CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

DEPARTMENT OF TOXIC SUBSTANCES CONTROL

TECHNOLOGY CERTIFICATION PROGRAM

Technology:

# Turner Designs TD-4100 On-Line Hydrocarbon Monitor

Manufacturer:

Turner Designs, Sunnyvale, California

Contract No. 94-T0732

## Evaluation Report

15 April 1997

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## FOREWORD

Effective January 1, 1994, Section 25200.1.5 of the California Health and Safety Code authorizes the State of California to certify the performance of environmental technologies that offer an environmental benefit. This includes measurement technologies. As part of this program, the State Department of Toxic Substances Control has evaluated a continuous on-line fluorescence monitor, Turner Designs Model TD-4100, for the detection of aromatic hydrocarbons in water. This report was prepared to show the results of this evaluation. The evaluation is based on a detailed review of validation materials submitted by the manufacturer and on specified original data generated by an independent laboratory, whose findings the evaluation team considered reliable.

## INTRODUCTION

A number of laboratory methods exist for the measurement of petroleum hydrocarbons in water, but continuous, real-time monitoring under field conditions is difficult. For some time, fluorescence-based methods have been known to be suitable for the detection of the fuels in water under field conditions (Ref. 28), because the aromatic hydrocarbons which are contained in raw petroleum, gasoline, diesel fuel, fuel oils, and other refined and residual pertroleum products have distinctive absorption and emission wavelengths. Detection of the monoaromatic hydrocarbons in the lighter fuels such as gasoline requires short wavelengths (ultraviolet) for excitation and emission. In contrast to detection, measurement of petroleum fuels in water is more difficult, because the fuels are complex mixtures with wide variation in hydrocarbon composition and other chemical and physical characteristics. Since the solubility of the petroleum hydrocarbons in water is low, any monitoring method must contend with the presence of dispersed product and the contamination of surfaces in the product stream. A fluorometer would offer a rapid and sensitive means of detecting petroleum-based hydrocarbons in water and would be suitable for on-line monitoring applications, provided that it is calibrated for the products to be monitored and capable of excluding interfering fluorescent materials, and if it is engineered to overcome these physical challenges and provide a sufficiently stable signal. Fluorometry usually does not require a pretreatment of the water samples. If sufficient specificity is designed into the equipment, through continuous, on-line monitoring of an influent or effluent stream, hydrocarbons in the aqueous stream can be immediately noticed, and with appropriate calibration and circuitry, can trigger an alarm.

## SUMMARY OF SCIENTIFIC PRINCIPLE

The technology is based on the principle of fluorescence detection of aromatic hydrocarbon molecules. An ultraviolet (UV) light source of a given wavelength energizes molecules with certain specific characteristics. These molecules absorb light energy of one or several specific wavelengths (excitation wavelengths) and emit light energy of one or several longer wavelengths (emission wavelengths). Fluorescence produces an emission fingerprint that is unique to each aromatic hydrocarbon. In sensitivity and simplicity of operation, fluorescence techniques can compete with other techniques that are based on light absorption (UV or IR) or light scatter. The measured intensity of the fluorescence (F) is proportional to the intensity of the excitation light source (I) and the concentration of sample (C) ($F = K \times I \times C \times k$, where $K$ = instrument amplification, $k$ = an instrument constant). As fluorescence increases with concentration, a quantitative estimate of the fluorescent material in the sample can be made, subject to several constraints which are discussed further below. A two-point calibration between raw fluorescence of the target hydrocarbons and their concentration is used by Turner Designs, as a sufficiently linear relationship exists over one order of magnitude, more or less, about a target concentration. This usually is the concentration where the instrument triggers an alarm and the user needs to take some action.

## BRIEF DESCRIPTION OF THE TECHNOLOGY

Turner Designs TD-4100 Continuous Online Monitor is a fluorometer that detects and measures aromatic petroleum hydrocarbons both in the dissolved and the dispersed state (droplets or particulate), through their fluorescent signature based on the scientific principle described above. The technology consists of a light source which is configured to generate uv or near-uv excitation light. The light passes though an excitation light filter chosen by Turner Designs based on the matrix and analyte(s) specified by the user. A free-falling sample stream is exposed to the filtered light. The flow cell shapes the geometry of the sample stream but the stream does not come in contact with an optical window. Therefore the flow cell is essentially non-fouling. The emitted light from fluorescence is collected at a 90 degree angle. In this manner, detection is restricted to light emitted from fluorescent molecules in the sample stream. The emitted light passes through an optical filter of specific wavelength and is measured by a photomultiplier. Readout is through an LCD screen which displays user-selectable readout in raw fluorescence .

The light source provides maximum excitation at the desired wavelength as determined by the excitation filter. A reference path provides source light to the photomultiplier tube which alternates between measurements of the source, dark current, and the emitted light. This eliminates error due to changes in the photomultiplier dark current. The water sample passes through a de-aerator tube to remove entrapped air from the treatment or pumping process. The de-aerator is arranged such that it will not affect volatile organic compounds in the sample stream. From the de-aerator the water falls by gravity through the sample block where the stream is exposed to the excitation light source. The principal components of the fluorometer are shown in Figure 1.

The Turner Designs TD-4100 On-Line Hydrocarbon Monitor is equipped with an alarm to alert the user of a change in petroleum hydrocarbon concentrations at the preset level or activating other system controls. This level is initially set for the user when the instrument is delivered but can be re-set by the user on a basis of safety considerations or regulatory limits. In emergency cases, instead of sampling the aqueous stream and waiting for laboratory results, the operator can immediately affect the monitored aqueous stream and prevent the intake or discharge of petroleum hydrocarbon-based pollutants. The Turner Designs TD-4100 On-Line Monitor has been applied to waters ranging from clear, filtered water to highly contaminated industrial process and wastewaters (Ref. 16).

## MATERIALS AVAILABLE FOR THIS EVALUATION

The following documents were available for this evaluation:

1. Application for California Technology Certification, with description of product to be certified. (Letter by Turner De-

signs to G. Wolfgang Fuhs, August 30, 1994.)

2. Fluorometric Facts: Oil in the Environment, Turner Designs, 16p., with 68 References; submitted in 1994. (Analysis of the peer-reviewed literature and Turner Designs in-house studies on the detection of crude oils and petroleum product by fluorescence in freshwater and ocean environments, including case histories in spill tracking through mobile use; relevant facts on properties and fate of petroleum products in water and consequences for fluorometer calibration.)

3. Certification of Turner Designs TD-4100 On-Line Hydrocarbon Monitor, letter by Turner Designs to G. Wolfgang Fuhs dated November 15, 1994, 12p. (Develops proposed product claims for certification.)

4. Turner Designs, Test Procedure, with test log form, Model 4000-AU (TRASAR 340)/TD4100 Digital Fluorometer, dated November 15, 1994. With Test Log, Model 4000-AU Digital Fluorometer, dated May 25, 1994. (Quality control protocol for TD-4100, including protocol for burn-in, electronics and wet testing.)

5. TD-4100 Optical Kits, Turner Designs, undated. (Parts listing of filter kits offered by Turner Designs by product category to be monitored, with wavelength peaks/ranges of excitation and emission light filters. This is a listing of default filter combinations; actual filter selection is based on tests with sample stream to be monitored, see text).

6. Turner Designs TD-4100 Field Test: Final Report, On-Line Oil on Water Monitor Trial, Ground Water Remediation Site, East Ridge Mall, San Jose. (Comparison of TD-4100 readings with laboratory analysis, 43 data points reported. Study performed on field site with the participation of Dames and Moore, Consultants and an inde-

Figure 1. Schematic of light path in TD-4100

pendent certified laboratory. See text for discussion.)

7. On-Line Monitoring of Oil in Water Using Fluorescence. (Turner Designs overview over applications of TD-4100; does not contain data.)

8. TD-4100 Instrument Specifications. (Published specifications of TD-4100.)

9. TD-4100 Gasoline and Diesel Spike Tests on Ohio River Waters (Confidential Information), March 1996. (Four spike tests of 4 to 5 data points each., with correlations and graphic indications of practical detection limits.)

