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Silicone Sensing Phase for Detection of Aromatic Hydrocarbons in Water Employing Near-Infrared Spectroscopy

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The use of silicone for detection of aromatic hydrocarbons in water using near-infrared spectroscopy is proposed. A sensing phase of poly(dimethylsiloxane) (PDMS) was prepared, and a rod of this material was adapted to a transflectance probe for measurements from 850 to 1800 nm. Deionized water samples contaminated separately with known amounts of benzene, toluene, ethylbenzene, and *m*-xylene were used for evaluation of the PDMS sensing phase, and measurements were made in a closed reactor with constant stirring. Equilibrium states were obtained after 90, 180, 360, and 405 min for benzene, toluene, ethylbenzene, and *m*-xylene, respectively. The PDMS sensing phase showed a reversible response, presenting linear response ranges up to 360, 290, 100, and 80 mg L^{-1}, with detection limits of 8.0, 7.0, 2.6, and 3.0 mg L^{-1} for benzene, toluene, ethylbenzene, and *m*-xylene, respectively. Reference spectra obtained with different rods showed a relative standard deviation of 0.5%, indicating repeatability in the sensing phase preparation. A relative standard deviation of 6.7% was obtained for measurements performed with six different rods, using a 52 mg L^{-1} toluene aqueous solution. The sensing phase was evaluated for identification of sources of contamination of water in simulated studies, employing Brazilian gasoline type A (without ethanol), gasoline type C (with 25% of anhydrous ethanol), and diesel fuel. Principal component analysis was able to classify the water in distinct groups, contaminated by gasoline A, gasoline C, or diesel fuel.

Contamination of the environment due to anthropogenic activities is a global problem that has caused growing concern in many segments of society. One of these activities relates to the production, storage, and transportation of petroleum derivatives, such as gasoline and diesel fuel, and organic solvents, as spills and leaks of these liquids can contaminate soils, superficial water, and groundwater. Among the substances that can be found in petroleum derivatives or can be used as solvents, aromatic hydrocarbons, due to their toxicity, have attracted considerable attention. In particular, efforts have been focused on the determination of benzene, toluene, ethylbenzene, and the xylenes, a class of aromatic hydrocarbons known as BTEX.

The techniques employed to perform the determination of these compounds are usually based on gas chromatography or high-performance liquid chromatography. Solid-phase extraction (SPE)[1,2] is frequently employed in conjunction with these chromatographic techniques, for the preconcentration of the hydrocarbons from contaminated water. Despite its good performance, the SPE procedure requires reextraction of the contaminants with an appropriate solvent before injection of the sample into the chromatograph. Solid-phase microextraction (SPME) has been proposed to have advantages over SPE, as the extracted contaminants can be directly injected into a gas chromatograph.[3,4] Although advantageous, these methods require sophisticated instrumentation and. therefore, present difficulties in field monitoring.

Optical fiber chemical sensors have been also proposed for the determination of aromatic hydrocarbons in contaminated waters,[5–10] presenting, among other advantages, the possibility of miniaturization for field applications. These sensors usually employ a polymer-clad silica fiber, and measurements are based on the evanescent waves principle. The polysiloxane cladding of the fiber extracts the hydrocarbon from water in a way similar to SPME, and as a consequence, its characteristics (refractive index and ability of absorbing radiation) are modified, changing the properties of the propagating wave, as the evanescent field of the

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standing wave penetrates into the cladding, interacting with it.[11–12] The selectivity of the polymer cladding to different types of hydrocarbons can be designed by choosing different substituent groups (for example, alkyl and phenyl groups) on the polysiloxane, and sensors have been proposed for determination of chlorinated,[13] aliphatic,[14] and aromatic hydrocarbons.[15] Usually, the detection system is based on mid-infrared (MIR)[8,10] or near-infrared (NIR)[11–15] spectroscopies. Although absorption bands in the MIR region are ~10−100 times more intense than in the NIR region, the latter spectroscopic technique employs simpler and more robust instrumentation, which favors field applications. Furthermore, most of the remote probes used in MIR region show poor transmission characteristics due to the usual materials employed in their construction, impairing its application.

