (C10 to C36) and volatile organic hydrocarbons will be analyzed by a contract laboratory, TestAmerica (West Sacramento Lab), following their internal SOP's based on EPA SW846 Method 8015B,C providing reporting limits of 50 ppb for this hydrocarbon range. In summary, for the diesel samples 2 - 1L amber glass bottles are needed for each sample and no preservatives are added to the bottles. For the gas sample, three 40 ml vials that include HCL as a preservative must be filled until the water crowns over the top of the vial.

The lid is flexible and is meant to accept the over filled vial to remove heads pace and bubbles. In addition, a trip blank vial will accompany all sample collections and shipments to assess for any potential contamination. Reference samples along with sampling blanks, will be shipped to the contract lab in batches at approximately three day intervals during deployments or post-cruise for profiling tests.

#### ***4.4.2. Spectrofluorometric characterization (EEMS)***

A SPEX ISA Fluoromax-2 scanning spectrofluorometer will be used to generate EEM spectra for all reference samples. The 150W Xe instrument lamp will be allowed to stabilize for 30 min before analysis of each sample batch. Excitation and emission grating wavelength calibration and lamp intensity will be verified and recalibrated at a minimum of once per day by verifying peak excitation lamp band at 476 nm and a water Raman band at ex/em 350/397 and intensity, respectively, as described in the instrument manual. EEM will be determined over an excitation range of 220-500 nm at 5 nm intervals and emission range of 300 – 550 nm at 1 nm intervals. A bandpass of 5 nm will be used on both excitation and emission optics with an integration time of 0.1 s. Fluorescence emission scan intensities will be corrected for lamp intensity and photomultiplier efficiency and dark counts subtracted. At the beginning and end of each analytical batch, MilliQ water, 10 ppb BB3 and 10 ppb QS will be analyzed sequentially to provide index of baseline and lamp intensity drift enabling standardization across analytical batches. Unfiltered samples will be read to provide better correspondence between test instrument readings and EEMS characterization. Spectrasil quartz cuvettes will be used for all sample analysis.

Dark count subtracted peak fluorescence intensity will be regressed against challenge compound concentration at each test level to define the standard response factor. Excitation and emission windows for each instrument (as provided by manufacture) will be mapped onto EEMS space and fluorescence intensity similarly regressed and compared to regression of instrument reads versus challenge concentration in order to identify sources of response variation observed.

#### ***4.4.3. Colored Dissolved Organic Matter (CDOM)***

Sample preparation:

Approximately 50 ml of the CDOM designated subsample will be subsequently filtered using 47 mm GF/F filters (0.7  $\mu$ m pore size) with low vacuum pressure (<5 in Hg) using a bell jar and acid-cleaned, combusted glass-ware. The first 10 ml of sample will be used to rinse the filter and collection beaker and discarded. The remaining 40 mls of filtrate will be poured into a 50 ml BD Falcon storage centrifuge tube, capped, wrapped with Parafilm, labeled, and stored in a refrigerator (4° C) until analysis.

Sample Spectrophotometric Analysis:

The sample and 200-300 ml of MilliQ will be equilibrated to room temperature (failure to match the blank and sample temperature results in an artifactual feature in the spectrum at long wavelengths). The spectrophotometer will be allowed to warm up (30-40 min) before scanning and the scanning set for 1-2 nm intervals, with a 4-6 nm slit width. When using a dual-beam spectrophotometer, zero will be set with MilliQ water in cuvettes in both the sample and

reference positions (dual-beam instrument) or by setting 0 and 100% transmission with a MilliQ blank (single-beam instrument). Matched 10 cm quartz or optical glass cells will be used for a dual-beam spectrophotometer and a single cell in a single-beam spectrophotometer. A rescan of the blank will be run to verify that the instrument has not drifted and to define the amplitude of noise. The sample will be mixed by rocking the centrifuge tube before decanting the sample. The sample cuvette will be emptied and rinsed with 10-15 ml of sample to ensure that there are no air bubbles in the light path. Scans will be run between 250 and 800 nm (quartz) or 350 and 800 nm (optical glass) and electronic files will be saved for each sample. The cuvette will then be rinsed with MilliQ between samples. A MilliQ blank will be run between every 5th sample. When using a single-beam spectrophotometer, it will be reset the 0 and 100% T. For dilute samples (those that are not significantly yellow in color when viewed down the 10 cm pathlength of the cuvette or have OD < 0.2 at 400 nm), triplicate scans of each sample will be run and average the scans to reduce the effect of noise.