10. TD-4100 On-Line Monitor, Applications in Northern California Refinery Condensate Monitoring, 998-4115, May 1994. (Refinery steam condensate analysis, fluorescence data and GC data by oil company laboratory, two graphs. Turner Designs client s proprietary information)

11. TD-4100 Instrument Detection Limits for Benzene, BTEX, Phenol, Gasoline, Diesel, Crude Oil, November 1994, 34p (Turner Designs Applications Group Test Report, Confidential Information). (Deionized water spiked with gasoline or 1000 ppm No. 2 diesel in isopropanol, BTEX 1:1:1:1 in isopropanol, benzene, and phenol; repeated calibrations with each, raw calibration data and graphic estimations of detection limits are provided.)

12. Detection Limits of the TD-4100 for Diesel and Gasoline, provided by Turner Designs to Ruth Chang, dated February 8, 1995, 9p. (Confidential Information). (Data of the same type as in Ref. 15, includes copies of corresponding pages of laboratory notebook.)

13. TD-4100 On-Line Hydrocarbon Monitor, Operating Manual, dated September 18, 1995, 88p. (Comprehensive manual provided to users by Turner Designs,includes calibrations, operation, field checks and safety aspects.)

14. California EPA Technology TD-4100 Certification, Application Group Test Report, by M. Means and G. Sung, Rev. 9/29/95. With Chlorophyll *a* Sensitivity Test Parameters, dated November 22, 1994 (Confidential Information). (Tests performed by Turner Designs to support performance claims; calibrations with raw data and graphic presentations, dynamic range, stability, and turbidity response.)

15. Turbidity Interference Test for Algae Measurement: TD-4100 Chlorophyll turbidity Analysis (Turbidity *vs*. Chlorophyll Concentration and Turbidity *vs*. Raw Fluorescence), dated July 28, 1995, 15p. (Contains raw data, spectral scans and graphic presentations.)

16 TD-4100 Technology Update Notes No. 1, 2, and 3, 6 p. (Applications updates, no new data.)

17. Instructions for sending Samples and Sample Information Request Form. Turner Designs, 1996. (Protocol and sample submission form for use by customers for the evaluation of sample streams by Turner Designs.)

18. Analyses of Phenol in Waters Containing Humic Materials, dated April 8, 1996, 10p. (Confidential Information). (A study performed by Turner Designs to determine optimum excitation and emission wavelengths for the detection of phenol in client-derived samples of water in the presence of humic matter, with original scans. The actual procedure of optimizing optical filtering, which is clearly evident from the material, is proprietary.)

19. Hydrocarbon Detection in Water Using the TD-4100 Continuous On-Line Monitor, undated. (Presentation by Turner Designs, contains some summary graphs.)

20. TD-4100 On-Line Hydrocarbon Monitor Installation Guide, dated May 2, 1995, 12p. (Instructions for site preparation and installation of TD-4100.)

21. Chemical Examination Reports by Alpha Analytical Laboratories, Inc. Samples collected daily from 4/13/94 to 5/13/94. Report signed by Bruce L. Grove, Laboratory Director. Includes documentation of California Environmental Laboratory Certification No. 1551 with list of approved analytes.

22. Analysis of Jet Fuel, Diesel, and Gasoline in Waters containing Humic Materials, dated March 13, 1996 (Confidential Information), 7p. (Data analogous to those in Ref. 23. Spectral scans of samples provided by clients to determineoptimum excitation and emission wavelengths for monitoring. )

23. TD-4100 On-Line Monitor Installation Form, 2p. (Form completed by service technician at time of installation; function check results, settings used in field calibrations, and record of user training provided; the completed, signed and dated form is kept by Turner Designs and consulted when responding to consumer inquiries.)

24. TD-4100 On-Line Hydrocarbon Monitor, a letter from Turner Designs to Ruth R. Chang dated April 12, 1996 (Confidential data).Chlorophyll *a* Sensitivity Test Parameters, dated November 22, 1994 (Confidential Information). TD-4100 Raw Fluorescence and Monitek Calibration Curve for Feed Oil Concentration (Confidential Information), 2p.; Comparison to Freon-IR Method, CPI Inlet Water and Sea Water Ratio Test, February 28, 1995 (Confidential Information). (Response to queries by evaluation staff on filter selection and associated QA; contains excitation/emission spectra of samples; Calibration data and graph, comparison of two methods, for monitoring feed oil of unknown origin. Thirty-one data points by several methods, data and graphs, raw oil in sea water.)

25. Research and Analysis of an Oil Ballast Monitoring Device by Engineering Clinic, Harvey Mudd College, Claremont, CA dated May 1, 1995, 40p. (Confidential Information). (Independent study by Harvey Mudd College for Arco Marine Inc. See text for discussion.)

26. Maher, W. A. Use of Fluorescence Spectroscopy for Monitoring Petroleum Hydrocarbon Contamination in Estuarine and Ocean Waters Bull. Environ. Contam. Toxicol. 30, 413-419, 1983.

27. Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd revised edition, Vol. 5, 1964. (p. 797, on fluorescence)

28. Nietsch, Berther: Indication of Petroleum Products in Natural Waters by Fluorescence (in German) Mikrochimica Acta 171-178, 1956. (Qualitative fluorescence tests successfully detect a variety of sources and potential sources of petroleum contamination of the River Danube and drinking water sources of the City of Vienna, Austria, with references to earlier studies.)

29. Letter from Turner Designs to Dr. Ruth Chang dated June 26, 1996. (Contains user contacts.)

The purpose of this evaluation was to validate performance claims by Turner Designs for the TD-4100 instrument. The evaluation team analyzed the materials submitted by Turner Designs. These included reports of field studies performed with Turner Design participation or independently, comparison of data generated with the TD-4100 with those obtained by other methods, especially U.S. EPA-approved laboratory methods. The team also called for specific experiments which were conducted and documented by Turner Designs. In two visits to Turner Designs facility, the team solicited, obtained, and reviewed original data and other validation documents and records and witnessed the calibration and functioning of the instrument in the company s laboratory setting. Furthermore, a users survey of instrument owners and operators was conducted through telephone interviews.

## TECHNICAL EVALUATION: GENERAL CONSIDERATIONS

The common features of fluorescence emission spectra of several crude oils and refined oil products were reported in the literature (26). Oils containing predominantly aromatic compounds with two and three rings produce a fluorescence emission maximum at approximately 330 nm and those with more than three rings produce fluorescence at approximately 380 nm. With excitation wavelengths as short as 254 nm and fluorescence measured at 280 nm, benzene and the other five components of BTEX can be detected, with benzene having the lowest quantum yield per mole of the constituents of BTEX. Turner Designs reported relative intensities for each BTEX component when normalized to benzene for benzene, toluene, ethylbenzene, and *o*-, *m*-, *p*-, xylene were 1:4:3:9:7:31, respectively (Ref. 24). Since these aromatics fluoresce in their natural state, no sample preparation is needed. No extractions or chemical modifications of the sample are required to monitor aromatic hydrocarbons. The measurement of fluorescing aromatic hydrocarbons thus provides a rapid means of monitoring petroleum contamination in complex water matrices. The absorbing target molecules can be excited with the light source whereas synthetic oils and greases will not be detected unless they have aromatic components or contain a fluorescent dye or tag.

Continuous monitoring results are affected by changes in the background and changes in the composition of the hydrocarbon product monitored.

Evaluation concentrated on the following aspects of the technology:

(1) Instrument Design: Physical features and operability.

(2) Sensitivity: the ability to detect the substance of interest in a matrix of concern at a specified concentration level. The detection limit and the dynamic range of the instrument.

(3) Selectivity: the ability of the equipment to detect compounds of interest in the presence of interfering substances as affected by the choice of light sources and of excitation and emission wavelengths through the selection of filters.

(4) Operating conditions: experimental parameters and other environmental conditions under which the product claims have been validated.

(5) Matrix effects: determination of analyte recovery from various sample matrices and approached to the minimization of these effects.

(6) Manufacturability: the ability of the manufacturer to produce instrumentation with consistent results and acceptable precision and accuracy.

