

A Fluorescence Based Measurement Technique to Quantify Water Contaminants at Pipe Surfaces During Flow

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This paper provides a detailed account of the development of a fluorescence based measurement technique for measuring the mass of contaminant on solid surfaces in the presence of water flow. A test apparatus was designed and developed for the purpose of studying adsorption and desorption of diesel to and from a copper test surface in the presence of contaminated and fresh water flow, respectively. A calibration technique was developed to correlate the measured fluorescence intensity to the mass of diesel adsorbed per unit surface area (the excess surface density) and the bulk concentration of the diesel in the flow. Both bulk composition and the excess surface density measurements were achieved via a traverse of the fluorescent measurement probe perpendicular to the test surface. The measured diesel excess surface density varied between zero and 0.02 kg/m^2 for the variation in the bulk mass fraction and Reynolds number of the flow.

Keywords: Adsorption, contaminant, diesel, excess layer, fluorescence, measurement technique, transport, sorption, water

INTRODUCTION[#]

Since the signing of the Executive Order establishing the Office of Homeland Security, Federal agencies have been working on ways to improve the security of the general public. One way in which the National Institute of Standards and Technology (NIST) is doing

its part is by helping the U.S. Environmental Protection Agency (EPA) devise ways to safeguard the nation's drinking water supply. This paper describes an effort to fundamentally understand the attachment and detachment mechanisms of contaminants to solid plumbing materials under dynamic water flow conditions. The results of this work provide EPA with an

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[#]Certain trade names and company products are mentioned in the text or identified in an illustration in order to adequately specify the simulation procedure. In no case does such an identification imply recommendation or endorsement by the National Institute of Standards and Technology (NIST), nor does it imply that the products are necessarily the best available for the purpose.

investigative tool to support the development of a response to water contamination events and a potential detection technique for timely warning of plumbing contamination.

Fluorescence has been used for early detection of a variety of water contaminants (EPA, 2012). Meder et al. (2012) have used fluorescence to detect microorganisms in water. Mathew (1997) developed a fluorescent detector to identify hydrocarbons in ground water. Bixler et al. (2014) developed a fluorescence technique for real time measurement of urobilin in waste water. All of these studies focus on measuring the contaminant within the water and not on a plumbing surface. Consequently, a technique is required to evaluate a plumbing surface for contaminant in order to decide if it is necessary to replace or not.

The purpose of this study is to apply a NIST fluorescence based measurement technique that was developed for measuring the mass of lubricant at the wall during boiling of refrigerants (Kedzierski, 2001) to measuring the mass of number 2 diesel on a copper pipe surface in the presence of flowing water/diesel mixture. In this way, we not only gain vital fundamental modeling information but we lay the groundwork for a possible early detection/monitoring system for sticky contaminants. Two major efforts have been focused toward the development of an in situ fluorescent measurement technique. First, a calibration technique was developed specifically for quantifying the amount of diesel on a copper pipe surface. Second, a water loop was designed and constructed consisting of a test chamber for subjecting small samples of pipe substrate materials to known concentrations of diesel/water solutions under controlled dynamic flow conditions. The present study presents measurements for only diesel on a copper surface. However, Kedzierski (2016) extends the measurement database for diesel accumulation and removal as a function of free-stream diesel concentration to iron and polyvinyl chloride using the same measurement technique and test apparatus. In addition, the technique could be adapted to any contaminant that fluoresces or that could be made to fluoresce. In general, many hydrocarbons and some microorganisms naturally fluoresce, while other contaminants may be modified to fluoresce.

EXPERIMENTAL APPARATUS AND UNCERTAINTIES

The standard uncertainty (u_i) is the positive square root of the estimated variance u_i^2 . The individual standard uncertainties are combined to obtain the expanded uncertainty (U), which is calculated from the law of propagation of uncertainty with a coverage factor. All measurement uncertainties are reported at the 95% confidence level except where specified otherwise.

Figure 1 schematically shows the flow loop for measuring diesel on pipe substrates. The primary components of the loop are the pump, the reservoir, and the test chamber with the test section. The inside surfaces of the approximately 96 mm by 1.6 mm rectangular flow cross-section of the aluminum test chamber, shown in Fig. 2, were black anodized to minimize stray light reflections. The channel was designed to have the same flow area as a 13 mm diameter copper tube. The test chamber had a circular cavity to accept the solid pipe test section. The height of the channel was 1.6 mm so that the probe could be flush to the top of the test section while maintaining proximity to the test surface for measurement purposes without being an obstruction to the flow. A centrifugal pump delivered the contaminated water to the entrance of the rectangular test chamber at room temperature. The pump head was removable so that it could be easily replaced in order to test a different contaminant. The flow rate was controlled and varied by varying the pump speed with a frequency inverter. A heat exchanger immersed in the reservoir was supplied

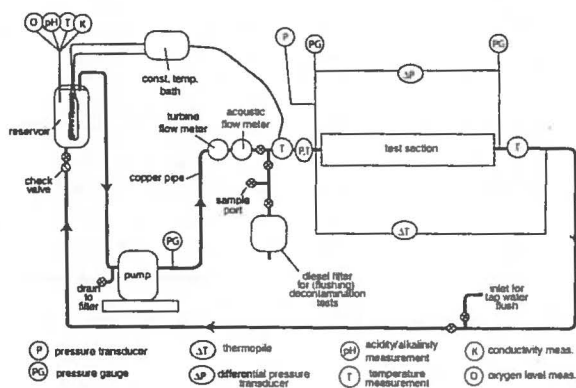


FIGURE 1
Schematic of test loop.