Parameterizing absorption:

The absorption spectrum of CDOM follows an approximately exponential decline in the visible (400-700) wavelengths. Absorption from optical density will be calculated by subtracting the optical density at 750 nm to correct for residual scattering and converted as:

$$a[\lambda] = \frac{2.3(OD[\lambda] - OD[750])}{d} \quad (1)$$

where  $a[\lambda]$  is absorption ( $\text{m}^{-1}$ ) at wavelength  $\lambda$ ,  $OD$  is optical density (dimensionless), and  $d$  is pathlength (0.1 m).

Because the magnitude of the parameters that describe the CDOM fit are dependent on the range and means of the curve fitting, it is critical to employ the same protocol. A non-linear fit over the range 400 – 700 nm (Equation 2) will be used. This equation minimizes the effect of the unfavorable signal to noise ratio at long wavelengths on the goodness-of-fit at the wavelengths of most interests (i.e. the excitation wavelengths in the 400 – 500 nm range); is less sensitive to thermal artifacts at long wavelength; and is less sensitive to the range of wavelengths used than the linear fit (Equation 3).

$$a[\lambda] = a[400]e^{(-S\lambda)} \quad (2)$$

$a[\lambda]$  is absorption ( $\text{m}^{-1}$ ) at wavelength  $\lambda$ ,  $a[400]$  is absorption ( $\text{m}^{-1}$ ) at the anchor wavelength of 400 nm, and  $S$  is the spectral slope ( $\text{nm}^{-1}$ ). Note that wavelength must be expressed as  $\lambda - 400$  before fitting for the anchor value to be at 400 nm.

An alternative for those without a non-linear fitting package is to log-transform the absorption data and fit to the linear equivalent.

$$\log(a[\lambda]) = \log(a[400]) - S\lambda \quad (3)$$

Note that the anchor wavelength must be expressed as the anti-log for reporting. Because the linear fit is sensitive to the dispersion due to noise at long wavelengths, this is best fit only for the interval 400-500 nm.

The parameter estimates and standard errors for  $a[\lambda] S$  and the value of  $R^2$  will be reported.

#### **4.4.4. Chlorophyll *a***

Chlorophyll grab samples will be analyzed on a Turner Designs 10AU fluorometer from samples filtered on 2.5 cm GF/F filters and frozen at -20 °C until analyzed according to Parsons, T. R., Y. Maita, and C. M. Lalli. 1984. A manual of chemical and biological methods for seawater analysis. Pergamon Press, New York. 174 p. Optimum filtration volumes will be determined on site; Baltimore Harbor will likely require 25 mL's and offshore Gulf of Mexico 250 mL's. All chlorophyll analyses will be performed by the Chesapeake Biological Laboratory according to their existing SOP's. The laboratory is a State of Maryland certified lab and has undergone previous audits by ACT during prior evaluations. Samples will be shipped to CBL in liquid nitrogen dry shippers to ensure they remain frozen at the required temperature.

#### **4.4.5. Turbidity**

Turbidity concentrations of reference grab samples will be determined by a Hach 1100AN benchtop turbidity sensor in NTU. The lab analyzer will be calibrated with certified standards prior to use and a QA check of the standard will be run during each analytical batch. Samples will be collected in pre-cleaned 50 ml polypropylene centrifuge tubes, gently mixed prior to reading and analyzed within 2 hours of collection. The same instrument will be used at each test site.