## TECHNICAL EVALUATION: CONSIDERATIONS SPECIFIC TO THIS PRODUCT

### *Instrument Design*

The use of a non-contact, falling-stream flow cell allows the continuous monitoring of the sample stream. It is obvious that this feature reduces maintenance requirements compared to designs which use a windowed flow cell. The free-falling column of water is irradiated with suitably filtered light and monitored for fluorescence at a 90-degree angle at specific emission wavelengths to detect and measure aromatic hydrocarbons using a sensitive optical detector (Fig. 2).

Proprietary electronics convert the raw fluorescence signals into time-averaged readable units which the user chooses as either Fluorescence Units or Concentration. Readout is on a LCD screen mounted in the instrument or through 4-20 mA wiring for remote monitoring in parts per billion (ppb) or parts per million (ppm). The intended application of this instrument is primarily in-field measurements to eliminate the requirement for laboratory analysis in many instances, and in detecting and preventing accidental out-of-compliance events, thus financially justifying the acquisition of the device.

The TD-4100 is intended to perform as a continuous, on-line monitor for aromatic hydrocarbons in water. It is designed to alert the operator of the occurrence of the target hydrocarbons above a preset level and to set off an alarm. There are System Function Alarms and Sample Level Alarms. System Function Alarms indicate malfunction of system components. Sample Level Alarms indicate that the sample reading is outside the pre-set range. Using two parallel circuit breakers, the user may choose a set point (sample concentration) and a control range either above or below the set point (zero alarm, early warning alarm, and high-level alarm). These control relays can be set either normally on or normally off. They can be used to activate a solenoid valve or activate an alarm in a normally open or normally closed mode. They can shut down an effluent treatment system in case of an upset.

Compact data loggers which are available from independent vendors can be connected to the TD-4100 for data storage and batch ransfer or to provide the owner or a regulatory agency with on-line information.

In its site visits, the evaluation team confirmed the design criteria, calibration, and response of the TD-4100 to gasoline and witnessed the functioning of the alarm system.

Manufacturer s in-plant tests for the validation of claims were carried out by equipping a production model TD-4100 with a water tank in which a 6-liter volume of water was recycled through the unit. In long-term testing, the use of a windowless flow cell virtually eliminates impact from accumulations of oil, bacteria, dirt, and other deposits on optical surfaces, but stability of the signal, in the laboratory as well as in the field, can be affected by buildup of material in the delivery tube which affected stream geometry. Manufacturer is aware of this problem. It is addressed in written instructions which users need to follow. Instructions for installation (Ref. 20), operation and routine maintenance of the instrument (Ref. 13, 16), are included with each unit.

*Sensitivity*

The Method Detection Limit of the TD-4100 has been defined by Turner Designs as the average baseline (field background) level plus three times the standard deviation (99% confidence level). For this purpose, the baseline signal was determined by taking the short-term averaged readout from the matrix 10 times during a 5-min period and calculating the standard deviation of these readings. To determine the detection limit for gasoline, Turner Designs installed a Gasoline Optical Kit (Part No. 4100-902), added precisely measured quantities of gasoline (in isopropanol) to the distilled water or natural surface water. To distilled water, 1 ppb to 500 ppb of gasoline were added. This test was repeated once each day over 5 days. By this procedure, Turner Designs determined a detection limit of

Figure 2. The TD-4100 non-fouling, non-contact falling stream flow cell.

gasoline in distilled water of 1 ppb (Ref. 14, Supplemental Evaluation: TD-4100 5-Day, inter-day, Minimum Detection Limit Study).

Turner Designs shows that 10 readings were taken at the blank and each concentration level; five data sets were obtained on five different days. Of the 10 readings in each data set, only two or three readings with 1 ppb of gasoline met the MDL criterion, the remainder had signals below the noise level plus three standard deviations. Of the readings at 5 ppb, 90 percent met the MDL criterion.On the basis of these results, we consider 5 ppb, not 1 ppb, a valid detection level in distilled water. The detection limit for gasoline in surface waters was estimated by a user at an Ohio River water intake (Ref. 9) and by Turner Designs staff in a California surface water (Tracy River, Ref. 14). Both waters had a background fluorescence twice that of distilled water. The detection limit for gasoline in these waters by this method was around 20 ppb. In both distilled water and river water, the linear correlation coefficients of the fluorescence reading and the concentration were greater than 0.98 over the measured range. Linearity of the relationship is discussed further below in this Section. For clean water, also the correlation coefficient between data generated by the TD-4100 and by the GC reference method (U.S. EPA Method 8020) was shown to be greater than 98% (Ref. 14).

Differences in aromatic content of gasolines may affect the fluorescence signal. This effect was not studied in detail as a part of this evaluation.

With excitation at 254 nm and emission at 365 nm, diesel shows a greater response than gasoline, and Turner Designs claimed a detection limit of 1 ppb. In tap water and contaminated water, however, the detection limit can be 100 ppb or higher (Ref 12, 16). The detection limits for crude oil and BTEX (specifically benzene) and phenol in deionized water are reported by Turner Designs to be in the ppb range (Ref. 15, 18). With the BTEX filter kit at 254 nm excitation and 280 nm emission wavelengths, the detection limit was shown to be 100 ppb for BTEX, 1000 ppb for benzene, and 100 ppb for phenol (Ref. 11). With a wide-band filter, Turner determined a detection limit for crude oil in deionized water of 10 ppb. Depending on matrix effects in ambient waters, the actual detection limit will be higher. The process adopted by Turner Designs of determining and minimizing the effect of UV-absorbing and fluorescing substances for each user installation of the TD-4100 is discussed below in the Section on Matrix Effects.

*Dynamic Range*

Turner Designs Claim No. 4 in effect states that the TD-4100 has a dynamic range which allows accurate determinations of hydrocarbon concentrations over three orders of magnitude. The relationship of fluorescence to concentration is not linear, but for practical purposes linearity is satisfactory over ranges of one to two orders of magnitude. The following experimentation was available to address this claim.

A Gasoline Optical Kit was installed, gasoline in isopropanol was added to the water in increments from low ppt concentrations to the point when quenching was observed. With optimal setting of the instrument, tests were first run at three different voltage levels, 330V, 430V, and 530V and three more tests were run at 330V. At 330V, the range (about 220 raw fluorescence units) extended to 1000 ppb of gasoline. As the electrical signal from fluorescence increases with increasing voltage, the measurement range at 430V extended only to 150 ppb (corresponding to 4,000 units) and at 550V it extended to 20 ppb (4,000 units). The calibration curve from 0 to 2,500 ppm is convex, but linearity of the response for gasoline in clean water at 330V is good between 100 ppb to 1000 ppm or, more generally, within one order of magnitude about any chosen target concentration. Depending on the sources and matrices of the water, the instrument s detection of gasoline ranged from 5 ppb to 1000 ppm. These results support that, barring unusual matrix effects, the TD-4100 has a working dynamic range for gasoline from 5 ppb to 1000 ppm. (Quantitation with the TD-4100 may not be reliable up to 1000 ppm with heavy hydrocarbons, see p.15).

Repeated calibrations performed in Ohio River water (Ref. 9) showed excellent linearity for gasoline over the 0 to 200 ppb range, and for diesel fuel over the 0 to 100 ppb range. Turner Designs reported correlation coefficients of raw fluorescence units vs. spiked concentrations were from 0.97 to 0.99 (Ref. 12).

*Selectivity*

Fluorometers selectively respond to compounds with fluorescence that is transmitted through the optical filter to the detector. By changing a matched pair of excitation and emission filters, the TD-4100 may monitor either a narrow or a broad range of compounds in a fuel mixture. Typical excitation and emission wavelengths used in TD-4100 Optical Kits used by Turner Designs are shown in Table 1 (Ref. 5).

It is Turner Designs declared practice to select for customers optical configurations that allow the monitoring of aromatic hydrocarbons in the presence of detergents, algal biomass, and suspended solids to minimize effects on readings from these sources. Users must be aware of the effects of changing patterns of analytes and background in the local sample stream.