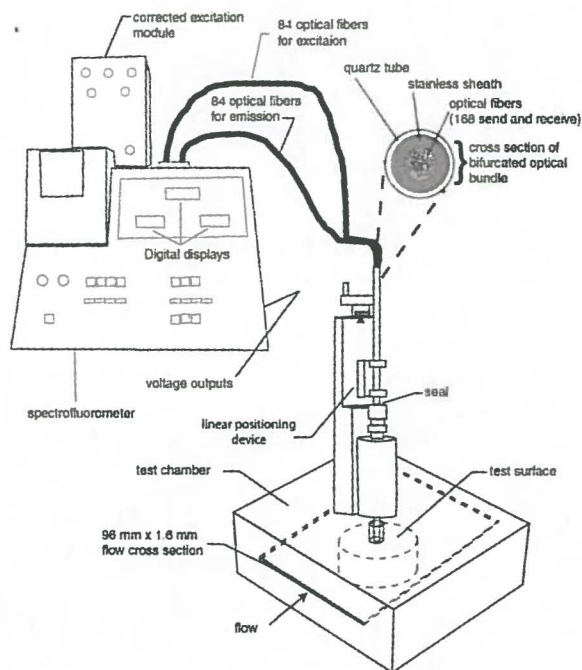


FIGURE 2
Schematic of spectrofluorometer, test section, and linear positioning device.

with brine from a temperature-controlled bath to maintain the entrance temperature to the test chamber at ambient temperature (293.8 K). This was done to ensure that the diesel was at the same temperature as it was during the fluorescence calibration to avoid the temperature effect on fluorescence (Miller, 1981). An additional temperature-controlled bath was used to maintain the fluorescence standards at the same ambient temperature.

Residential copper pipe was used to plumb together the various components of the loop. Redundant volume flow rate measurements were made with an ultrasonic doppler and a turbine flowmeter with expanded uncertainties of $\pm 0.12 \text{ m}^3/\text{h}$ and $\pm 0.03 \text{ m}^3/\text{h}$, respectively. As shown in Fig. 1, three water pressure taps before and after the test chamber permit the measurement of the upstream absolute pressure and the pressure drops along the test section with expanded uncertainties of $\pm 0.24 \text{ kPa}$ and $\pm 1.5 \text{ kPa}$, respectively. Also, a sheathed thermocouple measured the water temperature at each end of the test chamber to within an uncertainty of $\pm 0.25 \text{ K}$. The dissolved oxygen level, the conductivity, and the pH,

were monitored at the water reservoir with associated B-type uncertainties of $\pm 0.5\%$, $\pm 50 \mu (\Omega \text{cm})^{-1}$, and ± 0.3 , respectively.

Figure 1 also shows the inlet and exit taps that were used to flush the test section with fresh tap water. In preparation for flushing, the test section was isolated with valves from the rest of the test loop. Then the fluid was drained from the test chamber and returned to the reservoir. Next, a tap water supply was connected to a test chamber port. The other test chamber port was connected to a filter to absorb any diesel before it was sent to a drain.

Figure 2 shows a view of the spectrofluorometer that was used to make the fluorescence measurements and the test chamber with the fluorescence probe perpendicular to the flattened pipe test surface. Figure 3 shows a simplified schematic of the right angle spectrofluorometer consisting of a xenon light source, an excitation and an emission monochromator, and an emission photomultiplier tube (detector). The spectrofluorometer was designed to accept $45 \text{ mm} \times 10 \text{ mm} \times 10 \text{ mm}$ fluorescent samples or cuvettes filled with fluorescent material. A special adapter with lenses and mirrors, which replaced the cuvette holder, was fabricated to remotely excite and measure fluorescence via a bifurcated optical bundle. Two optical bundles consisting of 84 fibers each originated from the spectrofluorometer. One of the bundles transmitted the excitation light, i.e., the incident intensity (I_0), to the test pipe surface. The other bundle carried the emission, i.e., the fluorescence intensity (F), from the test

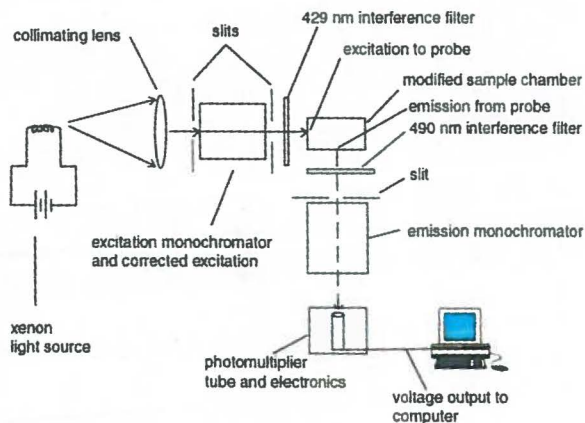


FIGURE 3
Schematic of right angle spectrofluorometer.

surface to the spectrofluorometer. The optical bundles originating from the spectrofluorometer merge transmitting and receiving fibers randomly into a single probe before entering the test section chamber. The sensor end of the fluorescence probe is sheathed with a quartz tube to protect it from reacting with the contaminant in the test fluid.

As the name suggests, right angle spectrometry was designed to limit the interference of the excitation signal on the emission signal by orientating the detector perpendicular to the beam of the emission monochromator. Considering this, the parallel configuration of the excitation and emission at the measuring end of the bifurcated optical bundle as shown in Fig. 2 is not ideal but was necessary for this application. The parallel configuration allows the reflection of the excitation from the copper surface to be transmitted through the emission fiber optics and to the detector. This can be a serious limitation given that the reflected excitation can overwhelm the emission signal even if the emission wavelength (λ_m) and the excitation wavelength (λ_x) differ because: (1) the excitation intensity can be several orders of magnitude greater than that of the fluorescence emission, and (2) the filtering process of the emission monochromator is not complete enough to entirely remove the reflected wave. The filtering process of the monochromator supplies the detector with an intensity that is distributed about the desired wavelength but with relatively small tails at larger and smaller wavelengths. Consequently, if the excitation intensity is very large, the tails of the excitation distribution can be greater than the peak emission intensity. A successful remedy for reducing the interference of the excitation signal was to place a 10 nm bandwidth bandpass interference filters at the exit of the excitation monochromator and one before the entrance to the excitation monochromator. Figure 3 schematically shows the placement of the bandpass interference filters.

The excitation wavelength and the emission wavelength were set to 434 nm and 485 nm, respectively, for all tests. As describe in Kedzierski (2006), the choice of these wavelengths ensured that a significant and measurable emission signal was obtained with no

measurable overlap of the excitation and emission spectra.

TEST FLUIDS

Commercially available number 2 diesel was used rather than a chemically simpler surrogate in order to demonstrate the use of the technique with an actual potential contaminant. Although organizations like the Water Research Foundation and American Water Works Association are primarily focus on pervasive contaminants like lead (Brown et al., 2015); nevertheless, studying diesel is justified because it is sticky so it can represent something toward a worst case scenario for contaminant removal by flushing. Diesel was also a desirable test contaminant because it has been found to exhibit a strong fluorescence.