NIR comprises the wavelength region of the electromagnetic spectrum from 780 to 2500 nm, and the absorption bands arise mainly from overtones and combinations of fundamental vibrations of C−H, O−H, and N−H bonding. In aqueous solutions, the more intense and broad absorption from combination and overtone bands of the O−H group that occurs almost over all the NIR spectral range masks the less intense C−H absorption bands of the organic compounds, impeding the direct determination of hydrocarbons in water. In addition, the concentrations of saturated aqueous solutions of aliphatic and aromatic hydrocarbons are very low, beyond the quantification limit of NIR spectroscopy. Due to these aspects, extraction of the organic compounds from water by a polysiloxane cladding of the optical fiber evanescent wave sensor plays a fundamental role, as it avoids the interference of water as it preconcentrates the organic compounds to be determined. The main drawback of methods based on the evanescent wave principle is in regard to the frequent necessity of employing long optical fibers (up to 30 m) in order to improve the quantification limit.[15] In addition, special attention must be paid to the optical arrangement in order to admit and collect suitable radiation power. The sensors developed so far are based on the use of a narrow band of radiation in the NIR region and limits their selectivity to distinguish hydrocarbons and hydrocarbon mixtures such as combustibles derived from petroleum.

Chemometric techniques, such as principal component analysis (PCA), have been widely employed for pattern recognition, being applied for classification of different samples, such as those from the beverage, food, pharmaceutical, and petrochemical industries. Regarding petrochemical samples, premium and regular gasoline have been classified by employing PCA with data obtained by using gas chromatography/mass spectrometry,[16] and the NIR spectroscopy/PCA approach has been applied to classify metropolitan and countryside diesel fuels[17] and petroleum products.[18]

This work describes an optical sensor that uses a poly-(dimethylsiloxane) (PDMS) rod as the sensing phase for detection of aromatic hydrocarbons in water, employing NIR spectroscopy. In contrast to previous contributions, which were based on evanescent waves, a simpler approach for measurements is proposed that employs a transflectance probe, in which silicone rods can be easily coupled. Benzene, toluene, ethylbenzene, and m-xylene were used to evaluate the PDMS sensing phase, and the technique was applied to identification of the type of contamination present in water intentionally spiked with Brazilian gasoline type A (without ethanol), gasoline type C (with 25% v/v of anhydrous ethanol), and diesel fuel.

EXPERIMENTAL SECTION

Reagents. Benzene, toluene, ethylbenzene, and m-xylene were used as purchased from Merck. Distilled−deionized water was used to prepare the simulated contaminated water samples. Gasoline A was obtained from Refinaria do Planalto (REPLAN Petrobrás, Paulínia, SP, Brazil), and gasoline C and diesel fuel were acquired at a local fuel station. Silicast T2 and its curing agent were supplied by Dow Corning Inc.

Sample Preparation. Aqueous solutions of the aromatic hydrocarbons were prepared by transferring ~500 μL of the organic solvent (benzene, toluene, ethylbenzene, or m-xylene) to a 500-mL flask completely filled with distilled−deionized water. The flask was sealed, and the mixture was continuously stirred for 12 h at 22 °C. Although by following this procedure saturated aqueous solutions of the aromatic hydrocarbons were expected to be obtained (except for benzene), the actual concentrations of the organic compounds in water were indirectly determined by measuring total organic carbon (TOC 5000 Shimadzu). Contaminated water samples with different concentrations of hydrocarbons were then prepared by proper dilution of the saturated solutions. Aqueous samples contaminated with gasoline C (contains 25% of ethanol) were prepared by mixing 10, 25, 50, 75, 100, and 150 mL of the combustible into 1000 mL of water in an extraction funnel. For water contamination by gasoline A or by diesel fuel, 25 mL of the combustible was added to 1000 mL of water. The mixtures were shaken for 5 min and allowed to stand for 8 h for separation of the organic and aqueous phases. A 500-mL aliquot of the saturated aqueous solutions was transferred to a closed reactor to perform the experiments.

Sensing Phase Preparation. The PDMS polymer was prepared as recommended by the manufacturer. The monomer and the curing agent (10:1 w/w) were mixed and gently homogenized to minimize the generation of air bubbles. The mixture was transferred to PTFE templates, with different heights (1.0, 5.0, and 10 mm), and placed under vacuum for 2 h in order to expel the air bubbles produced during the homogenization. The polymerization was then allowed to occur for 36 h. After this period of time, the plates were transferred to vacuumed oven at 60 °C for 6 h. With the aid of a cork borer, PDMS rods with diameters of 3.2, 5.5, and 7.0 mm were obtained.