### **4.5. Ancillary In situ Environmental Data**

At the moored test site, a calibrated CTD package will be attached to the test instrument rack and positioned at the same depth as the instruments to provide an independent record of conductivity and temperature measured at 15-minute intervals. Each mooring will also be equipped with an RBR TR-1060 temperature sensor to establish an accurate temperature history for the site. This sensor has a stated accuracy and resolution of 0.001 °C and 0.0005 °C, respectively. Each TR-1060 will be independently calibrated and certified prior to the use in this Verification. Lastly, the mooring will be equipped with a YSI 6600 EDS sonde outfitted with sensors for temperature, conductivity, chlorophyll, and turbidity. Chlorophyll and turbidity sensors contain anti-biofouling wiping system. In-situ measurements will be generated every 15 minutes over the duration of the moored field tests.

In conjunction with each water sample collection, technicians will record basic site-specific conditions on standardized log sheets including: date and time, weather conditions (e.g., haze, % cloud cover, rain, wind speed/direction), air temperature, recent large weather events or other potential natural or anthropogenic disturbances, tidal state and distance from bottom of sensor rack, and any obvious problems or failures with instruments. Datasheets will be

transmitted on a weekly basis to the ACT Chief Scientist, for data archiving and ACT personnel performance QA/QC.

Each test site will either establish or identify the closest meteorological station (and river discharge gauge where appropriate) that can record air temperature, humidity, directional wind speed, precipitation on a continuous basis to help identify the timing and intensity of any event based changes at the field test locations.

Ancillary data will be used in a qualitative sense to understand the history of weather patterns and changes in ambient water quality conditions. These data will not be used for any direct calibration, correction, or statistical comparison to the reported test data.

## 5.0. Verification Schedule

Note that the below schedule is provisional and actual dates for each milestone may vary.

- The Final ACT Hydrocarbon Sensor Performance Verification Contract will be sent to Manufacturers by May 1, 2011.
- Signed contracts are due back to ACT Headquarters by May 15, 2011.
- All relevant deployment equipment and 1 or 2 sets of complete instrument packages should be delivered to the Moss Landing Marine Lab test site by May 12, 2011.
- A Training Workshop on the actual will be held at MLML on May 18-20, 2011. Manufacturers will train ACT staff in the set-up, calibration, and use of their instruments during a 3-4 hour training session for each manufacturer.
- The laboratory test for the verification will take place at MLML from May 23-27, 2011.
- Instruments will be mailed from MLML to Stennis Space Center, University of S. Mississippi (c/o Dr. Kjell Gunderson) by June 15, 2011 in preparation for the profiling field test in the Gulf of Mexico.
- Gulf of Mexico profiling field test application will occur during July 9-12, 2011.
- The mooring test application will occur in Baltimore, Maryland during August 2011.
- Instruments will be mailed from Baltimore to the Bedford Institute of Oceanography (c/o Dr. Paul Kepkay) for the wave-tank, crude-oil test by October 1, 2011. The Bedford lab test of crude oil compounds will be conducted during the month of October 2011.
- ACT Chief Scientist, Technical Coordinators, Technical Advisory Committee, and Quality Manager, will meet for 3 days to analyze results and evaluate the Performance Verification processes in January 2012.
- ACT Performance Verification Statements for each individual instrument will be drafted and sent out for review by, Technical Advisory Committee, Technical Coordinators, Quality Manager, Partners, and Stakeholders in February 2012.

- Final Performance Verification Statements will be sent to Manufacturers in March 2012.
- One page comment letters from Manufacturers are due two weeks after receiving the final reports.
- Final Performance Verification will be released to the public in April 2012.

## 6. Data Recording, Processing and Storage

This section describes methods employed during data recording, processing, and storage to minimize errors and assure high quality analyses in the Performance Verification Statements.

### 6.1. Documentation and Records

A variety of data will be acquired and recorded electronically and manually by ACT staff in this Verification. Operational information and results from the reference method will generally be documented in a field/laboratory record book and on the data sheet/chain-of-custody forms (see below). An electronic copy of these raw data will be transferred to the ACT Chief Scientist weekly, who will store it permanently along with the rest of the study data.