Considering the complexity and the variability of diesel, the diesel for the project was restricted to a single batch. In this way, we can ensure the consistency of the properties of pure number 2 diesel^{II} fuel such as its liquid density and fluorescence characteristics.

A 2% by mass diesel mixture was prepared with local Gaithersburg, MD tap water and the mixture was left to form a colloid for approximately 3 months to provide sufficient time for the diesel and the water to reach equilibrium. While the method of preparation may not reflect the most likely contamination scenario, the methodology does provide a consistent test fluid for examining the effect of flow rate on contamination because the flow rate is varied for fixed fluid properties. The measured dissolved oxygen level, the conductivity, and the pH, of the water at 24°C before mixing with diesel were found to be, 86.4%, 358 $\mu\Omega/\text{cm}$, and 7.04, respectively. Number 2 diesel fuel was used from a single batch throughout the experiment to avoid property variations that might be caused by batch variations due to it being a complex mixture of hydrocarbons. Kedzierski (2006) provides the measured viscosity and density of the pure diesel liquid.

Because diesel is a complex mixture, its hydrolysis results in a dispersed phase of differing components that reside in separate regions of the colloid depending

^{II} "Pure diesel" is used here to denote that the particular batch of diesel, which will be consistently used throughout this project, is not mixed with water.

on the density, dispersion size, and hydrophobic nature of each component. If quiescent, the test reservoir had a stable Brownian suspension within the bulk water, which likely differed chemically from the dispersed phase that floated on top of the bulk liquid, and that which rested on the bottom of the reservoir. The result of and the evidence for a chemical breakdown of the diesel is given in Kedzierski (2006), which shows that the peak fluorescence emission for the emulsified water diesel mixture taken from the reservoir exists at a wavelength that is 25 nm greater than that of pure diesel. Because of the hydrolysis of diesel, positive and/or negative bias errors are likely to occur in the mass measurement depending on the individual spectra of the fluorescing components of the hydrolyzed diesel. For example, a positive bias error may result because nonfluorescent components that contributed to the diesel mass during the calibration may not deposit on the surface. Likewise, a negative bias error may occur because the peak intensity of the fluorescent material on the test surface has shifted from that of the calibration.

The hydrolysis of the diesel and the configuration of the inlet and the outlet of the reservoir influence the flow in the test section. As shown schematically in Fig. 1, the opening of the pump suction line in the reservoir is situated approximately 10 mm below the liquid-air interface. This design entrains the hydrolyzed diesel floating on the water surface with that in the bulk water, and on the bottom of the reservoir into the pumped flow. The return flow entering the bottom of the reservoir ensured good flow mixing. Figure 4 depicts the colloidal flow within the test section and the fluorescent measurement probe above it for the contamination and decontamination test conditions. The size of the droplets in the dispersed flow is exaggerated for illustration purposes. Both test conditions are shown to have an excess layer thickness (l_e) of undiluted hydrolyzed diesel adsorbed to the test surface. Because the molar mass of the diesel is unknown, the surface excess density (Γ) is defined in the work on a mass basis as (Kedzierski, 2001):

$$\Gamma = l_e(\rho_d - \rho_b x_b) \quad (1)$$

The density of liquid diesel is ρ_d . The density of the bulk mixture ρ_b is evaluated at the bulk mass fraction of the mixture (x_b). The surface excess density is

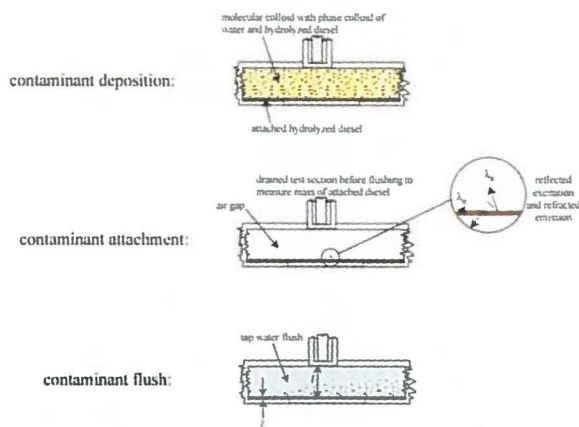


FIGURE 4 Cross-sectional illustration of test section during contamination and flushing.

roughly the mass of diesel attached per surface area. The Γ and l_e are the primary measurements of this study.

MEASUREMENTS AND UNCERTAINTIES

Fluorescence/Mass Calibration

Fluorescence as a means for detecting a contaminant has its advantages in that its absorption and fluorescence spectra are like a fingerprint that can be used in its identification. Consequently, by isolating the wavelength of light that the contaminant fluoresces, its intensity can be used to identify its mass. This is true even when the contaminant is mixed with another fluorescent or nonfluorescent substance as long as the fluorescent substance does not absorb and emit at the same wavelengths as the contaminant. For this reason, the tap water was examined and it was not found to fluoresce at any wavelength for any excitation wavelengths between the range of 200 nm and 800 nm. Consequently, interference from water is not possible via it contributing to the intensity of the fluorescence signal.

The calibration technique that was developed here for detecting the mass of diesel on a copper surface exposed to a flowing dilute mixture of diesel in water is introduced in the following. Two different calibration methods had to be combined due to the additional

complexity caused by immiscible liquids. Both calibration techniques were used to quantify different functional aspects of the Beer-Lambert-Bouguer law (Amadeo et al., 1971), which forms the basis of the calibration equation. The first method is essentially the same as the original NIST calibration method that was used to detect lubricants on boiling surfaces (Kedzierski, 2002). This methodology was used to obtain the relationship between diesel composition and fluorescence intensity for a fixed light path length (fixed probe height above the test surface).¹¹ The second method, that was developed in this study, relies on a perpendicular traverse of the flow stream with the measurement probe. To achieve this, a linear positioning device with a graduated knob was adapted to the quartz tube as shown in Fig. 2. The second method (traverse method) is used to calibrate the effect of contaminant thickness (path length) and the proximity of incident intensity. The traverse method is essential for splitting the total measured fluorescent intensity into two components: that from the diesel on the test surface and that from the diesel in the bulk flow stream. In this way, the mass of diesel on the test surface and the composition of the fluid stream are determined.