In certain process streams, phenol appears as a contaminant of benzene. Although benzene can be effectively detected by the TD-4100 equipped with BTEX filter kits (280 nm emission), for the separation of phenol and benzene Turner Designs offers a special optical kit with emission at 270 nm. With this kit, 1 ppm of benzene is detected in the presence of 1 ppm phenol (Ref. 14). Chlorinated hydrocarbons, aliphatic hydrocarbons, and non-aromatic petroleum products are not detected by the fluorometer (Ref. 3).

Turner Designs demonstrated the procedure for evaluation of clients samples for the selection of optimal wavelengths to the team; examples are presented in the following section.

*Matrix Effects*

To configure a TD-4100 for a customer, to detect the hydrocarbons of concern under matrix-specific conditions, Turner Designs scans samples submitted by the cus-

Table 1- Wavelength Configurations for Turner TD-4100 Fluorometer

| Compound | Excitation Wavelengths (nm) | Fluorescence Wavelengths (nm) | Lamp |
|---|---|---|---|
| BTEX | 254 | 280 | Clear Quartz |
| Gasoline | 254 | 330 | Clear Quartz |
| Diesel | 254 | 365 | Clear Quartz |
| Crude Oil (Wide Band) | 300-400 | 410-610 | Near-UV |
| Crude Oil (High Blank) | 300-400 | 400 | Near-UV |
| Chlorophyll | 340-500 | 680 | Blue |

tomer in the range 200 to 650 nm. Excitation and emission filters are selected and matched in the spectral ranges which result in minimal background effects while maximizing the detection of the target compounds. Turner Designs provides sampling kits and instructions to prospective customers for obtaining these samples (Ref. 17). Failure on the part of customers to follow these instructions and provide accurate information can result in inaccurate analytical results and incorrect setup and operation of the TD-4100. Also the basic sensitivity level is set by Turner Designs for the conditions specified by the customer. In this manner, the probability of false positive and false negative results is significantly reduced.

(a) Humic Substances

Fluorescing humic substances occur naturally in soil, surface waters, and ground waters. Fluorescence in natural waters was noticed by scientists as early as 1931, but this fluorescence was from humic substances and algae; fluorescence measurements to detect petroleum products date back to 1956 (Ref. 28 and literature cited there). Therefore, a fluorometer for petroleum hydrocarbons needs to discriminate against fluorescence from other sources. Humic materials in water are characterized by maximum excitation at 245 nm and emission around 400 nm. Turner Designs has presented testing data which demonstrate their method of successfully separating signals from humic acids from those of jet fuel, gasoline, diesel fuel, and phenol to ppb levels in water (Ref. 18, 22).Variations in background fluorescence from variations in the type and concentration of humic materials, however, still can affect the overall signal, and therefore the user should be prepared to confirm critical results by another analytical method. In sea water, added humic acid (5000 ppb) has little effect on emissions at 330 nm and 380 nm.

(b) Turbidity

Turbidity is addressed in Turner Designs claim no. 5. By its nature, detection and measurement by fluorescence of aromatic hydrocarbons in water is less affected by turbidity, suspended solids, suspended gas than measurement by light scatter or light absorption. Turner Designs evaluated turbidity effects by adding non-fluorescing technical-grade titanium oxide powder to the water. A Gasoline Optical Kit was calibrated on a 500 ppb gasoline secondary standard in distilled water and configured to give an alarm at 500 ppb. Grab samples were taken at each addition and analyzed for turbidity by a Nephelometer. The NTU level was monitored up to 1000 NTU, without observing particle settling problems. (NTU are turbidity units measured by a Nephelometer.) The test was repeated four times. Results of this study indicated a change of less than about 5% in the measurement of 500 ppb gasoline in water when the turbidity changed from 0.1 NTU to 300 NTU. The change was less than about 10% when the turbidity increased from 100 to 500 NTU (Ref. 14).

(c) Interference from Chlorophyll-Bearing Particles (Algae)

Fluorescence techniques are very sensitive to chlorophylls. Equipped with proper filters (excitation 560 nm, emission 680 nm), the TD-4100 can detect 100 ppt of chlorophyll *a* (Ref. 14). Turner Designs tested Interference from turbidity in algal biomass measurements by adding carbon, dirt, and coal to water containing an average concentration of 15.9 ppb chlorophyll a (800 raw fluorescence units). The fluorescence reading remained within 5% up to a turbidity of 350 NTU. At higher turbidities, some particles were settlingout. At higher chlorophyll levels (2,700 raw fluorescence units), however, the reading decreased more than 10% at 70 NTU (Ref. 15). Therefore, the exact effect on turbidity on chlorophyll *a* is not clear. In addition, the effect of suspended solids on fluorescence is related to both turbidity and particle size. As with other measurements, particles can cause errors from light scattering. (Effects of particle size were not further investigated here). A user reported interference from particulate matter in biologically treated wastewater (see below). Baseline adjustment or pretreatment are possible solutions.

(d) Quenching effect and interferences

Users should be aware that fluorescence measurements can be affected by quenching. Quenching reduces fluorescence by self-absorption and other mechanisms and, depending on its causes, can contribute to non-linearity of the fluorescence signal with concentration. The effect depends on the composition of the sample, the light source, and the excitation and emission wavelengths.

The presence of other materials that absorb light at the excitation or emission wavelengths, or at both wavelengths will cause a reduction in sensitivity but may not contribute to non-linearity. Changes in pH would effect the fluorescence response for ionizable species, particularly when fluorescent metal chelates are formed. The effect of pH could be significant, especially in industrial waste waters. We recommend that the pH of the water should be measured as a routine practice. Other factors, such as dissolved oxygen, salinity, solids, sunlight, and concentration of diverse substances are all known to affect fluorescence (Ref. 2, 27). This reinforces the notion that in on-line monitoring applications with the TD-4100 users need to be aware of the nature and possible interferences in their sample stream and concentration ranges of concern, work with Turner Designs to establish feasibility and optimize operating conditions, and develop a plan for validating from time to time the TD-4100 responses through appropriate sampling and laboratory analysis.

## RESULTS OF VALIDATION STUDIES

The efficacy of the fluorometer was assessed in several studies, including comparison of readings obtained in the field by the TD-4100 with results obtained by the analysis of samples by standard reference methods including U.S. EPA Methods 8015A for gasoline, 602 for BTEX, and 8020 for PAHs. Results of these field studies were as follows:

1. A study was designed at a refinery to test the effectiveness of continuous on-line monitoring for the detection of xylenes leaking into heat exchangers. The TD-4100 was installed to record the fluorescent signal of xylenes in the steam condensate stream. The refinery, independent of Turner Designs, took grab samples for BTEX analysis by the GC method in its company laboratory. Xylene was the major contaminant. Field data were generated over a five-week period. Data of raw fluorescence versus xylene concentrations determined by GC were used to develop a correlation. The correlation coefficient between U.S. PAH Reference Method 8020 and the fluorescent readings was 0.98 (Ref. 10, 19, 24).

2. Turner Designs installed a TD-4100 monitor with an air purge system to demosntrate the feasibility of on-line hydrocarbon monitoring of pumped groundwater at the East Ridge Mall remediation site in San Jose, CA (Ref. 6). Study design was reviewed by staff of the Regional Water Quality Board. The trial lasted four weeks. Grab samples were taken at the TD-4100 outlet once every work day by Turner Designspersonnel and submitted to Alpha Analytical Laboratory, an independent California-certified laboratory, for gasoline and BTEX testing. BTEX compounds were analyzed by EPA method 8020 and TPH-gasoline by EPA method 8015A(Ref. 21). The calibration mixture for BTEX was benzene, toluene, ethylbenzene, and *p*-xylene at a

1:1:1:1 ratio. The instrument monitored the composite inlet to the treatment system (well designations GW1 and GW2) and returned this stream to the effluent side of an oil-water separator. The report shows forty-four data points. The repeatability of the TD-4100 readings was within 5%. the laboratory precision was given as 20%. The range of the BTEX laboratory results was from 6 to 8,000 ppb, the TPH-gasoline results ranged from 50 to 26,000 ppb. Correspondence between the fluorescence peaks and the TPH-gasoline results, however, was complete; correlations between TPH-gasoline concentrations and TD-4100 Raw Fluorescence readings from the two wells, GW-1 and GW-2, were 0.98 and 0.92, respectively. (Ref. 6).