Apparatus. Measurements were performed by employing a Luminar 2000 Brimrose near-infrared spectrophotometer. The instrument is based on an acoustic-optical tunable filter, capable of reaching high scan speeds. A tungsten lamp was employed as light source, and detection was made with an InGaAs detector, covering the spectral range from 850 to 1800 nm. A transflectance

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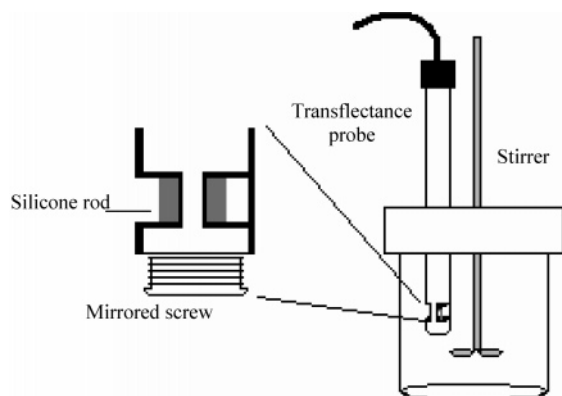
Figure 1. Experimental setup employed for measurements, showing detail of the transflectance probe with the PDMS sensing phase.
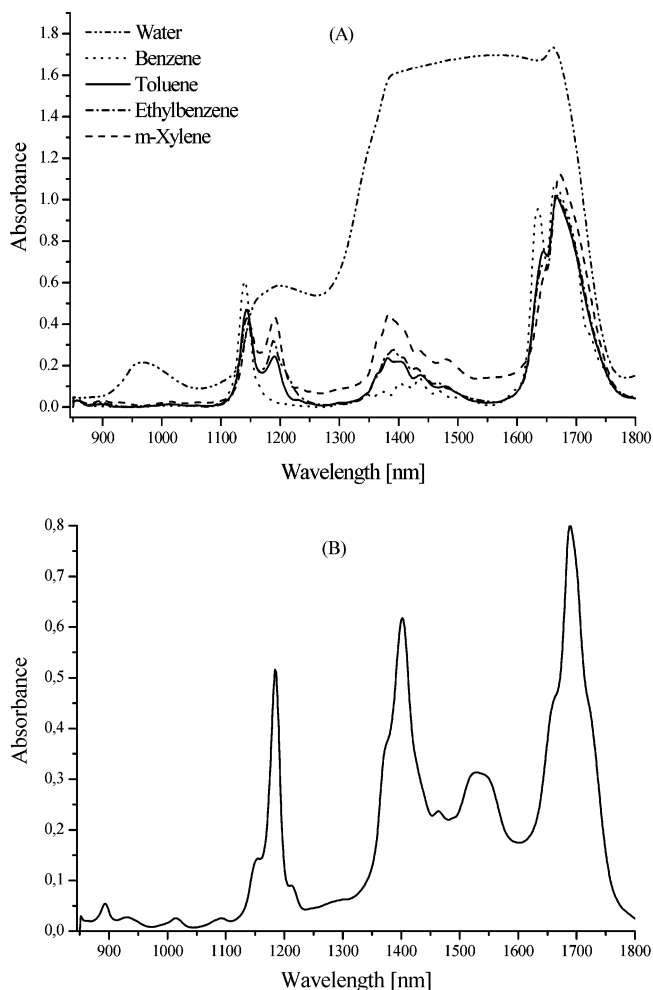

Figure 2. Spectra of deionized water and aromatic hydrocarbons obtained by employing the standard 10-mm optical path transflectance probe (A) and spectrum of the silicone sensing phase adapted to the probe and immersed in water (B).

optical fiber probe (Brimrose, model 685, 12-mm shaft diameter), with variable optical path from 1 to 10 mm, was employed, into which the PDMS rods were adapted for measurements. To adapt a rod in the probe, the end mirror (which defines the optical path) was unscrewed, the rod was inserted in the tip of the probe, and the mirror was then replaced, holding the PDMS rod as shown in Figure 1. Each spectrum was acquired as an average of 100 scans, in a procedure that takes ~10 s.