Figure 5 shows the vessel that was used in the first method to calibrate the fluorescence intensity received from the bifurcated optical bundle against the mass fraction of diesel. The lid of the 150 mL black, anodized, metal jar had a port for evacuation¹ and filling of the test sample and a fitting to seal around the stainless tube that pierced the lid. The stainless tube had a quartz tube and a quartz bottom welded to its end and it was the same type that was used in the test chamber of Fig. 2. A disk of copper pipe material was placed on the bottom of the jar. By using the same material and surface roughness, the disk and the test pipe had the same reflective properties. Copper from a flattened pipe was evenly oxidized by electrolysis and soldered to the top of the calibration disk that had circumferentially machined grooves for sealing in the test chamber. The same disk was used as the calibration disk and the test surface to compensate for unknown surface effects. The distance between the top of the cali-

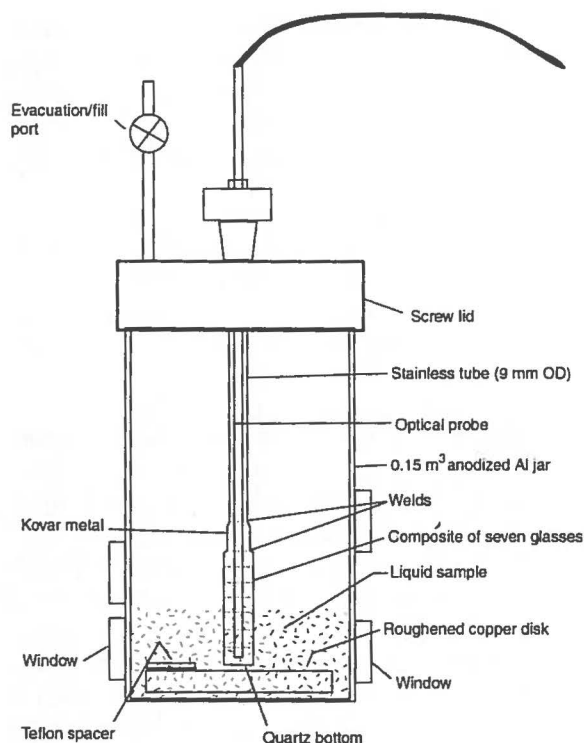


FIGURE 5
Schematic of fluorescence/composition calibration jar.

bration disk and the bottom of the quartz tube was set with the aid of a 1.6 mm Polytetrafluoroethylene (PTFE) gauge disk and micrometer dial indicators. This fixes the path length of the fluorescence and the mass of fluorescent liquid below the probe. During calibration, the jar and the portion of the quartz tube above the lid were covered with black insulation to prevent the optical probe from receiving ambient light. The probe rested on the inside-bottom of the quartz tube.

Three jars were used to calibrate the mass fraction of diesel to the fluorescent intensity. Two jars were used as standards to set the lower (0) and upper (100) limits of the intensity signal on the spectrofluorometer. A jar that contained only pure water was used to zero the intensity. Because light intensities are additive, the

¹¹The first method would have been sufficient had the bulk composition of the flow remained the same as it was charged in the reservoir. Due to the immiscibility of the two fluids, the bulk composition of the flow differs from that in the reservoir.

¹It has been found that weak evacuation of a vessel containing diesel does not measurably change its fluorescent characteristics.

zeroing ensured that the reflected excitation wave and other effects were not attributed to fluorescence. A second jar that contained pure diesel was used to set the intensity on the spectrofluorometer to 100. The third jar was used to measure and record the intensity of various mixtures of diesel and nonfluorescent n-decane of different concentrations. N-decane was used instead of water because it was miscible with diesel and also non-fluorescent. As an additional precaution, all raw-measured intensities (F_i) were numerically normalized by the intensity from the zero-jar (F_0) and the maximum-jar (F_{100}):

$$F = \frac{F_i - F_0}{F_{100} - F_0} \quad (2)$$

where the intensity of the contamination data was adjusted (see Kedzierski, 2006) by no more than 0.3% to account for the small (typically within ± 1 K) difference in temperature between the test section and the bath containing the maximum- and the zero-jars. The maximum correction for the flushing data was greater (1.5%) than for the contamination measurements due to the colder temperature of the house tap water.

Evacuation of the jar was done to prevent fluorescence quenching by oxygen (Guilbault, 1967). N-decane was used because it is miscible with diesel. Calibration measurements proceed by successively adding or removing diesel in appropriately small increments. As shown in Kedzierski (2006), the fluorescence intensity was fitted linearly with respect to the diesel mass fraction to within a residual standard deviation of $\pm 1.2\%$.

The second calibration method involved pure diesel alone and varying the thickness of the diesel below the quartz probe to determine the effect of the proximity of the incident light (I_0) and its path length (l). For these tests, the probe was traversed through the diesel and diesel thickness below the quartz probe was synonymous with the path length. As shown in Fig. 2, a linear positioning device with a graduated knob was used to locate the quartz tube relative to the test surface and thus measure the path length of the incident light through the diesel. The measured fluorescent intensity versus the path length was non-linear as shown in Kedzierski (2006). Given that the intensity versus mass fraction followed a linear relationship, the nonlinear aspect of the intensity versus l was due to the variation in the incident intensity with l . For this

reason, further calibrations were done with fixed diesel film thickness and variable path lengths and it was observed that $\frac{1}{F} \frac{dF}{dl}$ was approximately constant for all ranges of the F and l traverse data for fixed diesel film thickness. This demonstrates the exponential dependence of I_0 with the proximity of the probe to the diesel (l) and that this was the cause of the nonlinear calibration with respect to l . The I_0 path length effect is known as excitation absorbance (Herman, 1998), which results from the diesel nearest to the light source receiving more excitation than the diesel that is further away.

The linear form of the Beer-Lambert-Bouguer law (Amadeo et al., 1971) was used to correlate the measured intensity of the fluorescence emission (F) to the mass of diesel:

$$F = 2.3I_0\epsilon cl\Phi \rightarrow [\epsilon cl \leq 0.05] \quad (3)$$

Here c is the concentration of the fluorescent diesel, which can be rewritten as a product of the bulk contaminant (diesel) mass fraction (x_b) and the bulk liquid mixture density (ρ_b) divided by the molar mass of the contaminant (M_c). Kedzierski (2006) shows that the linear criteria for eq. (3) ($\epsilon cl \leq 0.05$) is satisfied for 78% of the calibration data and the absorbance (ϵcl) did not exceed 0.063. In addition, the use of the full, nonlinear Beer-Lambert-Bouguer law did not reduce the residual standard deviation of the fit. Consequently, use of the linear form of the law is justified.

