Environ. Sci. Technol. **1999**, *33*, 814−819

Partition Infrared Method for Total Gasoline Range Organics in Water Based on Solid Phase Microextraction

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A new method is described for determining total gasoline-range organics (TGRO) in water that combines solid-phase microextraction (SPME) and infrared (IR) spectroscopy. In this method, the organic compounds are extracted from 250-mL of water into a small square (3.2 cm × 3.2 cm × 130 μm thick) of Teflon PFA film. This film, a perfluoroalkoxyethylene polymer, lacks C−H bonds and makes it possible to quantitate the extracted organics directly in it via their C−H stretching vibrations. Three gasoline-range fuels, unleaded gasoline, aviation gas, and lighter fuel (petroleum naphtha), were chosen to evaluate the SPME/IR procedure. Preliminary experiments show that method detection limits are in the 0.5−1.5 ppm range for spiked solutions, and precision is relatively good (6−11% RSDs). Linear dynamic ranges of calibration extend to the water solubility limits for all fuels studied. Finally, the potential of this SPME/IR method for determining TGRO in natural "real world" water samples was investigated by extracting wastewater contaminated with gasoline. In this procedure, a commercially available gas chromatography standard was used to calibrate the SPME/IR method. The results obtained from the SPME/IR determination of the TGRO in two wastewater samples were in reasonable agreement with those obtained from standard purge-and-trap gas chromatographic analysis.

Introduction

The determination of total petroleum hydrocarbons (TPH) in water is an important means of monitoring for fuel contamination arising from spills or leaking storage tanks. Often, petroleum contamination in water is divided into two classes: the gasoline-range organics (GRO) which arise from fuels such as gasoline, aviation fuel, and petroleum naphtha, and the diesel-range organics (DRO) which arise from fuels including diesel fuel and no. 1 fuel oil. Although both classes of contaminants are common pollutants in ground and surface waters, it is generally acknowledged that the GRO are more environmentally malignant because they have a larger percentage of the potentially more toxic aromatic compounds (i.e., the BTEX compounds, benzene, toluene, ethylbenzene, and the xylene isomers). Thus, the analysis of wastewater, ground and surface waters for total gasoline-range organics (TGRO), is especially required wherever these products are used.

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Currently available standard techniques for TPH in water focus on the determination of the higher molecular weight fractions such as oil and grease (*1*). These methods make use of solvent extraction procedures followed by either gravimetric or infrared (IR) spectrometric determination of the aggregate oil or grease. Although simple and sensitive (e.g., detection limits in the 0.5 ppm range), these standard methods have two serious disadvantages in that they use large quantities of solvents (e.g., hexane or trichlorotrifluoroethane), and they are unsuitable for the determination of total gasoline-range organics because of volatility losses. Currently, the most appropriate method for determining TGRO would be the use of purge-and-trap preconcentration followed by gas chromatography (GC) analysis. Although this procedure does not specifically determine total hydrocarbons, the use of an appropriate GC detector which has a nearly-uniform compound response (e.g., a flame ionization detector) can be used to conveniently infer total hydrocarbon concentration. Unfortunately, purge-and-trap/gas chromatographic instrumentation is required which is expensive, technically sophisticated, and time-consuming to operate (e.g., requiring ca. 2 h).

In this work, we present preliminary information on the development of a new solventless partition method for determining TPH in water using solid-phase microextraction coupled with infrared transmission spectroscopy (SPME/IR). Solid-phase microextraction is a process which involves selectively partitioning analytes from the aqueous phase into a polymeric solid phase (*2*). In the application of IR spectroscopy to SPME, the partitioned analytes are determined directly in the solid phase by measuring their IR absorption. The technique thus eliminates the difficulty of using IR transmission for determining compounds in aqueous solutions arising from the spectral interference of water. Previous studies in this laboratory demonstrated the use of SPME/IR with Parafilm M for the selective and sensitive determination of 10 volatile organics including the BTEX compounds (*3*).

In this study, we demonstrate the usefulness of SPME/IR for the measurement of TPH in water by developing a method for TGRO. In this SPME/IR method, the organics are partitioned from the aqueous phase into a small square of Teflon PFA, a perfluoroalkoxyethylene polymer which lacks C−H bonds. This polymer not only successfully extracts petroleum hydrocarbons from water but also provides a clear spectral window in the C−H stretching region (ca. 3000 cm^{-1}) for identification and quantitation of these compounds. The previously identified solid phase useful for SPME/IR, Parafilm, is a polymer composite which absorbs infrared radiation strongly in the C−H stretching vibration region of 3035−2768 cm^{-1}. Thus, this region is spectrally opaque in that film and not useful for selectively identifying aggregate organics via their C−H stretching. Additionally in this study, we present preliminary data on the use of SPME/IR for determining TGRO in "real world" water samples.