Procedure. Figure 1 depicts the system employed for absorbance measurements. Solutions of contaminated water samples were transferred to the 500-mL double-walled glass reactor, maintained at 22 °C by an external water bath. The reactor was completely filled with the aqueous sample, avoiding any headspace, which could allow loss of the volatile organic compounds. In addition, a flat lid with an O-ring was employed to tightly close the reactor. The sample solution was mechanically stirred at 600 rpm during the measurements. The PDMS rod was adapted to the transflectance probe, which was immersed into the aqueous sample. O-rings were also employed to fix the probe and the stirrer to the lid, avoiding loss of the volatile hydrocarbons. Spectra were acquired every 60 s for samples contaminated with gasoline or diesel fuel and every 150 s for aqueous aromatic hydrocarbon samples for a period necessary to reach a steady-state signal. For all absorbance measurements, the spectrum of the PDMS rod adapted to the probe and immersed in deionized water was employed as reference, providing the I_0 intensities for absorbance calculations.

RESULTS AND DISCUSSION

Measurement Principle. The direct determination of low contents of hydrocarbons in water by NIR spectroscopy is not possible due to the high absorbance of the O−H group, which prevails over the weaker C−H absorption. Figure 2A shows absorbance spectra of the pure compounds, which were acquired by employing the transflectance probe with an optical path of 10 mm. Water presents a broad and intense band extending from 1300 to 1750 nm, hiding, for instance, the spectra of BTEX, making impracticable its determination in aqueous samples, as mentioned.

Similarly to sensors based on the evanescent wave principle that employ an optical fiber with silicone cladding to extract the hydrocarbons from water, the sensor proposed in this work employs a silicone rod as sensing phase. Figure 2B shows the spectrum of a silicone rod adapted to the transflectance probe,

which was immersed in water. The spectrum presents intense peaks at 1184, 1402, and 1690 nm mainly due to the presence of CH_3 groups of the PDMS polymer. When the probe, with the PDMS rod adapted, is immersed in aqueous solutions of BTEX, the aromatic hydrocarbons are extracted from water by the PDMS sensing phase, where they are also concentrated. This process also avoids the interference of water on the measurements, becoming the basis of the proposed sensing scheme for detection of aromatic hydrocarbons in water. Figure 3 shows the spectra recorded after immersing the probe for 60 min in aqueous solutions containing benzene, toluene, ethylbenzene, and *m*-xylene. These spectra result after subtraction of the absorption spectrum of PDMS sensing phase (shown in Figure 2B). All four hydrocarbon spectra present a peak around 1140−1150 nm, which arises from aromatic CH stretching. However, except for benzene, a small peak around 1200 nm is observed due to nonaromatic CH stretching, which increases from toluene to *m*-xylene, as the numbers of C−H bonds of the methyl and ethyl groups increase. In addition, the profiles of the peaks around 1700 nm are also different, as a consequence of the different groups attached to the aromatic ring. Figure 3 also shows the spectrum of a 146 mg L^{-1} aqueous toluene solution obtained with the standard transflectance probe, plotted after subtraction of the spectrum of the
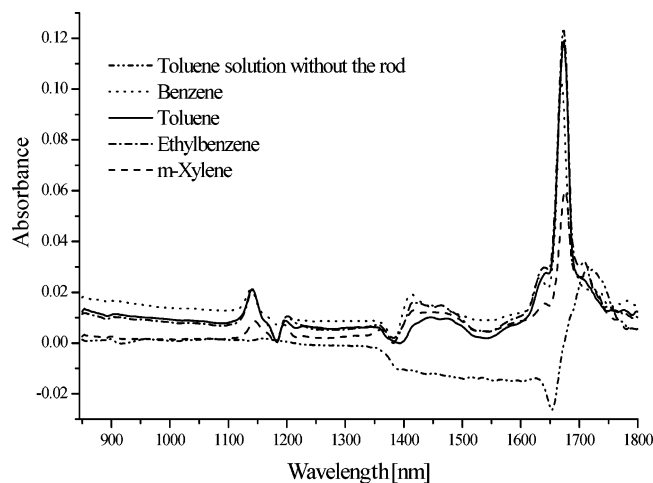
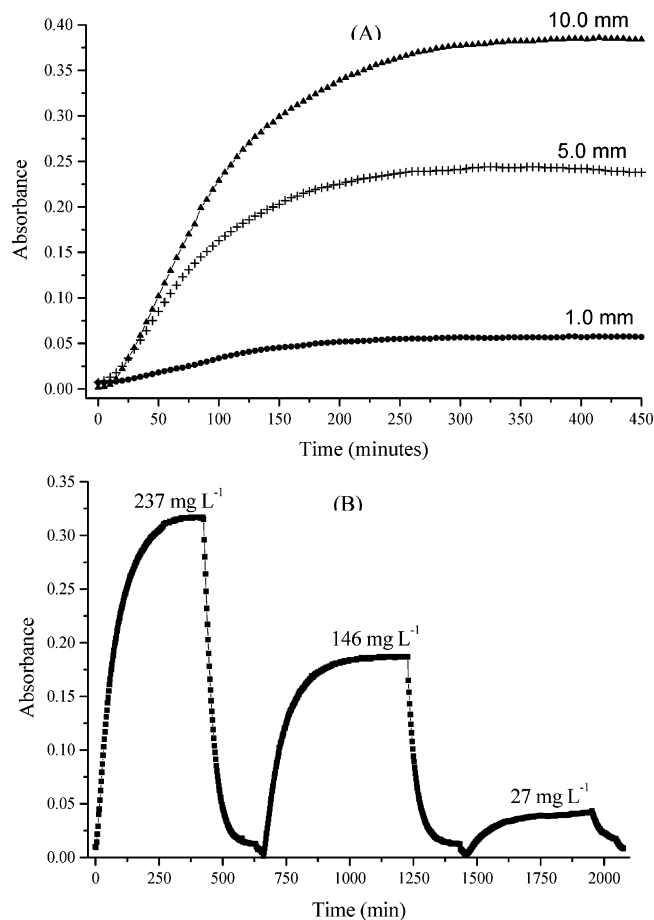**Figure 3.** Spectra of a 146 mg L^{-1} aqueous solution of toluene obtained with the probe without the PDMS rod and obtained with the PDMS sensing phase (10-mm optical path, 3.2-mm diameter) immersed in aqueous solutions of benzene (137 mg L^{-1}), toluene (146 mg L^{-1}), ethylbenzene (98 mg L^{-1}), and *m*-xylene (74 mg L^{-1}).