The mixture densities were calculated on a linear mass weighted basis. The quantum efficiency of the fluorescence (Φ), the extinction coefficient (ϵ), the intensity of the incident radiation (I_0), and the M_c are all unknowns that are lumped into two regression constants and an exponential term to give the regressed calibration of F against x_b for diesel as:

$$F = \frac{2.3I_0\Phi\epsilon}{M_c} l x_b \rho_b = 1.04735 \left[\frac{\text{m}^2}{\text{kg}} \right] l x_b \rho_b e^{-209.23 \text{ m}^{-1} l} \quad (4)$$

Equation (4) shows that $2.3I_0\Phi\epsilon M_c^{-1} = 1.04735 \left[\text{m}^2 \text{kg}^{-1} \right] e^{-209.23 \text{ m}^{-1} l}$. The uncertainty of the calibration given in eq. (4) is approximately $\pm 0.2\%$ of F for the 95% confidence level.

Figure 6 shows that the resulting calibration for the flow conditions is linear. The regression of the same

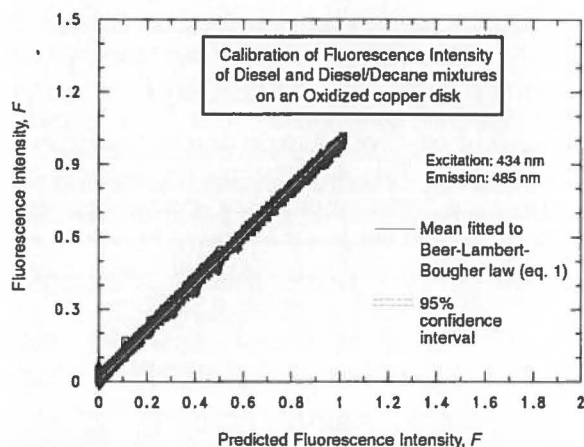


FIGURE 6 Overall calibration of Beer-Lambert Bouguer law for diesel on Cu disk.

measurements against the Beer-Lambert-Bouguer law (Amadeo et al., 1971) gave a greater fit uncertainty suggesting that the linear fit is more appropriate.

Application of Calibration

Given that Γ and l_e are the primary measurements of this study, the main use of the calibration is to solve for these parameters. For the case where the diesel remains completely immiscible with water and has a strong affinity for metal surfaces, an excess layer of pure diesel will form on the pipe surface of thickness l_e .

Equation 3 can be rearranged to solve for the diesel excess layer thickness by setting the mass fraction, and the mixture density to reflect the properties of pure diesel:

$$l_e = \frac{F}{2.3I_0\Phi\epsilon M_c^{-1}\rho_d} = A_0 + A_1 l \quad (5)$$

As shown in Fig. 7, l_e can be regressed to eq. (5) using measurements of F for given values of path length (l) and plotted versus l . The two example F versus l data sets shown in Fig. 7 were obtained by moving the optical bundle closer to the test surface in order to vary the path length. As illustrated by the open circles, most of the resulting values of l_e for a given data set were directly proportional to l ; hence, a linear relationship with respect to l including fitting constants A_0 and A_1 is shown on the rightmost side of eq. (5).

Although, eq. (5) can be used to calculate as many values of l_e as long values of F and l can be supplied, it is valid only for when the path length and the excess layer thickness coincide (for non-zero bulk compositions) because it has been derived for pure diesel. This condition can be met by setting l to l_e in the rightmost portion of the eq. (5) and solving for l_e :

$$l_e = \frac{A_0}{1 - A_1} \quad (6)$$

For traverse data sets that are not linear for the full range of l , as illustrated by the open square symbols in Fig. 7, only the data that is approximately linear near the wall was used to generate constants A_0 and A_1 .

Equation 6 is necessary only for a non-zero bulk mass fraction (x_b). For flushing tests, where $x_b = 0$, eq. (5) is valid for all $l \geq l_e$. Consequently, the excess surface density of diesel for flushing tests is obtained from an average of the l_e obtained from eq. (5) and the traverse measurements.

As shown in Kedzierski (2006), roughly 85% of the l_e measurements have a relative uncertainty of less than 25% for the 95% confidence level. For these measurements the average uncertainty of l_e is approximately $\pm 7\%$ of l_e . Overall, the average uncertainty of l_e was approximately ± 0.2 mm. Because of the relatively small uncertainty in the calibration of F with eq. (4), the dominant component of the uncertainty of l_e is due to the uncertainties associated with the constants in eq. (6), which were obtained from traverse measurements like those shown in Fig. 7.

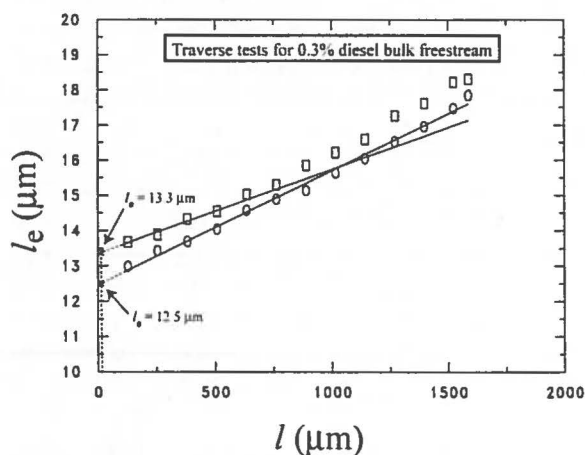


FIGURE 7 Demonstration of excess layer thickness measurement.

The bulk mass fraction can be obtained by dividing the total fluorescence signal (F) into its components along the path length while assuming a uniform bulk mass fraction. The total intensity is the sum of that contributed by the bulk concentration ($F_l(x_m=x_b)$) for the entire path length and that in the diesel excess layer ($F_{le}(x_m=1)$) minus the intensity that would have been due to the bulk concentration but did not occur because it was displaced by the excess layer ($F_{le}(x_m=x_b)$)

$$F = F_l(x_m=x_b) - F_{le}(x_m=x_b) + F_{le}(x_m=1) \quad (7)$$

Substitution of eq. (4) into the components of the above equation and grouping like terms gives:

$$F = 2.3I_o\Phi\epsilon M_c^{-1} [lx_b\rho_b - l_ex_b\rho_b + l_e\rho_d] \quad (8)$$

Here ρ_d is the density of liquid diesel.