Experimental Section

Extraction Films and Apparatus. The polymer solid phase used for the extraction procedure was a commercially available bulk perfluoroalkoxy Teflon (Teflon PFA) film of 130-μm thickness obtained from Berghof/America (Concord, CA). Before cutting into small squares for the SPME/IR procedure, each bulk piece was dry sanded with 400-grit wet/dry sandpaper in four different directions on both sides. A small sanding block was used to provide even pressure.

10.1021/es980777g CCC: $18.00
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Published on Web 01/23/1999

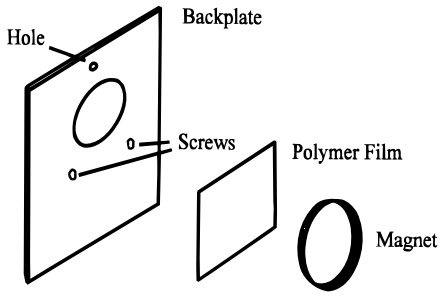

FIGURE 1. Schematic diagram (exploded) of SPME/IR holder.

The film piece was then cut into 32-mm squares which had a resultant calculated volume of 130 μm^3 per square.

Metal holders were fabricated to support the PFA film during the extraction procedure and to acquire the IR spectra. The holder, shown in Figure 1, consisted of a 14-gauge steel plate 44.5 mm long and 51 mm wide with a 19.1 mm diameter hole in the center corresponding to the IR aperture. The film was secured to the metal plate over the hole with a ceramic ring magnet of 25 mm inner diameter and 35 mm outer diameter (Cenco−Central Scientific Co., Franklin Park, IL). Two screws inserted in holes drilled near the bottom of the plate prevented the magnet from slipping during extraction.

Glass jars with Teflon-lined lids (250-mL total volumes) were used as the extraction vessels (Cole-Parmer, Vernon Hills, IL). Each vessel was modified by drilling two 2-mm diameter holes through the lid and inserting 18-gauge wire to form a hook. A small hole near the top of the metal plate provided a means of suspending the film holder assembly from the lid of the jar into the aqueous solution. Silicon sealant, applied externally to the lid of the extraction vessel, was used to cover the drill holes and wire to reduce loss of volatile compounds. Experiments using purge-and-trap/GC analyses show that there is no measurable adsorption of analytes onto the film holder assembly or the Teflon-lined lid (down to the SPME/IR method detection limits of ~1 mg/L).

Reagents and Samples. Unleaded gasoline and aviation gasoline (AV GAS 100LL) were obtained from local sources. The lighter fuel (petroleum naphtha) is a commercially available product and was purchased from a grocery store in Grand Forks, ND. Standard stock solutions were prepared by spiking the appropriate amount of fuel into methanol and then diluting with distilled water in a volumetric flask. The final methanol concentration did not exceed 0.5% of the solution volume.

Gasoline-range organic calibration mixtures, GRO-mix (EPA) and GRO-mix (WISC), were purchased from Restek Corp. (Bellefonte, CA). Since the hydrocarbon mixtures were received as methanol solutions, the aqueous stock solutions were prepared by pipetting directly into distilled water.

Two stock solutions were used for each calibration curve. Calibration standards were prepared in volumetric flasks by diluting aliquots from the stock solutions with distilled water. All solutions were used within 10 min to avoid evaporative loss of volatile analytes.

Two samples of petroleum-industry wastewater contaminated with GRO were obtained from a local source. Total solids were determined for these samples by gravimetric analysis following drying at room temperature.

Infrared Spectrometry. The IR spectra were acquired on an ATI Mattson Genesis FTIR spectrometer (Madison, WI) equipped with a room-temperature deuterated triglycine sulfate detector (DTGS). All spectra were obtained at a scan rate of 6.25 kHz with 4 cm^{-1} resolution. The spectrometer used a triangular phase apodization function and 2X zero-filling. Sixteen scans were signal-averaged for both the sample and background spectra. Savitzky-Golay smoothing was applied to the absorbance data using a 19-point quintic polynomial method to determine the weighting factor.

Quantitative calibration information was obtained from spectral band heights. These heights were calculated by subtraction of the baseline absorbance values from the peak absorbance values. Linear interpolation across the base of the absorbance band was used to determine each baseline value.

Purge and Trap Gas Chromatography. Reference analyses for the wastewater samples were performed on an OI Analytical 4460A purge-and-trap system coupled to a Hewlett-Packard 5890 Series II gas chromatograph with flame ionization detection. The GC was equipped with a 30-m, DB-5 capillary column of i.d. 0.32 mm and a film thickness of 0.25 μm (J&W Scientific, Folsom, CA).