water, indicating the unfeasibility of direct determination of hydrocarbons in water. A comparison between the spectra shown in Figure 2A and Figure 3 reveals that the absorbed compounds in the solid PDMS sensing phase present distinct spectral features. The main absorbance regions remain approximately the same, while the spectral profile changes considerably. Probably, this is the result of strong interactions between the aromatic molecules and the structure of the PDMS. In addition to these results, it is important to mention that the immersion of the probe with the PDMS sensing phase by 60 min in saturated aqueous solutions of nonaromatic hydrocarbons, such as isooctane and *n*-hexane, produced signals of low intensities, which cannot be distinguished from the blank signals, as these compounds present very low solubility in the PDMS polymer, which improves the selectivity of the sensor for aromatic hydrocarbons.

Sensor Optimization. The kinetics and intensity of the sensor response are governed by the diameter and height of the PDMS rod, as these parameters determine the interval of time for attaining steady state and signal magnitude. Although the porosity and the surface area of the rod also affect the sensor response, these parameters were not investigated, as the PDMS sensing phase was prepared as recommended by the manufacturer, and as a consequence, its composition was maintained the same throughout the work. The absorbance intensities as a function of time, obtained with 10-mm-long PDMS rods having three different diameters (3.2, 5.5, and 7.9 mm), showed that wider rods cause a time lag before a measurable absorbance signal can be detected, because the toluene (or any aromatic hydrocarbon) extracted from contaminated water needs to diffuse through the PDMS rod until reaching the optical path of the transflectance probe. As a consequence, the time necessary to reach a steady-state signal is longer and its final intensity decreases as the diameter of the rod increases, as the organic compound, for the same initial concentration in water, will be more diluted in the PDMS sensing phase. The smallest possible diameter for the rod was 3.2 mm, restricted by the diameter of the optical fiber probe. Figure 4A shows the signal profiles obtained as a function of time for measurements of aqueous toluene solutions carried out with 3.2-mm-diameter

Figure 4. Spectra of an aqueous solution containing toluene obtained with PDMS sensing phases with diameters of 3.2 mm and optical paths of 1.0, 5.0, and 10 mm (A) and absorbance signals as a function of time for aqueous solutions of toluene (PDMS rod with 3.2-mm diameter and 10-mm optical path) (B).

rods having different optical paths lengths (1.0, 5.0, and 10 mm). As expected, the absorbance intensity of the steady state increases as the optical path increases, while the time for reaching the steady state remains constant. This result is in accordance with the fact that the organic compound undergoes a radial diffusion through the PDMS polymer rod. It is also important to note that the same behavior was verified for all the hydrocarbons studied in this work.