3. A study was designed to demonstrate whether the TD-4100 could track the rise and fall of oil concentrations in treated water from an oil/water separating hydrocyclone. This study was performed by Turner Designs in conjunction with a hydrocyclone manufacturer at their test facility (Ref. 28, 31). The feed water was dosed by weight with lubricating oil by staff of the other company. Up to a concentration of 160 ppm in the feed water, the linear correlation coefficient ($r^2$) between the fluorescence reading and the oil concentrations was greater than 0.99. Monitek readings (which are ultrasonic measurements of suspended droplets and solid particles in the water), were also compared to fluorescence readings, but owing to lack of specificity, the Monitek readings did not correlate as well with oil as the fluorescence measurements.

4. Another field test to measure off-shore crude oil from a platform was performed independently by an oil company in the Gulf of Mexico (Ref. 24). The purpose of this study was to demonstrate the ability of the TD-4100 to monitor continuously the discharge of crude oil in produced water and to compare these results with those from the Freon-IR method (modified EPA Method 413.2 for oil and grease analysis). A total of 31 data points were reported. Up to a concentration of 350 ppm crude oil in water, the linear correlation coefficient between fluorescence readings and the Freon-IR method was 0.9.

5. Research was conducted at a college engineering facility to conduct a comparative evaluation of several monitoring devices for oil in ballast water of cargo vessels. This study was undertaken by an independent organization under contract with a major potential user (Ref. 25). The investigation addressed issues of reliability, accuracy, durability, availability of maintenance, and compliance with federal regulations for discharges of ballast water. Five different systems were evaluated. Although Turner Designs claims that the detection range of the TD-4100 is 1 ppb to 1000 ppm, at concentrations above 50 ppm the oil would cling to the sides of the container from where the sample stream was drawn. As a consequence, measurements above 50 ppm were not considered reliable. The TD-4100 was recommended for selection from the five designs to replace the existing systems, because it was found to be the most accurate and reliable monitor in the critical 0 to 50 ppm range, and as a consequence, would allow the operator to comply with U.S. and international regulations.

*Operating Conditions*

Operating conditions may significantly affect fluorescence measurements. It is important that standards and unknowns be treated in the same manner and measured under the same conditions. The stability of a standard should be checked under the exact measurement conditions that will be used in practice. Users should carefully follow the Operations and Maintenance Manual provided by the manufacturer (Ref. 3, 4, 17 and 16). To generate results with good precision and accuracy, operating conditions considered sensitive to the measurement are discussed in the following.

A. Temperature

Fluorescence decreases when the temperature of the sample increases. The temperature coefficient of the fluorescence depends on the chemical species, on phenomena such as hydrogen bonding, nature of the excited state, and acid-base equilibria. Turner Designs suggests that the sample temperature should not change more than 10°C before recalibration. If the temperature of the sample changes more than 10°C between calibrations, Turner Designs suggests that a sample heater or cooler be used to keep at temperature constant between calibrations. (Fluorescence may change 3% per degree Celsius, Ref. 2.) Temperature also affects the solubility and particularly the transfer of oil from emulsion to free liquid form. The maximum acceptable sample temperature is 140°F (60°C). The operating temperature range for TD-4100 is 40°F to 120°F (4°C to 49°C). Therefore the instrument should not be operated in direct sunlight.

B. Instrument Calibration, Measurements, and Maintenance (Ref. 13, 16)

*Instrument Calibration:* An accurate calibration standard is essential for successful quantitation. The basic sensitivity of the TD-4100 is initially set at the factory. This initial setting provides sensitivity for the detection of aromatic hydrocarbons at concentrations around 1 ppm, with a dynamic range of 3 orders of magnitude. The factory setting for the basic sensitivity level must be changed from the initial setting if the water to be monitored has significantly lower (ppb) or higher (1000 ppm) aromatic hydrocarbon content or has a high baseline signal when installed at the customer site. Once the basic sensitivity level is set for the site-specific conditions, it should not be necessary to adjust the basic operating level unless optical filters of different wavelengths or a different type of lamp are used.

An appropriate blank and calibration standard with a known hydrocarbon concentration are used for initial instrument calibration. Typically a water sample from the site with little or no aromatic hydrocarbons is designated as the blank. There are three methods of calibration for field measurements: qualitative calibration, quantitative calibration with a primary standard, and quantitative calibration with a reference standard.

*Qualitative measurements:* A calibration standard is not required. A threshold concentration, as defined by the user, will be expressed as a relative percent level to the blank (*i.e.*, percent increase relative to the blank). Using information based on the noise levels of the sample stream and the instrument, the operator sets the desired threshold level in the software. With this setting, the instrument will trip the alarms without calibration.

*Quantitative measurements:* Since the principal use of the TD-4100 is to trigger an alarm for follow-up by the user, a two-point calibration is generally used to establish a linear relationship between raw fluorescence of the targeted hydrocarbons and their concentration (Ref. 17) with the understanding that the linear relationship holds within one to two orders of magnitude of the signal. Calibration is by one of the following three methods: (1)The Neat Hydrocarbon Technique: Neat hydrocarbon, *e.g.*, gasoline, is spiked into one gallon of blank water from the waste stream to create a known standard. The standard is then measured by the instrument and assigned the standard concentration value in the software to match the raw fluorescence signal; (2) Fluorescent Equivalent Technique: A known fluorescent dye is added to one gallon aliquot of blank water from the waste stream to correct for different types of hydrocarbons. The fluorescence dye standard is used to calibrate the instrument as in the neat hydrocarbon technique.; and (3) Reference Method Technique: A sample is measured and simultaneously a grab sample of the water is collected and analyzed by a reference method, such as GC or GC/MS. Based on the result obtained with the reference method, the operator calibrates the unit to match the raw fluorescence reading of the instrument. For best results, the concentration of the calibration solution should be near the desired alarm level or approximately 50% of the maximum to be measured. Calibration is carried out as needed, usually about once per month depending on the sample stream and local conditions, using the procedure established by Turner Designs. If the instrument is to be used for quantitative measurements, fluorescence readings should be calibrated against another analytical method.

*Maintenance:* For routine maintenance, the user is instructed to replace the light source every 6 months. The air-curtain carbon canister, which provides a constant pressure of clean and dry air to the instrument, is replaced every two months, or in longer intervals depending on the quality of the air supplied to the instrument. The plumbing needs to be cleaned periodically, depending on the water in the monitored stream, to avoid buildup of algae or sediment in the pathway with resulting effects on the geometry of the sample stream (Ref. 16). Routine maintenance for the internal and the external parts of the instrument is described in the maintenance manual supplied by Turner Designs (Ref. 3, 13, 16). Cleaning of the piping which supplies the sample stream with brushes supplied by Turner Designs should be as required to maintain sample stream geometry, and in clean sample streams at least quarterly. Instrument calibration and routine maintenance procedures were demonstrated to the evaluation team on the occasion of a site visit to Turner Designs facility.

*Stability:* In performance claim no. 6, Turner Designs assumes a stable calibration with less than 5% drift over 90 days when the unit is maintained according to instructions and guidelines provided. Stability of the instrument was studied by recycling through the instrument 6 liter of water for 90 days. The unit was blanked with distilled water and calibrated on a 1000 ppb gasoline secondary standard in water. Readings were taken weekly. During the test period, a fresh 1000 ppb solution was prepared each week to provide the constant concentration. A naphthalene derivative of 1000 ppb was set up to monitor instrument stability because it is less volatile than gasoline. Although the TD-4100 uses a non-contact flow cell, the readings of the TD-4100 were affected by the reduction of the falling stream through buildup of solids, possibly a bacterial film, in the delivery system; in the study readings decreased in the order of 20% over seven weeks. Upon cleaning, readings returned to within 5% of the original.

In a second experiment, the TD-4100 held its calibration for a ten-week period within 5%. Therefore, the claim of stability over a 90-day period can be sustained only with proper maintenance. With this understanding it can be stated that the stability of the instrument is acceptable for long-term monitoring in the field for as long as several months.