Immediately prior to analysis, the wastewater samples were diluted approximately 2.5:1 with distilled water in order to ensure that the resulting analytical signals were within the linear dynamic range of the GC/FID instrument. A 10-mL volume of sample was spiked with a 5-μL aliquot of methanol containing 133 mg/L of monochlorobenzene (Fisher Scientific) to function as an internal standard. Triplicates of each sample were then purged for 11 min with helium at a flow rate of 40 mL/min. Volatile organics were collected on a 25-cm, type E trap (Supelco Inc., Bellefonte, PA), and then thermally desorbed at 180 °C for 4 min in order to transfer the organics to the gas chromatograph. During the desorption mode, the GC oven was held at 30 °C for 5 min. The temperature was subsequently ramped to 200 °C at 10 °C/min and held at 200 °C for 3 min. Injector and detector temperatures were 200 and 250 °C, respectively.

SPME/IR Extraction Procedure. Prior to extraction, a single-beam IR spectrum of each PFA film was acquired to serve as background reference. The PFA film/holder assembly was then attached to the lid of the extraction vessel. The solution to be extracted was poured into the vessel which contained a metal stir bar. All extraction volumes were 250 mL which minimized headspace and analyte losses due to volatility. The lid was immediately screwed tightly to the glass, and the solution was stirred using a ceramic-topped, magnetic stir plate. Previous research has shown that the rate of analyte partitioning into the solid phase is significantly affected by solution stir rate (*4*). To ensure all the solutions were stirred at similar rates, the height of each vortex was measured, and the stir rates adjusted until the heights were all similar.

Following an extraction, the PFA film/holder assembly was removed from the extraction vessel, and droplets of water adhering to the film surface were quickly blotted with a Precision Wipe (Kimberly Clark, Roswell, GA). The film holder was then placed in the sample compartment of the spectrometer. It should be noted that this process required 5−10 s. An IR spectrum of the PFA film with the partitioned analytes was acquired. Fourier transform of the sample spectrum ratioed to the background spectrum yielded an absorbance spectrum of the extracted analytes. Upon completion of the SPME/IR procedure, the Teflon PFA films were either discarded or reused after a minimum 48 h of air-drying. If a film was reused, its IR spectrum, referenced to air, provided a means of determining whether all the residual components had completely evaporated.

Results and Discussion

Teflon PFA. Teflon PFA is a commercially available polymer that is generally used for protecting laboratory surfaces. It is not sold, per se, as a solid phase material for use in separation science. Thus, as received from the manufacturer it is a visually transparent film that is highly polished. Figure 2 shows three infrared transmittance spectra of Teflon PFA from 4000 to 400 cm^{-1}. As can be seen in any of the spectra

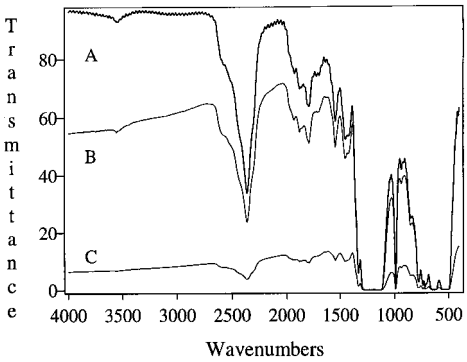

FIGURE 2. Infrared transmittance spectra of Teflon PFA. Spectrum A is of a film as obtained from the manufacturer. Spectrum B is of a film after abrading both sides with sandpaper to an absorbance value of 0.2 AU at ca. 3000 cm^{-1}. Spectrum C is of an over-sanded film (absorbance 1.0 AU).

shown in Figure 2, clear optical regions of the film include 4000−2690 and 2200−2000 cm^{-1}. The remaining regions, 2690−2200 and 2000−400 cm^{-1}, absorb infrared radiation strongly and are therefore opaque.

Prior to use, it is necessary to "condition" the Teflon PFA film by sanding both sides in order to eliminate the smooth, parallel surfaces. A spectrum of the Teflon film as received is shown in Figure 2A. It reveals a sinusoidal modulation in the 4000−2690 cm^{-1} area arising from internal interference of the infrared radiation as it passes through the film. This "fringing" is exaggerated because of the polished nature of the film and results in a serious degradation in the detection limit. The spectrum shown in Figure 2B is of Teflon PFA film after abrading both surfaces with 400-grit sandpaper. Although the absorbance baseline is slightly elevated (at 0.2 AU in the 4000−2690 cm^{-1} region), the fringing pattern has been virtually eliminated.

It should be pointed out that care must be taken not to oversand the surfaces. Oversanding results in a decreased light throughput because of reflection of the IR radiation from the fine scratches on the surfaces of the film. Unfortunately, this loss of throughput can also cause a degradation of the detection limit. The spectrum shown in Figure 2C is of an overly sanded Teflon film that has a baseline absorbance greater than 1.0 AU in the 4000−2690 cm^{-1} region, which provides less than 10% light transmittance. In general, the films were sanded just enough in order to obtain baseline absorbances of ca. 0.2 AU.