Sensor Performance. Figure 4B depicts the response profile of the sensor as a function of time after three series of measurements with aqueous toluene solutions of different concentrations. This profile was obtained by immersing the probe in the 237 mg L^{-1} toluene solution, which was stirred until the steady-state signal was obtained. Afterward, the probe was removed from the solution and left in air, allowing the loss of the hydrocarbon by the PDMS rod to the ambient, recovering the baseline signal. Thereafter, the probe was immersed in the 146 mg L^{-1} toluene aqueous solution and the same procedure described above was followed. The reversible response of the sensor under the experimental conditions employed may be observed, suggesting the possibility of its use in continuous monitoring. The same behavior was observed by placing a sensor, previously immersed in an aqueous toluene solution, in pure water, although a longer interval of time was necessary to recover the baseline signal. Therefore, additional
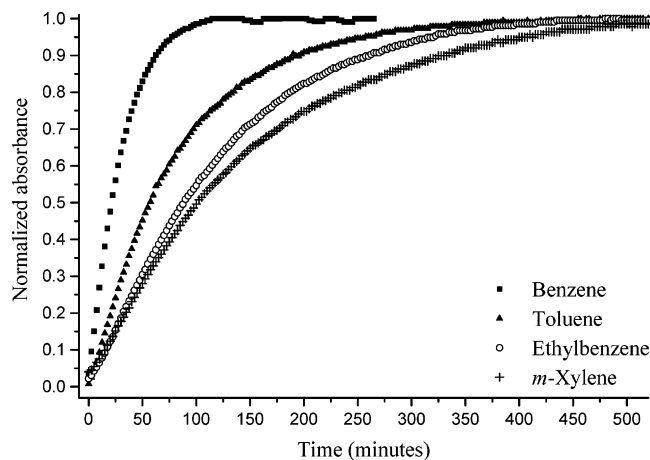
Figure 5. Response profile of the sensor (3.2-mm diameter, 10-mm optical path) for benzene (137 mg L^{-1}), toluene (146 mg L^{-1}), ethylbenzene (98 mg L^{-1}), and m-xylene (74 mg L^{-1}) aqueous solutions. Absorbance measured at 1674 nm.

Figure 6. Analytical curves for benzene, toluene, ethylbenzene, and m-xylene obtained at immersion times of 30, 30, 100, and 100 min, respectively. Absorbance measured at 1674 nm; PDMS rod of 3.2-mm i.d. and optical path of 10 mm.

investigations with the sensor in continuous flow conditions would be necessary to evaluate its performance for this task.

It is also important to note in Figure 4B that distinct steady-state signals are reached for different concentrations of the organic compound in water, indicating no saturation of the sensing phase at the equilibrium state, which is governed by the partition coefficient of the hydrocarbon between the water and PDMS rod. If the PDMS sensing phases were saturated, the same absorbance signal would be obtained at the end of the experiments, regardless of the initial concentration of the aromatic compound in water, and the time necessary to achieve the equilibrium state would be longer for the more dilute solutions.