When the expression for the linearly mass fraction weighted ρ_b is substituted into eq. (8), its solution is quadratic in x_b with only one root that is less than or equal to 1.

$$x_b = \frac{1}{2} \left(\frac{1}{1 - \frac{\rho_d}{\rho_w}} \right) - \frac{1}{2} \sqrt{\left(\frac{1}{1 - \frac{\rho_d}{\rho_w}} \right)^2 - \frac{4 \left(\frac{F}{2.3I_o\Phi\epsilon M_c^{-1}} - l_e\rho_d \right)}{(l - l_e)(\rho_w - \rho_d)}} \quad (9)$$

where ρ_w is the density of liquid tap water. The average uncertainty of x_b was approximately ± 0.002 . Kedzierski (2016) presents an alternative and equivalent form of eq. (9) for the calculation of x_b .

Air Gap Calibration

A secondary methodology was developed that relies on the gradient of F rather than its absolute value in order to confirm the measurement of l_e as obtained from eq. (5) or eq. (6). The advantage of a gradient approach would be the elimination of a bias or error on the measurement of F if it existed. As shown in Fig. 4, part of the excitation is reflected from the diesel-air interface and is not available to induce fluorescence. Consequently, the calibration must be adjusted to account for the air gap during the drained

test chamber measurements. Kedzierski (2006) provides the derivation of the air-gap l_e and the result is given here as:

$$l_e = \frac{-0.0121 \text{ m} \frac{dF_{ag}}{dl} M_c}{2.3I_o\Phi\epsilon x_m\rho_m} = -0.01156 \frac{\text{kg}}{\text{m}} \frac{\frac{dF_{ag}}{dl} e^{209.23 \text{ m}^{-1}}}{x_m\rho_m} \quad (10)$$

MEASUREMENT RESULTS

Excess Layer Thickness

The test apparatus shown in Fig. 1 was used to submit an oxidized copper disk to exposure tests with two different bulk concentrations of diesel in tap water under varying flow conditions. More specifically, contamination measurements over an approximate 200 h time period were made for five different Reynolds numbers varying from 0 to 7000:

$$\text{Re} = \frac{4\dot{m}}{\mu_b p_w} \quad (11)$$

where the wetted perimeter of the channel was 195 mm, the viscosity of the mixed bulk flow (μ_b) was calculated using a nonlinear mixture equation, and the mass flow rate ($\dot{m}$) was obtained from the turbine meter. Flushing measurements were done for a fixed Re of approximately 5000. The range of Reynolds numbers result from using a range of volume flow rates that a half-inch diameter tube would experience in typical buildings. After each contamination tests, the test surface was cleaned with acetone and clean tap water. Kedzierski (2006) provides tabulated measurements for both the raw and reduced data.

Figure 8 provides the measured diesel layer thickness as caused by an exposure to a flowing water/diesel (99.8/0.2) mixture, i.e., diesel at approximately 0.2% bulk mass fraction (2000 ppm). The exposure time is the duration of exposure of the test surface to the flow starting from when the clean surface was first exposed to a particular flow condition. For all flow rates and exposure times, the average l_e for $x_b=0.2\%$ obtained from the eq. (6) methodology was approximately $2.3 \mu\text{m}$.

Figure 9 provides the measured diesel layer thickness as caused by an exposure to a flowing water/diesel (99.7/0.3) mixture, i.e., diesel at approximately

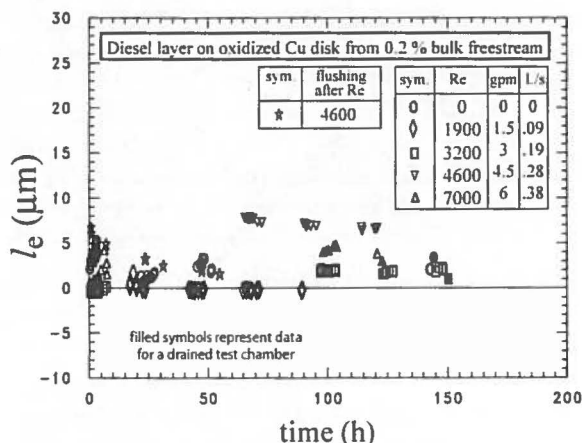


FIGURE 8
Effect of exposure time and flow rate on thickness of the diesel excess layer for a 0.2% bulk freestream mass fraction.

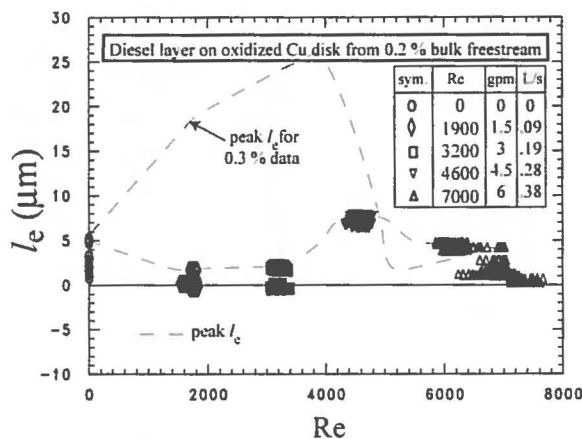


FIGURE 10
Diesel excess layer thickness as a function of Re for water/diesel (99.8/0.2).

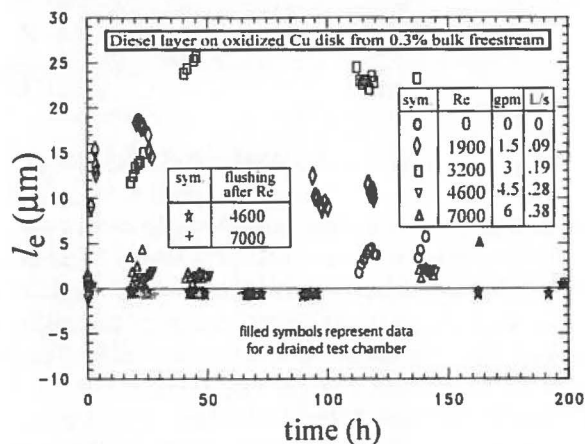


FIGURE 9
Effect of exposure time and flow rate on thickness of the diesel excess layer for a 0.3% bulk freestream mass fraction.