*Training Policy:* As standard practice, Turner Designs dispatches an engineer to commission each instrument on-site and to provide the customer with standardized (usually two-day) training in the operation of the instrument. A TD-4100 On-Line Monitor Installation Form is completed with information on the settings of the instrument on-site and kept as a reference in the customer s file at the manufacturer s facility. The manufacturer also offers training at their facilities and consultation by telephone (Ref. 3).

## MANUFACTURABILITY - QUALITY ASSURANCE IN MANUFACTURING

TD-4100 is designed for an outdoor environment. All exposed components are made of materials for corrosion protection to best industrial practice known to Turner Designs. Standard features, options, and specifications of TD-4100 are in test procedure descriptions furnished with each unit (Ref. 3, 8).

Procurement and quality control of light filters for excitation and fluorescence is at the center of Turner Designs operations and is in part proprietary. The optical filters are interference filters. Their integrity and quality (transmission and band pass profile) are checked upon receipt against the specifications agreed upon between Turner Designs and the manufacturer or vendor. The filters supplied with each instrument are subjected to a function test prior to shipment to the user (Ref. 24).

Turner Designs has further asserted that it tests the power system, plumbing, and function of each unit before shipment. A final Q.C. check list is dated with signature of the testing engineer. The source lamp is rated at 8,000 hours. The safety features of an explosion-proof model are available as options but not installed in standard units (Ref. 3). A copy of the warranty statement is attached to each unit. The unit is equipped with password protection for master and user IDs.

## USER SURVEY

The experience of eight users of the TD-4100 was conducted in a telephone survey. The questions posed to the users were: (1) Is the instrument correctly designed for the user s application? (2) How long has the instrument been in use? (3)What is the user s application? (4) What compounds and ranges of concentrations are being monitored? (5) Does the instrument effectively achieve the stated purpose? (6) Have the results obtained with the TD-4100 been compared with results obtained by other methods? (7) Are there other comments on the instrument s performance?

Eight users were interviewed by phone. Among these, two applied the device for the monitoring of storm water, two for waste water, and four for industrial processing streams.

The instruments had been in use for periods from 3 weeks to 18 months. In each case, Turner Designs had selected the light source and optical filters to meet the need of the customer s application. All instruments had been set at a target concentration level for 24-hour continuous monitoring of hydrocarbons in water, specifically: (1) monitoring PAHs in boiler condensates for the purpose of checking leakage of gasoline or petroleum fuels used in a steam generator; (2) monitoring hydrocarbons in stormwater to detect discharges or spills of diesel fuel and gasoline in the aircraft industry; (3) monitoring petroleum-derived PAHs in a sewage discharge; and (4) monitoring fuel and gasoline in various industrial waste waters and mining waters. Detection levels ranged from 500 ppb to 50 ppm. In every case users stated that they had achieved their intended purpose and that the TD-4100 provided better sensitivity than was required for their monitoring, supporting Turner Designs Claim No. 1. Where results obtained with the TD-4100 were compared to those obtained by the appropriate reference methods, they were found comparable with respect to data points correctly classified as above or below the target or alarm levels, supporting Turner Design s claims no. 2, 3, and 4. In fact, the most common use of the TD-4100 was to trigger the taking of a sample for confirmation of the problem indicated by the instrument. The users found the TD-4100 well built and working well. A common problem was the sediment buildup in the plumbing system from solids-containing sample streams which changed the geometry of the sample stream, which in turn affected the fluorescence signal. One user found a change in readout when the sample stream was changed from an untreated sewage discharge to effluent from a biological treatment plant. The change was due to the suspended biomass in the second stream. These experiences point to the need for maintenance of the sampling system and a possible need for background readjustment, recalibration, or change of optical filters in response to changes in the sample matrix.

In addition to the users in this survey, U.S. Navy personnel had used earlier models of Turner Designs hydrocarbon fluorometers with similar filter configurations on a research vessel in San Diego Harbor for several years. They reported that the principles on which the technology is based are sound, and that their data correlate very well with laboratory analyses, even with highly variable influent streams.

## PROTECTIVENESS CONSIDERATIONS AND ENVIRONMENTAL BENEFITS

The design of the TD-4100 allows for continuous monitoring and an automatic alarm or out-of-control signaling to shut down a process, or both. This is a potential environmental benefit not available through alternative monitoring approaches which require periodic sampling and laboratory analysis. The TD-4100 may be able to detect short-term excursions which may go undetected by standard periodic sampling programs.

The TD-41000 does not generate waste during continuous operations (between scheduled maintenance events). This is an advantage over standard sampling and laboratory methods that require the handling and transport of samples, the potential generation of other wastes during the preparation of samples for laboratory analyses, and the disposal of unused portion of sample.

The operation manual identifies the principal hazards to the user. It includes warnings at each point in the operations or maintenance where they may be encountered, including exposure to the uv light source. These instructions appear adequate. Routine maintenance of the TD-4100 flow path is in most cases successfully accomplished with detergents and water using bottle brushes supplied with the TD-4100. If strong acid solution (1:1 mixture of concentrated hydrochloric acid and water) is used in cleaning, it must meet facility requirements for handling such acids including the use of proper personal protective equipment. *Reference to this 1:1 dilution of concentrated hydrochlorid acid as dilute is misleading and is to be avoided.* All wastes must be managed according to applicable regulatory requirements.

## SUMMARY

The Turner Designs TD-4100 On-Line Monitor is suitable for on-line field monitoring of analytes in water that emit a characteristic fluorescence in the wavelength of near UV and visible range. If the basic sensitivity level is properly adjusted to site-specific conditions, the analytes can be effectively detected in contaminated waters without sample preparation as required by traditional analytical methods. Based on the evaluation of the documents submitted, the evaluation team finds the following performance statements consistent with its findings for instruments that are properly installed according to manufacturer s instructions, including previously established site-specific requirements, and are properly maintained as suggested by the manufacturer. All statements are related to the detection of gasoline and BTEX. Analyses pertaining to polynucleated aromatic hydrocarbons (PNAs, PAHs) other than naphthalene were not presented for this evaluation.

(1) The TD-4100 provides direct, continuous, on-line detection of aromatic hydrocarbons in water. The instrument triggers alarms and/or control devices when aromatic hydrocarbons in water exceed user-defined limits.

(2) The TD-4100 reports the level of hydrocarbons in water as a relative change in raw fluorescence units or as an absolute change in concentration units of parts per billion (ppb) or parts per million (ppm).

(3) The TD-4100 detects 5 ppb of gasoline in distilled water and 20 ppb of gasoline in unfiltered, untreated surface river water whose background fluorescence is 200% greater than distilled water.

(4) The TD-4100 can accurately measure hydrocarbon concentrations in clean water that change as much as 1000-fold.

(5) The TD-4100 demonstrates the selective isolation for the detection and measurement of 1 ppm benzene in water in the presence of 1 ppm of phenol.

(6) The TD-4100 demonstrated less than about 5% change in quantitative measurement for 500 ppb of gasoline in water when the turbidity in water changed from 0.1 to 300 NTU, and less than about 10% change when the turbidity increased from 100 to 500 NTU.

(7) The TD-4100 maintains a stable calibration (drift within 5%) over 70 days of continuous operation and possibly longer, but requires maintenance in accordance with guidance provided in the operator s manual, including cleaning of the sample delivery system as detemined by local conditions.

In cases where the exact concentration of specific hydrocarbons is required, confirmatory results using the U.S. EPA Office of Solid Waste SW-846 Test Methods (8015A for gasoline, 8020/8021 for BTEX, and 8270, 8100 for PAHs) are needed. Due to the nature of fluorescence and fluorescing compounds, and the sensitivity of the fluorescence method, environmental conditions and possible chemical interferences in water should be thoroughly investigated, when a fluorometer is chosen as a monitor. To ensure the accuracy of analyses, split sample analyses (including the positive, the negative and samples for decision making) should be performed to compare results generated by the TD-4100 and the U.S. EPA-approved methods. If the TD-4100 is used in monitoring high-flow water or waste water streams, the intake needs to be constructed to take a representative sample. If this is the case and the operating conditions specified by the manufacturer are followed, the TD-4100 can be used effectively to monitor aromatic hydrocarbons in water. In an emergency, the software-controlled alarm system can automatically shut down a discharge containing an unacceptable level of target pollutants. This feature contributes to public health protection. When the instrument is calibrated properly, the TD-4100 can be used to monitor the concentrations of target compounds in water, in most cases, to meet regulatory requirements.