The response time of the sensor was evaluated for benzene, toluene, ethylbenzene, and m-xylene, by performing experiments with aqueous solutions of these compounds at comparable concentrations in water. Figure 5 shows the kinetic profiles of absorption of the four compounds (benzene 137 mg L^{-1}, toluene 146 mg L^{-1}, ethylbenzene 98 mg L^{-1}, and m-xylene 74 mg L^{-1}), which were normalized in order to provide a clearer interpretation. The measurements were performed by stirring the solutions in order to avoid the formation of a stationary layer at the polymer rod/aqueous solution interface, making the response independent of the coefficient diffusions of the hydrocarbons in water. The response times, measured at $t_{90\%}$ of the steady-state signal, for benzene, toluene, ethylbenzene, and m-xylene were 90, 180, 360, and 405 min, respectively. The different behavior for the four compounds can be explained based on their structures, which define their solubility and diffusion coefficients in the PDMS sensing phase. Benzene, which has no methyl or ethyl groups, shows the shortest response time, as it can diffuse faster through the PDMS rod. As methyl or ethyl groups are attached to the aromatic ring, the molecule becomes bulkier, decreasing its ability to diffuse into the polymer and increasing the response time, in the sequence toluene, ethylbenzene, and m-xylene. Despite the long time intervals necessary to reach the steady-state signal, which were much longer than those presented by sensors based on evanescent waves,[15] the intensities obtained after inserting the probe in contaminated water for 30 (benzene and toluene) and 100 min (ethylbenzene and xylene) were intense enough to
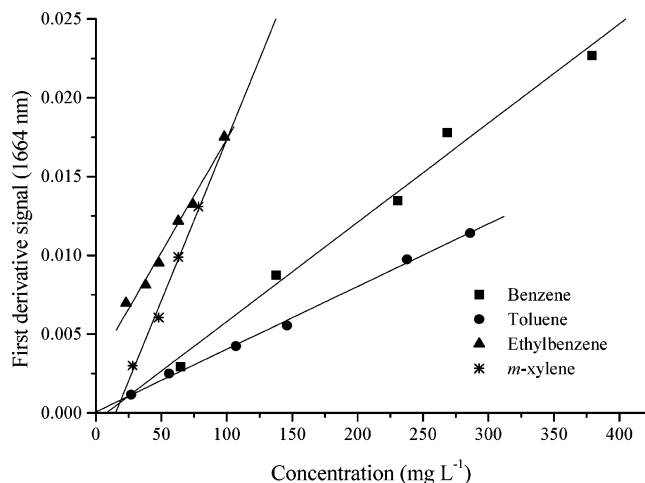
determine these compounds in water, as shown in Figure 5. Under these conditions, as depicted in Figure 6, linear responses ($r^2 >$ 0.993) up to 360, 290, 100, and 80 mg L^{-1} were obtained for benzene, toluene, ethylbenzene, and m-xylene, respectively, with detection limits (3σ/sensitivity) of 13, 20, 5.3, and 4.3 mg L^{-1}, respectively, when absorbance measurements were made at 1674 nm. However, after the steady state is reached, detection limits of 8.0, 7.0, 2.6, and 3.0 mg L^{-1} were achieved for benzene, toluene, ethylbenzene, and m-xylene, respectively. For evanescent wave-based sensors, detection limits of 0.9 and 0.4 mg L^{-1} for toluene and p-xylene, respectively, have been reported[6] when 11-m-long optical fibers are employed for measurements. Although measurements can be made in nonequilibration conditions, it is worthwhile to mention that this approach must be employed with caution in real-world conditions, as temperature, fluid dynamics, and fouling affect the extraction of the hydrocarbons by the silicone rod.

The precision of the sensor was evaluated by performing measurements with different rods using toluene aqueous solutions, with rods from different batches, and with the same rod. In this last case, the rod, after each measurement, was placed in an oven at 40 °C for 30 min in order to rapidly eliminate the absorbed toluene. The maximum values at 1664 nm of the first-derivative absorbance spectra were employed for comparison. By using different rods from the same batch, relative standard deviations of 6.7 and 5.5% were obtained for measurements with 52 and 208 mg L^{-1} toluene aqueous solutions, respectively (average of 6 measurements). A relative standard deviation of 3.6% was obtained for measurements with the same rod, using a 208 mg L^{-1} toluene aqueous solution. Experiments performed with different rods from two different batches by using a 116 mg L^{-1} toluene aqueous solution provided values for the first-derivative signals that did not show significance differences at the 99% confidence level (average of 6 measurements for each batch).

Application to Analysis of Contaminated Water Samples. The sensing phase was applied for identification of the source of hydrocarbons in waters deliberately contaminated by Brazilian gasoline type A (without ethanol), gasoline type C (with 25% v/v anhydrous ethanol), and diesel fuel. The normalized first-derivative spectra set obtained during 200−310 min, every 1 min, of exposure
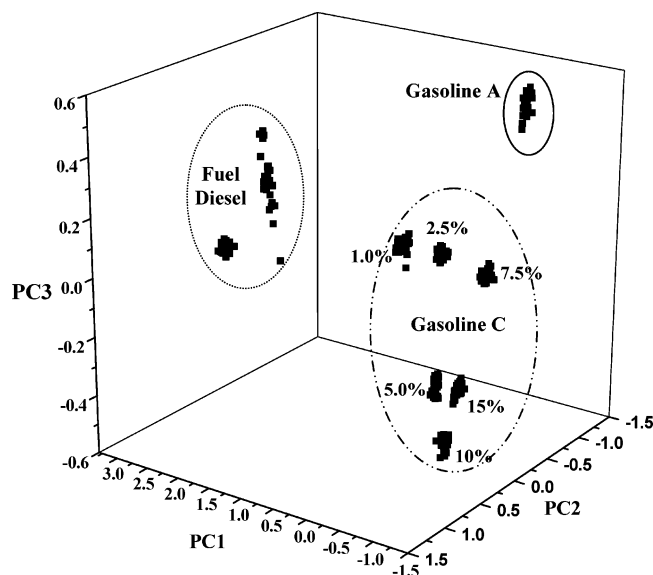
Figure 7. Graphic of scores of the three principal components of the aqueous samples contaminated with gasoline A, gasoline C, and diesel fuel (two samples).