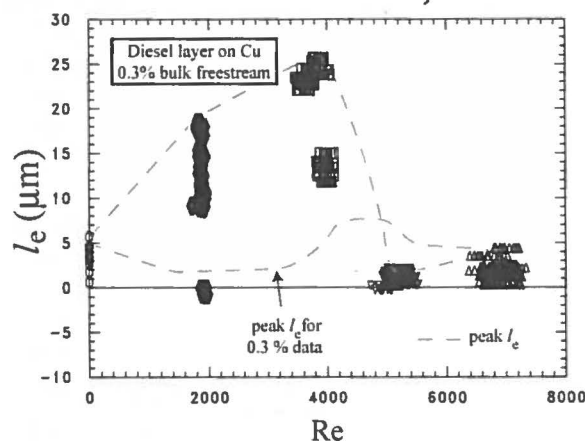


FIGURE 11
Diesel excess layer thickness as a function of Re for water/diesel (99.7/0.3).

0.3% bulk mass fraction (3000ppm). A much larger variability in the measurements is evident for the 0.3% mass fraction than for the 0.2% mass fraction condition. For all exposure times and Re, the average l_e for $x_b = 0.3\%$ was approximately $7.4\mu\text{m}$, which is $5.1\mu\text{m}$ (222%) thicker than the average thickness observed for the 0.2% mass fraction tests.

Figure 10 crossplots all of the excess layer measurements of Fig. 8 as a function of Re. Figure 10 shows that the maximum diesel excess layer thickness of approximately $8\mu\text{m}$ occurred at a Re near 4800. For

Re larger and smaller than 4800, the diesel excess layer was thinner. For example, the l_e for Re near 1900 and 3800 was approximately $1\mu\text{m}$, which is nearly eight times less than the maximum l_e . The l_e for Re greater than 6000 was approximately $3\mu\text{m}$. Figure 11 crossplots all of the excess layer measurements of Fig. 9 (the 0.3% mass fraction tests) as a function of Re. Figure 11 shows that the maximum film thickness of approximately $26\mu\text{m}$ occurred at a Re of approximately 4000. Consequently, a maximum for the diesel adsorption exists near a Re of 4000 for both freestream concentrations. The dashed lines given in Figs. 10 and

11 represent the maximum measured excess layer for each range of Re tests. The variation in Re for a given set of tests for "fixed" Re was caused by an approximate 1% variation in the water temperature during startup and the an approximate 15% variation in the water flow during the nearly 200h test duration.

Filled symbols in Figs. 8 and 10, shown between 150h and 200h, represent l_e measurements that were made at the end of the exposure tests after the test section was drained using the air-gap technique as a secondary measurement technique. For the water/diesel (99.8/0.2), mixture all three of the drain checks were within $\pm 1.5\mu\text{m}$ of the measurements that were made while the test fluid was flowing. For example, for the air-gap check obtained using eq. (10) for the Re near 7000 condition produced a l_e near $3\mu\text{m}$, while the last measurement made with eq. (6) produced a l_e near $3.7\mu\text{m}$. Similarly, eq. (6) produced a l_e of approximately $2\mu\text{m}$ for both the no-flow and the 3200-Re tests, while the eq. (10) check resulted in $3.5\mu\text{m}$ and $1\mu\text{m}$ for l_e , respectively. For the water/diesel (99.7/0.3) mixture, all three of the drain checks for the flushing data were also within $\pm 1.5\mu\text{m}$ of the measurements that were made while the test fluid was flowing giving $0.5\mu\text{m}$ and $-0.5\mu\text{m}$, respectively. However, the agreement between the empty and filled test chamber tests was not as good for the water/diesel (99.7/0.3) mixture for the 7000-Re contamination measurements. For example, the air-gap check for the Re near 7000 condition produced a l_e near $5\mu\text{m}$, while the last measurement made with eq. (4) produced a l_e near $2\mu\text{m}$.

Flushing tests done after the water/diesel (99.8/0.2) 4800-Re contamination tests are shown in Fig. 8. The flushing measurements start at an l_e near $6.5\mu\text{m}$, which agrees with the value of l_e at the end of the 4600-Re contamination tests, thus, confirming the repeatability of the measurement technique. The l_e decreased from approximately $6.5\mu\text{m}$ to approximately 1.5mm after flushing for approximately 55 h. This corresponds roughly to a $0.09\mu\text{m/h}$ removal rate and a 77% reduction of the total diesel thickness over 55 h.

The flushing tests shown in Fig. 10 performed after the 5000-Re water/diesel (99.7/0.3) contamination tests, likewise start at approximately the same l_e ($1.5\mu\text{m}$) as where the previous contamination test ended, again demonstrating good repeatability. After

approximately 20 h of flushing, the 5000-Re contaminant thickness was reduced to approximately -0.5nm . Given the uncertainty of the measurement, most all of the diesel has been removed by flushing with clean tap water. The removal rate achieved after the 5000-Re, 0.3% mass fraction (3000ppm) contamination tests ($0.1\mu\text{m/h}$) agrees closely with that achieved for the flushing tests done after the 4600-Re, 0.2% mass fraction (2000ppm) contamination tests. This suggests a constant removal rate of approximately $0.1\mu\text{m/h}$ of diesel from a copper surface for a flushing Re of 5000 that is independent of initial thickness and original contamination concentration. No removal rate could be calculated for the flushing tests done after the 7000-Re water/diesel (99.7/0.3) because the tests produced an l_e near -0.5nm for nearly all measurement times.

Freundlich Constants

For sorption systems, the Freundlich constant (K) relates the equilibrium solid-phase concentration (c_s) to the equilibrium concentration of the bulk liquid-phase (c_l) as (Schwarzenbach et al., 2003):

$$c_s = Kc_l^n \quad (12)$$

where the Freundlich exponent (n) determines the rate of sorption to the solid surface.

Equation 12 can be rewritten in terms of the excess surface density and the mass fraction of the bulk liquid as:

$$\Gamma = \frac{K}{a_s} \left(\frac{x_b \rho_b}{M_c} \right)^n = \hat{K} (x_b \rho_b)^n \quad (13)$$

where the constant a_s is the specific surface area of the solid defined as the surface area per mass of solid. Here K is normalized by the constant a_s and the molar mass of the contaminant raised to the n^{-1} power ($M_c^{n^{-1}}$) to give $\hat{K}$.