The results from the test instruments will also be recorded electronically. Test data will only be downloaded and analyzed upon completion of the field deployments. Once collected, one copy of these data will reside at the corresponding ACT test facility and a second copy at ACT Headquarters until the entire Verification is finished. The table below summarizes the types of data to be recorded and the process for recording data.

| <b>Data to be Recorded</b>                                       | <b>Responsible Party</b> | <b>Where Recorded</b>   | <b>How Often Recorded</b>                                | <b>Purpose of Data</b>  |
|--|--------------------------|---|--|---|
| Dates, times of sampling events                                  | Each ACT Partner         | Field record books/data sheets                                      | Each reference sample collection and laboratory analysis | Used to organize/check test results; manually incorporate data into spreadsheets - stored in study binder |
| Test parameters (site conditions)                                | Each ACT Partner         | Field record books/data sheets                                      | Each reference sample collection                         | Used to define site characteristics; manually incorporate data into spreadsheets - stored in study binder |
| Test instrument calibration data                                 | Each ACT Partner         | Laboratory record Book/data sheets                                  | Start/end of test  | Document correct performance of test instrument   |
| Test instrument data<br>- digital display<br>- electronic output | Each ACT Partner         | - Data sheets<br>- Instrument data acquisition system (data logger) | After completion of the 26-day field deployments         | Used as part of test results; incorporate data into electronic spreadsheets - stored in study binder      |
| Reference analytical results                                     | MLML Lab                 | Laboratory record Book/data sheets                                  | At the conclusion of each analytical sample batch.       | Used to check test results; manually incorporate data into  |

|                                      |          |                                     |   |   |
|--------------------------------------|----------|-------------------------------------|---|---|
|                                      |          |                                     |   | spreadsheets - stored in study binder                         |
| Reference calibration data           | MLML Lab | Laboratory record books/data sheets | Whenever zero and calibration checks are done | Document correct performance of reference method              |
| Performance evaluation audit results | ACT HQ   | Laboratory record books/data sheets | At times of performance evaluation audits     | Test reference method with independent standards/measurements |

## 6.2. Data Review

All data are to be recorded directly in the field/laboratory record book as soon as they are available. Records are to be written in water-proof ink, written legibly, and have any corrections initialed by the person performing the correction. Any corrections will be crossed out with a line (not blackened or white-out), and the correction made, with initials and date of correction. These data will include electronic data, entries in field/laboratory record books, operating data from the ACT Partner test facility, and equipment calibration records. Records will be spot-checked within two weeks of the measurement to ensure that the data are recorded correctly. The checker shall not be the individual who originally entered the data. Data entries shall be checked in general for obvious errors and a minimum of 10 percent of all records shall be checked in detail. Errors detected in this manner shall be corrected immediately. The person performing the review will add his/her initials and the date to a hard copy of the record being reviewed. The ACT Technical Coordinator (TC) will place this hard copy in the files for this Verification. In addition, data generated by each ACT Partner test site will be provided to the ACT Chief Scientist and reviewed before they are used to calculate, evaluate, or report results.

## 7. Quality Assurance/Quality Control

The Hydrocarbon Sensor Verification will be implemented according to the test protocols and technical documents (e.g. Standard Operating Procedures) prepared during the planning stages of the test. Prescribed procedures and a sequence for the work have been defined and all work performed during the Verification shall follow those procedures and sequence. Technical procedures include methods to assure proper handling and care of test instruments. All implementation activities are documented and are traceable to the test/QA plan and SOPs and to test personnel.

### 7.1. Laboratory Test Quality Control

All laboratory instrumentation at MLML used to analyze reference samples will be calibrated by a trained technician using established SOP's along with the instrument manuals supplied by the manufacturer. MLML will maintain a log of all calibration and reference QA/QC samples analyzed during the Verification. The logs shall include at least the following information: name and identification number of instrument, date of calibration, and calibration results. These logs shall be provided to the ACT Chief Scientist and maintained in a master calibration file as part of the QA/QC records. QA/QC samples will include:

- a. Recovery of Known Additions – Matrix Spikes. Use the recovery of known additions as part of analyses protocols for 10% of samples by using the concentrated solutions so volume change in sample is negligible.
- b. Analysis of Externally Supplied Standard. Whenever analyses of known additions do not result in acceptable recovery, analysis of externally supplied standards (certified reference materials) is necessary. Laboratory control standards are analyzed with concentrations between 5 and 50 times the MDL (Method detection level; the lowest reportable value) or near sample ambient levels, whichever is greatest.
- c. Analyses of Blanks.
  - a. Analyze a minimum of 5% of the sample load as blanks. These blanks should include:
    - i. Field Blanks – (see Section 7.2).
    - ii. Sampler Device Blank – (see Section 7.2).
    - iii. Filtration Blanks – (see Section 7.2).
    - iv. Reagent Blanks - mill Q,
    - v. Instrument Blanks dark counts and Raman intensity
- d. Calibration with Standards.
  - a. Measure at least three different dilutions of the standard when analysis is initiated. Verify the standard curve daily by analyzing one or more standards within the linear range, as specified in the individual method. Results are reported which are in the range of standard dilutions used.
  - b. Performance Evaluation Audit. Perform a verification of your calibration standard (see Section 7.3).
- e. Analysis of Duplicates. Analysis of duplicate sample is effective for assessing precision, which is accomplished by analyzing 5% or more of the samples in duplicate (see Section 7.2).
- f. Control Charts. Three types of control charts are used in laboratories: a mean chart for **standards** - laboratory control standards or calibration check standard; a mean chart for background or reagent **blank**; and a range chart for **replicate** analyses.
- g. Records of Standards and Chemicals: Records must be kept of all standards, solvents, and other chemicals used during analysis and extraction. This information must include: Name of Chemical/CAS#, Manufacturer, Lot#, the date received by laboratory, expiration date, the date the chemical was opened for use, and NIST-traceability. Material Safety Data Sheets must be on file in the laboratory and all safety and storage precautions related to those chemicals must be followed.
- h. Blind Sample Run: Ideally, all samples should be run as “blind” samples – by the sample number only.

## 7.2. Field Test Quality Control

Field quality control represents the total integrated program for assuring the reliability of measurement data. It consists of the daily field logs, quality control samples, and sample custody procedures.

### Field Logs

Standard, uniform field logs should be maintained for all fieldwork. These logs should report name of staff conducting fieldwork, date (month, day, and year), operating status of all equipment, and manual readings of environmental conditions.

### Field Quality Control Samples

To ensure that the reference sample collection and analysis procedures are properly controlled, field blanks and laboratory replicate samples will be taken once a week during the test period. These will be analyzed in the same manner as the collected reference samples and should comprise a minimum of 5% of the total samples collected and shipped.

1. Field Blank: Sample containers filled with distilled or deionized water are taken to the field and returned. This sample assesses contamination during transport and storage.
2. Sampler Device Blank: This sample is obtained by passing deionized water through a non-dedicated sampler, such as a portable pump, collection bottle, or rosette bottle. This blank is used to test contamination by a sampler.
3. Filtration Blank: Sample is collected by passing the deionized water through the field filtering apparatus to test the contamination by a filter and apparatus.
4. Field Duplicate: Two or more samples are collected simultaneously at a location to determine the variability associated with sample collection. This is to occur weekly at random during the test.

### Sample Custody

All reference samples will be accompanied by the sample collection sheet and Chain-of-Custody (COC) forms. The COC specifies time, date, sample location, unique sample number, requested analyses, sampler name, required turnaround time, time and date of transaction between field and laboratory staff, and name of receiving party at the laboratory. Proper labeling of sample bottles is critical. The COC is a mechanism by which a sample can be tracked through the various phases of the process: collection, shipping, receiving, logging, sample prep/extraction, analysis and final data QA/QC review.

### Sample Handling

All collected reference samples at each test site will be handled in the same manner. All environmental reference samples should be processed while wearing clean laboratory gloves to minimize potential sources of contamination. Each reference sample should be dated and coded according to site and sample sequence. The actual sample container should be labeled with a number for identification. The reference sample number should be used in all laboratory records and COC's to identify the sample. Transfer of reference samples from field personnel to laboratory personnel is also recorded on the COC and records are maintained in the laboratory with the names and signature of persons leaving and receiving the custody. All logs shall be

duplicated weekly. The original shall be retained at the ACT Partner site and a copy shall be sent to the ACT Chief Scientist. Samples stored for any period of time shall be routinely inspected by the TC to assure proper preservation and label integrity. Accumulated samples are to be shipped for analysis each week to minimize holding time.