## RECOMMENDED APPLICATIONS

### *Present Applications*

Based on the data and conditions evaluated, the unit should provide increased assurance of success in the monitoring of aqueous streams for petroleum hydrocarbons at a potentially reduced cost, especially in applications where a waste stream exhibits little variation with respect to the interferences such as turbidity, suspended solids, and humic substances. Moreover, since most discharges under the National Pollution Elimination Discharge System (NPDES) permits are required to achieve certain effluent limits for turbidity and suspended solids, it is very likely that a discharger would be notified independent of the operation of the TD-4100 if either of these parameters were to become so elevated as to have a significant effect on the readings provided by the TD-4100.

For discharges to surface waters, most monitoring requirements have been established utilizing grab and/or composite samples that are submitted for laboratory analysis. In many instances, it is likely that the fluorescence monitor could offer a higher degree of assurance that discharge limits for these chemicals were not being exceeded. Accordingly, the TD-4100 has found application for the monitoring of oil in groundwater.

For instance, at sites where petroleum must be removed from groundwater, the water is often treated and then discharged to a surface water body. These waste streams can generally be expected to exhibit little variability with respect to interferences. It is likely that upon proper calibration and proper orifice maintenance pursuant to the manufacturer s instructions, the unit will provide higher assurance than is now provided under current NPDES monitoring requirements. The primary reason for the increase in environmental assurance is the provision for instantaneous cessation of the discharge upon the detection of a discharge exceedance. In comparison, current requirements could allow a discharge exceedance to occur for 90 days or more until it is detected. Although laboratory analysis must still be relied upon for calibration, it is anticipated that validation could be accomplished using field standards.

One concern that must be adequately addressed is the representativeness of the sub-stream that the TD-4100 actually analyzes. Proper system design and installation should result in delivery of a representative sample to the TD-4100. This concern is particularly significant where the waste stream may not be well mixed or homogeneous, or if separate-phase hydrocarbons are expected in the waste stream.

*Potential Applications*

This unit has potential application in several areas of current environmental practice, including monitoring of municipal waste water and stormwater discharges, monitoring the effects of oil spills, and the characterization of contaminated sites, including the monitoring of leachates. Current practices in these areas of work entail the use of standard laboratory analysis for petroleum hydrocarbons as well as the analysis of BTEX and PAH compounds.

The unit may also provide data quality improvements in the areas of storm water monitoring and hazardous waste site characterization. The discharge of pollutants in stormwater runoff and the leaching of pollutants from soils both exhibit temporal trends. Current practice in the analysis of these phenomena rely upon composite sampling and/or sample homogenization. The unit provides an economical means by which to analyze the temporal trends inherent to understanding pollutants in natural environments.

Site characterization is another area where application of this technology could potentially result in cost savings and environmental benefits. For instance, current methods for determining the mass of pollutants that can leach from soil are very aggressive and do not approximate the conditions found in undisturbed soils. The unit could provide a means by which the leachable mass of pollutants could be determined by analysis of relatively undisturbed soil cores in a simple flow-through permeameter. The unit makes such an analysis feasible because of its ability to record variations in concentration in real time. Establishing a time series by standard laboratory methods would likely be prohibitively expensive. The leachable mass presents the most significant threat to groundwater resources, and a more accurate estimate of its actual value would likely result in more efficient site clean-ups. Similarly, application could be expected in groundwater monitoring at contaminated sites with tidal influences.

In storm water and municipal waste water monitoring, composite samples are often relied upon to characterize discharges. If the unit can be calibrated to analyze adequately for the appropriate chemicals chemicals in a stormwater discharge, it will likely provide better estimates of the discharged mass by allowing real-time integration of concentration data acquired by the instrument with flow data. Since storm water discharges exhibit extreme variability in many characteristics, further study of the unit s applicability is warranted prior to regulatory acceptance for this particular purpose.

Turner Designs has shown considerable experience in the construction of fluorometers for field and shipboard use for the determination of chlorophyll fluorescence, algal biomass, hydrocarbon measurements, and for process control based on these measurements.

## EVALUATION TEAM AND REPORT AVAILABILITY

The professional team for this evaluation included Ruth R. Chang, PhD (Biochemistry); Cynthia Dingman, B.S. (Clinical Science); Brad Job, P.E.; Water Resources Control Engineer (California Regional Water Quality Control Board, San Francisco Region); Bruce LaBelle, PhD (Chemistry); and G. Wolfgang Fuhs, Dr.sci.nat. (Team Manager).

Copies of this evaluation report are available from the Office of Pollution Prevention and Technology Development, California Department of Toxic Substances Control, 400 P Street, P.O. Box 806, Sacramento, CA 95812-0806, or from the team manager.

## APPENDIX

The following Final Notice of Certification was published in the California Regulatory Notice Register Volume 97, Issue 14-Z, p.698-700, of April 4, 1997

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

DEPARTMENT OF TOXIC SUBSTANCES CONTROL

Final Notice to Certify Hazardous Waste Environmental Technology

The California Environmental Protection Agency, Department of Toxic Substances Control (DTSC) has made a final decision to certify the following company s hazardous waste environmental technology:

*Turner Designs TD-4100 On-Line Hydrocarbon Monitor.*

Chapter 412, Section 25200.1.5, Health and Safety Code, enacted by Assembly Bill 2060, Weggeland 1993, authorizes the DTSC to certify the performance of hazardous waste environmental technologies. Only technologies that are determined not to pose a significant potential hazard to the public health and safety or to the environment when used under specified operating conditions may be certified. Incineration technologies are explicitly excluded from the certification program. The purpose of the certification program is to provide an in-depth, independent review of technologies at the manufacturer s level to facilitate regulatory and end-user acceptance and to promote and foster growth of California s environmental technology industry.

DTSC makes no express or implied warranties as to the performance of the manufacturer s product or equipment. The end-user is solely responsible for complying with the applicable federal, state, and local regulatory requirements. Certification does not limit DTSC s authority to require additional measures for protection of the public health and the environment.

By accepting certification, the manufacturer assumes, for the duration of certification, responsibility for maintaining the quality of the manufactured equipment and materials at a level equal or better than was provided to obtain certification and agrees to be subject to quality monitoring by DTSC as required by the statute under which certification is granted.

DTSC s notice of intent to certify was publishedon December 27, 1996 in the California Regulatory Notice Register Volume 96, No. 52-Z, p. 2272-2275. No comments in relation to the proposed certification were received during the public comment period. DTSC s final certification shall become effective on May 5, 1997.

Additional information supporting DTSC s final certification decision is available for review at:
California Environmental Protection Agency,
Department of Toxic Substances Control,
Office of Pollution Prevention and Technology Development,
P.O. Box 806, 301 Capitol Mall, 1st Floor,
Sacramento, CA 95812-0806,
Attn.: Dr.Wolfgang Fuhs (510) 540-3076.

A description of the technology to be certified, the certification statement, and the certification limitations for the technology of the company listed above follows.

## CERTIFICATION PROGRAM (AB2060) FOR HAZARDOUS WASTE ENVIRONMENTAL TECHNOLOGIES

### TECHNOLOGY CERTIFICATION

*Technology:*

TD-4100 On-Line Hydrocarbon Monitor.

*Manufacturer:*

Turner Designs, Inc., 845 West Maude Avenue, Sunnyvale, CA 94086, Tel. (408) 749-0994.