Because the present measurements do not sufficiently span the free stream concentration variable to accurately determine the Freundlich exponent, it was assumed that the diesel-water-copper system behaved as one with constant sorption free energies giving a linear isotherm with $n=1$. Using this assumption, the normalized "Freundlich constants" were obtained by averaging measurements for a particular Re test for

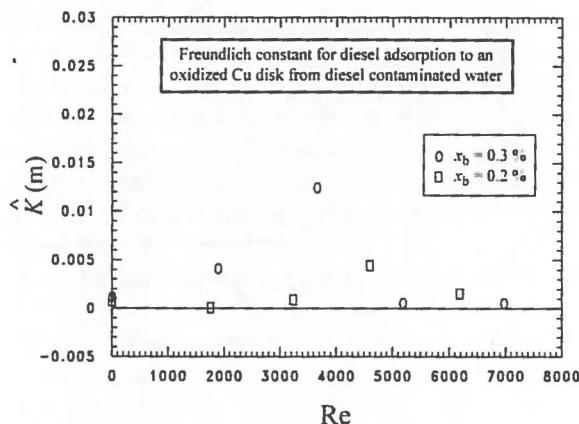


FIGURE 12
Normalized Freundlich constants for diesel adsorption to an oxidized Cu disk from diesel contaminated water.

exposure times greater than 50 h in order to approach an equilibrium or steady state value for $\hat{K}$. All of the l_e measurements, for a given Re test, appeared to be nearly constant after 50 h of exposure. Consequently, it was assumed that a balance between diesel deposition and removal had been achieved.

Figure 12 shows the normalized Freundlich constant as a function of Re for the two different bulk concentrations of this study. The uncertainty in $\hat{K}$ was estimated to be approximately $\pm 10\%$ of its value. The figure shows that $\hat{K}$ varies between near zero to values approaching 0.015 m. For Re less than 4000, the $\hat{K}$ behaves as expected with values for the 0.3% bulk mass fraction being larger than those for the 0.2% bulk mass fraction. However, for Re greater than 4000, the opposite behavior is observed, with $\hat{K}$'s for the 0.2% mass fraction being larger than those for the 0.3% mass fraction. Considering that a Re of 4000 is beyond the transition Re (from laminar to turbulent flow)² and within the transition region, no explanation can be offered at this time for the crossover phenomenon.

DISCUSSION

Because of its derivation from thermodynamics, the Freundlich constant given in eq. (12) is associated

with chemical and/or physical equilibrium between the liquid-phase and the solid-phase concentrations. The measured phenomenon of the present study cannot be expressed in terms of a solid-phase concentration. The solid is not soluble with respect to the contaminant. Rather, the contaminant is located at the solid surface. As a result, the normalized "Freundlich constant" given by eq. (13) ($\hat{K}$) may not necessarily represent thermodynamic equilibrium. The $\hat{K}$ may be influenced by physical forces other than Van der Waals like flow and pressure forces. For this reason, the variation of the normalized Freundlich constant with respect to Re for fixed liquid-phase concentration is not prohibited by thermodynamics.

It is difficult to estimate the effect of the hydrolyzed diesel on the measurements, but it has likely introduced an unknown bias error to measurements. Future test with fresh diesel and water mixtures that have not had time to hydrolyze would reduce or eliminate the bias error.

CONCLUSIONS

A detailed account of the development of a fluorescence based measurement technique for measuring the mass of contaminant on solid surfaces in the presence of water flow has been provided. A test apparatus was designed and developed to use the fluorescent properties of diesel for the purpose of studying its adsorption and desorption to and from an oxidized copper test surface. A calibration technique was developed to measure both the mass of diesel adsorbed per unit surface area (the excess surface density) and the bulk concentration of the hydrolyzed diesel in the flow.

The measured diesel excess surface density that was adsorbed to the surface varied between zero and 0.02 kg/m² for Reynolds numbers between zero and 7000. A maximum for the diesel adsorption was observed near a Re of 4000 for both nominal bulk mass fractions of 0.2% and 0.3% diesel. For the most part, the thickness of the diesel excess surface density remained less than 10 μ m. The exception to these excess layer measurements was the 0.3% bulk mass

²The transition Re would be 2300 if the hydraulic diameter concept prevails, and 3000 (Schlichting, 1979) if the flow is considered to be one between infinite flat plates.

fraction with $Re=4000$ measurements that peaked near $25\mu\text{m}$.

In an effort to model the adsorption of diesel to copper, normalized Freundlich constants were calculated based on a linear isotherm and found to vary between near zero and 0.015m . Most of the Freundlich constants were less than 0.005m . In addition, flushing tests suggest a constant removal rate of approximately $0.1\mu\text{m/h}$ of diesel from a copper surface that is independent of initial thickness and original contamination concentration. The measurements show that most all of the diesel has been removed to within the uncertainty of the measurement procedure by flushing with clean tap water.

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NOMENCLATURE

English Symbols

A	regression constants in eq. (5)
a_s	specific surface area, $\text{m}^2 \text{kg}^{-1}$
c	concentration, mol m^{-3}
I	fluorescence intensity
I_r	raw fluorescence intensity measurement
I_i	incident intensity, V
K	Freundlich constant, $\text{mol}\cdot\text{kg}^{-1}$
K_n	normalized Freundlich constant, m
L	path length, m
δ	thickness of excess layer, m
M	molar mass of contaminant, kg mol^{-1}
$\dot{m}$	mass flow rate, kg s^{-1}

Re	Reynolds number
n	Freundlich exponent
p_w	wetted perimeter of channel, m
T	temperature, K
U	expanded uncertainty
u_i	standard uncertainty
x	mass fraction of diesel

Greek symbols

Γ	surface excess density, kg m^{-2}
ϵ	extinction coefficient
λ	wavelength, m
μ	dynamic viscosity, $\text{kg m}^{-1} \text{s}^{-1}$
ρ	mass density of liquid, kg m^{-3}
Φ	quantum efficiency of fluorescence

English Subscripts

0	zero reference jar
100	maximum reference jar
ag	air gap
b	bulk
d	pure diesel
e	excess layer
m	emission, mixture
o	outlet or exit
s	solid surface
x	excitation
w	tap water

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