### **7.3. Audits**

Independent of the QA activities that are being conducted at each Partner test facility, the ACT Chief Scientist will be responsible for ensuring that the following audits are conducted as part of this verification a minimum of two ACT Partner test sites. Audits shall be performed by QA Manager, who shall be independent of direct responsibility for performance of the Verification.

#### Performance Evaluation Audits

A performance evaluation audit will be conducted of the MLML to assess the extent and compliance of their QA program and adherence to SOPs.

#### Technical Systems Audits

ACT's QA Manager will perform a Technical Systems Audit (TSA) at least twice during this Verification. The purpose of this audit is to ensure that the Verification is being performed in accordance with the test/QA plan, published reference methods, and any SOPs used by the Partner test facility. In this audit, the ACT QA Manager may review the reference methods used, compare actual test procedures to those specified or referenced in the test/QA plan, and review data acquisition and handling procedures. A TSA report will be prepared, including a statement of findings and the actions taken to address any adverse findings.

#### Data Quality Audits

ACT's QA Manager will audit at least 10% of the data acquired in the Verification to determine if data have been collected in accordance to the test/QA plan with respect to compliance, correctness, consistency, and completeness. The ACT QA Manager will trace the data from initial acquisition to final reporting.

#### Assessment Reports

Each assessment and audit will be documented, and assessment reports will include the following:

- a. Identification of any adverse findings or potential problems.
- b. Response to adverse findings or potential problems.
- c. Possible recommendations for resolving problems.
- d. Citation of any noteworthy practices that may be of use to others.
- e. Confirmation that solutions have been implemented and are effective.

#### **7.4. Corrective Action**

The ACT Chief Scientist, during the course of any assessment, audits, or review of laboratory results will identify to the party performing the specific activities any immediate corrective action that should be taken. If serious quality problems exist, the ACT Chief Scientist is authorized to stop work. Once the assessment report has been prepared, the ACT Chief Scientist will ensure that a response is provided for each adverse finding or potential problem and will implement any necessary follow-up corrective action. The ACT QA Manager will ensure that follow-up corrective action has been taken.

#### **7.5. QA/QC Document Control**

It is the responsibility of the ACT Chief Scientist to maintain QA/QC records, which shall include the following:

- a. Records of the disposition of samples and data.
- b. Records of calibration of instruments.
- c. Records of QA/QC activities, including audits and corrective actions.

#### **8. Roles and Responsibilities**

The Verification is coordinated and supervised by the ACT Chief Scientist and ACT Partner institution personnel. Staff from the Partner institutions will participate in this test by installing, maintaining, and operating the respective technologies throughout the test; operating the reference equipment, collecting the water samples, downloading the data from the instrument package, and informing the ACT Chief Scientist staff of any problems encountered.

Manufacturers' representatives shall train ACT Partner staffs in the use of their respective technologies and, at their discretion, observe the calibration, installation, maintenance, and operation of their respective technologies throughout the test. QA oversight is provided by the ACT QA Manager. In addition to aiding the development of these protocols, the external Technical Advisory Committee will be consulted during the evaluation in the event problems occur, will assist in the analyses of results, and will review the final Performance Demonstration Statement prior to release. Specific responsibilities are detailed below.

##### ACT Chief Scientist

The ACT Chief Scientist has the overall responsibility for ensuring that the technical goals and schedule established for the Verification are met. The ACT Chief Scientist shall:

- Prepare the draft Test Protocols/QA Plan and Performance Verification Statements.
- Revise the draft Test Protocols/QA Plan and Performance Verification Statements in response to reviewers' comments.
- Coordinate distribution of the final Test Protocols/QA Plan and Performance Verification Statements.
- Coordinate testing, measurement parameters, and schedules at each ACT Partner institution testing site.
- Ensure that all quality procedures specified in the test/QA plan are followed.
- Respond to any issues raised in assessment reports and audits, including instituting corrective action as necessary.