was submitted to PCA,[19] which was able to classify the water into distinct groups, contaminated by gasoline A, contaminated by different amounts of gasoline C. or contaminated by diesel fuel, as shown in Figure 7. The presence of ethanol in gasoline C improves the solubility of hydrocarbons in water, allowing us to classify waters contaminated with different amounts of gasoline C in different groups. A straightforward classification would be expected, in which a relationship between the amount of gasoline C employed to contaminate the water and the position of the respective group in the scores graph would occur. However, it must be emphasized that ethanol also changes the partition coefficient of the aromatic hydrocarbons between the aqueous and the silicone phases, leading to apparently anomalous results shown in Figure 7. This fact must be investigated in more detail and is out of the scope of the present work.

Considering that the sensor has shown a longer response time (equilibration times of 90−405 min, depending on the aromatic compound) than sensors based on an evanescent field (less than 30 min),[15] a procedure was investigated to employ the sensing phase for field measurements, which require a high-throughput performance. Five rods of PDMS sensing phase were immersed into 200 mL of aqueous samples saturated with the combustible (gasoline A, gasoline C, or diesel fuel), maintained under constant stirring in a closed vessel. After 20 min, the rods were removed from each solution at intervals of 5 min, readily adapted to the transflectance probe for immediately scanning the NIR spectra. Three spectra were sequentially recorded. The normalized first derivative of those spectra were submitted to PCA, which was able to classify the water into three groups, contaminated by gasoline A, gasoline C, or diesel fuel, a result that agrees with those shown in Figure 7. This simulation attests to the usefulness of the sensing phase for in-field measurements, as it can be used for monitoring and mapping water contamination. A proposed

procedure would encompass the sampling of a fixed volume of water collected at different points in a contaminated area in sealed vials, into which the PDMS rods would be immersed. As an equilibrium state is reached after, at most, 400 min, as shown in Figure 5, vials would be taken to the laboratory, where the measurements would be performed, as described above. An alternative faster procedure would employ ~20-min immersion time. From an analytical curve, obtained from data collected within this same time interval, it would then be possible to determine the total concentration of aromatic hydrocarbons in each water sample (by employing measurements at 1670 nm, for example). Although not continuous, these procedures are simpler than the chromatographic methods usually employed to perform this task while the long time interval necessary to achieve the necessary qualitative or quantitative detectability is compensated by increasing the number of samples that, in fact, can be simultaneously processed. Because the acquisition of the NIR spectrum is fast (less than 1 min), the procedure increases significantly the sampling throughput, allowing predictions in an average time of 3.5 min when, for instance, 20 rods are simultaneously dropped in 20 water samples and left to stand for hydrocarbon concentration for 50 min.

Although the detection achieved by the evanescent wave sensors is better than the silicone sensing phase herein described, it suffices to detect acute or even light contamination of water bodies. In fact, its detection limits are ~8 times worse than those reported for the evanescent wave sensors.[6] Further attempts to improve the sensitivity of the silicone sensing phase would include the exploitation of the ~10 times more sensitive spectral region (1800−2500 nm), where combination bands are located. Unfortunately, the spectrophotometer employed in the present studies restricts the useful wavelength range from 800 to 1800 nm.

CONCLUSIONS

The results obtained in this work indicate that the PDMS sensing phase can be useful for detection of aromatic hydrocarbon in contaminated water by using NIR spectroscopy. The low-cost, easy preparation of the silicone rod and the repeatability achieved among different sensing elements allows for it to be discharged after a single measurement, although its reversibility, which is easily achieved and extends its useful life, has been attested in this work. Furthermore, the proposed approach is simpler than those based on the evanescent field principle and also less expensive than chromatographic methods, allowing us to map a contaminated area by sampling water or by immersing PDMS rods in different points of the aquatic ambient. Finally, by employing PCA, it is possible to identify the type of contaminant of the water with a clear distinction between gasoline or diesel fuel being observed in this work.

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