*Technology Description*

The Turner Designs TD-4100 fluorometer is intended for the continuous monitoring in the field or in industrial environments of aqueous streams containing petroleum fuels or other petroleum-derived pollutants. It allows automatic out-of-control alarms or signaling to shut down the monitored flow. The technology is based on the principle of fluorescence detection in an aqueous stream irradiated with light from one of three available light sources. The light source generates UV or near-UV light that is passed through an excitation light filter chosen by the manufacturer. The selection of filters is based on information provided by the user regarding the characteristics and variability of the matrix and analyses of concern. The filtered excitation light enters a non-contact, non-fouling measurement cell containing a continuous flow, laminar, free-falling, aqueous stream. Any fluorescent compounds in the stream that can absorb the chosen wavelengths of excitation light, fluoresce at characteristic wavelengths. The fluorescence emissions pass through another filter, at 90 degrees from the excitation light, and are collected in a photomultiplier detector. A dual beam optical design alternates between measurement of the filtered source light, dark current, and the filtered fluorescence emission light. Proprietary electronics convert the raw signal into readable units, displayed on a LCD screen as either fluorescence units or concentration, or into a signal suitable as an input into a data logger. The compounds responsible for the signal are aromatic hydrocarbons of molecular weights ranging from benzene to polynucleated aromatics. Filtered excitation and fluorescence wavelengths, respectively, are for BTEX (including benzene), 254 nm and 280 nm; for gasoline, 254 and 330 nm; for diesel fuel, 254 and 365 nm. The manufacturer also offers excitation and fluorescence filter sets for crude oil (wide band), 300-400 and 410-610 nm; and for crude oil (high blank condition), 300-400 and 400 nm. The excitation and fluorescence filters are interference filters manufactured by others which meet Turner Designs specifications. The Turner Designs TD-4100 fluorometer is intended for the continuous monitoring in the field or in industrial environments of aqueous streams containing petroleum fuels or other petroleum-derived pollutants. It allows automatic out-of-control alarms or signaling to shut down the monitored flow.

*Certification Statement*:

Under the authority of Section 25200.1.5 of the California Health and Safety Code, the Department hereby certifies the TD-4100 On-Line Fluorometer manufactured by Turner Designs, Inc., 845 West Maude Avenue, Sunnyvale, CA 94086 as a Measurement Technology for the continuous on-line monitoring of gasoline, benzene, toluene, ethyl benzene, xylenes (BTEX) and other petroleum products in water by virtue of their aromatic hydrocarbon content.

The TD-4100 is semi-quantitative in that it detects petroleum-derived products and pollutants in terms of a preset fluorescence level or in terms of levels set by calibration with benzene, gasoline, diesel, or other petroleum product. Detection levels in deionized water are about 1000 ppb for benzene and 5 ppb for diesel fuel or gasoline. In ambient and industrial waters, detection levels of 50 to 200 ppb for diesel fuel or gasoline are more typical. The dynamic range typically extends over three orders of magnitude. The relationship between concentration and fluorescence over this range is non-linear, although, for practical purposes, linearity extends between one or two orders of magnitude about chosen target levels. Within appropriate concentration ranges, comparison of fluorescence readings with results of laboratory analyses has shown correlation coefficients of 0.98 or better. The TD-4100 has been shown to be capable of maintaining a signal stable within about 5 percent over ten weeks.

A critical element of the technology is the manufacturer s commitment to match light source, excitation and fluorescence filters to a user s needs in terms of type of product to be detected, level of detection, and type and level of site-specific interfering compounds (including interfering chemicals, changes in turbidity, or fluorescing particles such as algae), and establishment of an expected level of on-site performance base don these evaluations and prior to sale and installation of the equipment.

The use of a window-less measurement cell eliminates a principal source of signal attenuation. Stability of the signal is still dependent on a stable geometry of the sample stream which is affected if a deposit is allowed to build up in the piping system leading to the measurement cell. Periodic calibration checks, replacement of the source lamps, and other maintenance must be performed by the user in a manner prescribed by the manufacturer.

The TD-4100 is equipped with alarm and signal circuits to allow the automatic interruption of an industrial inflow or effluent and alert the operator when a preset level of the target hydrocarbon is exceeded. As the signal may be affected by changes in temperature, the user must consider temperature changes in outdoor use.

The variability of the background and composition of the hydrocarbons being monitored will affect the sensitivity, accuracy, and precision of measurements. Differences in aromatic content of gasolines may affect their detectability by fluorescence.

*Limitations of Certification*

DTSC makes no express or implied warranties as to the performance of the manufacturer s product or equipment. DTSC has not conducted any bench or field tests to confirm the manufacturer s performance data. Nor does the Department warrant that the manufacturer s product or equipment is free from any defects in workmanship or material caused by negligence, misuse, accident, or other causes.

DTSC believes, however, that the manufacturer s product or equipment can achieve performance levels set out in this Certification. Said belief is based on a review of the data submitted by the manufacturer and other information, and is based on the use of the product in accordance with the manufacturer s specifications.

This certification is subject to the conditions set out in the regulations to be developed pursuant to Section 25200.1.5 of the California Health and Safety Code, such as the duration of the Certification, the continued monitoring and oversight requirements, and the procedures for certification amendments, including decertification.

By accepting this Certification, the manufacturer assumes, for the duration of the Certification, responsibility for maintaining the quality of the manufactured materials and equipment at a level equal or better than was provided to obtain this Certification and agrees to be subject to quality monitoring by DTSC as required by the law under which this Certification is granted.

*Specific Conditions*

The manufacturer shall use their established procedures to evaluate specific light source and filter combinations to so as to optimize instrument response relative to known, interfering substances that may occur at a customer s site. This includes, for new waste streams, testing on samples of the actual waste streams at the manufacturer s facility. The manufacturer may substitute optical parts in response to monitoring requirements for specific sample streams. With regard to such substitutions, the conditions encountered during the evaluation on which this certification is based shall remain representative of Turner Design s response to customer needs and overall quality management.

The equipment shall be manufactured from materials with corrosion protection for outdoor use.

Through updates of user guides, Manufacturer shall inform the user of interferences and matrix effects which potentially affect the testing results as they become known to the Manufacturer.

Certification does not extend to the user s construction of a sampling intake to obtain representative samples from high-flow streams of water or waste water and user s maintenance of such structures.

In cases where the results are to be reported as the concentration of a specific analyte, the user should calibrate the instrument using that analyte, and confirmatory results obtained using applicable U.S. EPA Office of Solid Waste SW-846 Test Methods.

Users shall provide the manufacturer with adequate information on the characteristics and variability of their wastestream so that the manufacturer can properly configure and calibrate the instrument. Users shall follow the manufacturer s instructions for installation, operation, and maintenance. Thue user should be aware of potential changes in the characteristics of their wastestreams that may affect the ability of the technology to detect the analytes of concern. Users shall develop and follow a plan in accordance with their facility s quality management system for validating, at appropriate intervals, the performance of TD-4100 through sampling and laboratory analyses.

*Basis for Certification*

This certification is based on the evaluation of internal studies conducted by the manufacturer, demonstrations of the equipment at the manufacturer s facility during field visits by DTSC personnel, field trials conducted by independent parties both with and without the cooperation of Turner Designs  personnel, and reports from users. A listing of the documents available for this evaluation is contained in the Draft Evaluation Report. The manufacturer has declared that certain submitted materials contain proprietary information and should not be subject to public disclosure.

*Recommended Applications*

Recommended applications include preventing contamination of receiving waters with oily industrial effluents and stormwater, and similar pollution of surface drinking water sources and groundwater. In most situations, and subject to those which Turner Designs carries out in cooperation with each prospective user, the TD-4100 allows monitoring at or below regulatory levels.

The TD-4100 greatly improved the monitoring regime through its continuous operation, and may substantially reduce the need for periodic sampling, improve data quality, and add to the protection of public health and the environment. In case of an alarm, the TD-4100 can alert the operator so that immediate sampling of the monitored flow may be conducted to determine the nature of the offending pollutant.

*Regulatory Implications*

DTSC s certification does not change the regulatory status of hydrocarbon testing; it is intended, however, to facilitate and encourage the acceptance of this technology where a project s data quality objectives can be met by its use. To this end, regulatory programs are encouraged to consider DTSC s findings regarding this technology, depending on each program s objectives and constraints. State-regulated facilities may contact state permitting officers for use of the technology for operational monitoring. Other local and state government permitting authorities may take this certification under consideration when making their permitting decisions. Project managers may consider using this technology where its use can contribute to the project and its data quality objectives.