- Serve as the primary point of contact for manufacturers and ACT Partner Technical Coordinators.
- Ensure that confidentiality of proprietary manufacturer technology and information is maintained.

The ACT QA Manager shall:

- Review the draft Test Protocols/QA Plan and Performance Verification Statements.
- Conduct at least one technical systems audit (TSA) once during the Performance Verification.
- Audit at least 10% of the Verification data.
- Prepare and distribute an assessment report for each audit.
- Verify implementation of any necessary corrective action.
- Notify the ACT Chief Scientist if a stop work order should be issued if audits indicate that data quality is being compromised or if proper safety practices are not followed.
- Provide a summary of the audit activities and results for the Performance Verification reports.
- Review the draft Performance Demonstration reports and statements.
- Have overall responsibility for ensuring that the test/QA plan and ACT QMP are followed.
- Ensure that confidentiality of proprietary manufacturer technology and information is maintained.

ACT Technical Coordinators at each Partner institution shall:

- Assist in developing the Test Protocols/QA Plan.
- Allow facility access to the manufacturers and ACT Headquarters representatives during the field test periods.
- Select a secure location for the tests.
- Install, maintain, and operate the test hydrocarbon sensors at their respective test locations according to the specified instructions of the manufactures and these protocols.
- Perform sample collections and analyses as detailed in the test procedures section of the test/QA plan.
- One member of TC team will conduct 10% data audit as described in QA procedures. This will be done on all data logs and electronically entered data.
- Provide all test data to the ACT Chief Scientist electronically, in a mutually agreed upon format.
- Remove sensor systems and other related equipment from the test facility upon completing the Performance Demonstration test.
- Provide the ACT Chief Scientist and Quality Managers access to and /or copies of appropriate QA documentation of test equipment and procedures (e.g., SOP's, calibration data).
- Provide information regarding education and experience of each staff member involved in the demonstration.
- Assist in ACT's reporting of their respective test facility's QA/quality control results.
- Review portions of the draft Demonstration Statements to assure accurate descriptions of their respective test facility operations and to provide technical insight on demonstration results.

The Moss Landing Marine Laboratory shall:

- Perform reference sample measurements.
- Perform all QA/QC analysis as detailed in these Test Protocols.
- Provide the ACT Chief Scientist and QA Manager access to and /or copies of appropriate QA

- documentation of test equipment and procedures (e.g., SOPs, calibration data).
- Provide information regarding education and experience of each staff member involved in the demonstration.
  - Assist in ACT's reporting of their respective test facility's QA/quality control results.
  - Review portions of the draft Demonstration Statements to assure accurate descriptions of their respective test facility operations and to provide technical insight on demonstration results.

Manufacturers shall:

- Review the draft test/QA plan and provide comments and recommendations.
  - Approve the revised test/QA plan.
  - Work with ACT to commit to a specific schedule for the Verification.
  - Provide an operational sensor systems for each of the agreed upon test sites.
  - Attend an Instrument Training workshop in MLML to train ACT personnel on the set-up, calibration, use, and data management of their instruments.
  - Review and comment upon their respective draft Performance Verification Statements.
- Note: ACT reserves the right to dismiss any manufacturer from the Verification if it does not comply with agreed upon schedules or requirements.

External Technical Advisory Committee shall:

- Assist in developing the Test Protocols/QA Plan.
- Approve the final Test Protocols/QA Plan.
- Provide specific advice during testing.
- Review and comment upon draft Verification Statements.
- Approve final Verification Statements.

**9. External Technical Advisory Committee**

- Dr. Earle Buckley, North Carolina State University and ACT Advisor/QA Manager
- Dr. Michelle Woods, NOAA-AOML
- Dr. Kjell Gundersen, University of Southern Mississippi
- Dr. Paula Cobble, University of South Florida
- Dr. Brian Bergamashi, USGS, Sacramento
- Dr. Emmanuel Boss, University of Maine
- Dr. W. Scott Pegau, Alaska Oil Spill Recovery Institute
- Dr. Paul Kepkay, Centre for Offshore Oil Gas and Energy Research, Bedford Institute of Oceanography