Analytical Band Selection. Teflon PFA is a polymer which is devoid of carbon−hydrogen (C−H) bonds. Thus, it is possible to determine total organics absorbed into the film via their C−H stretching vibrations without spectral interference from the polymer itself. The bands in the C−H stretching region of 2850−3050 cm^{-1} encompass aromatic (3033 cm^{-1}), aliphatic-methyl (2965 cm^{-1}), and aliphatic-methylene (2932 cm^{-1}) C−H stretching absorbances (*5*).

Unleaded gasoline, aviation gas, and lighter fuel (petroleum naphtha) were selected as representative gasoline-range petroleum fuels. The distinctive composition of each fuel mixture is apparent in the purge-and-trap/GC chromatograms shown in Figure 3. As can be seen in Figure 3, the aviation gasoline contains a relatively large amount of aromatic compounds and a correspondingly small amount of aliphatics. The unleaded gasoline sample contains a slightly greater amount of aliphatics with a reduced amount of aromatics, and the lighter fuel contains a very high percentage of aliphatic compounds.

Comparative IR spectra of the C−H stretching region for the three fuels absorbed in Teflon PFA are shown in Figure 4. These spectra were obtained by extracting 7-ppm aqueous

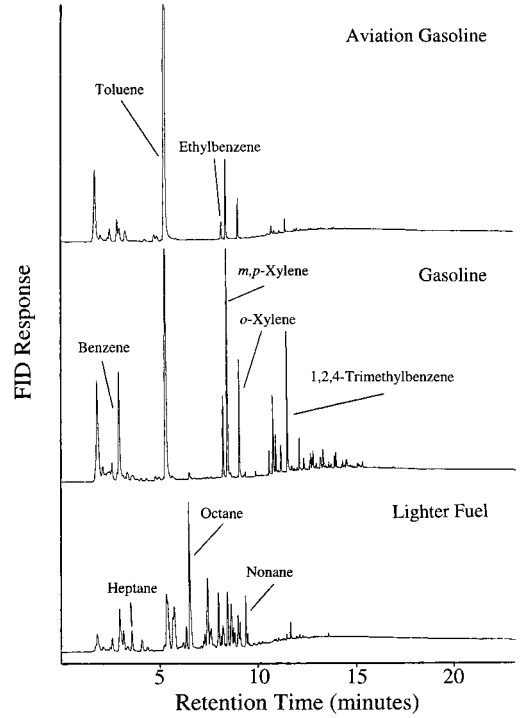

FIGURE 3. Purge-and-trap/gas chromatograms of 1.4 mg/L aviation gasoline, 1.4 mg/L unleaded gasoline, and 1.5 mg/L lighter fuel.

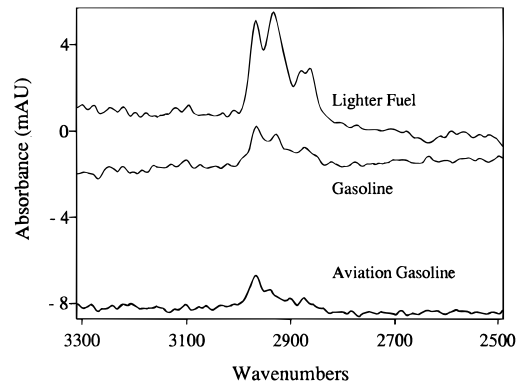

FIGURE 4. Comparative IR spectra of Teflon PFA following 30-min extractions of water solutions containing 7 mg/L fuel. The absorbance bands are due to C−H stretching from fuel components partitioned into the Teflon film.

solutions of each fuel for 30 min. As shown in this figure, the main analytical absorbance band for aviation gasoline in the Teflon PFA film occurs at 2966 cm^{-1}. Unleaded gasoline and lighter fuel also display absorbances at 2966 cm^{-1} but have a prominent alternate band at 2932 cm^{-1}. For this work, quantitative determinations for each of the three fuels were made from absorbance data at 2966 cm^{-1}. This wavenumber provided the most uniform response for the mixtures examined in this study.

Calibration. Equilibration time studies for these three fuels indicated that analyte partitioning from water into the Teflon PFA solid phase required more than 3 h. Since this time period is somewhat unreasonable for routine implementation, an extraction period of 30 min was chosen instead. It has been shown previously that quantitative information can be obtained from SPME techniques at nonequilibrium extraction times if the procedure is consistent (*3*, *6*). Of course, adverse consequences of performing SPME/IR extractions at times shorter than equilibrium is a sacrifice in the detection limits and a corresponding reduction in the linear dynamic range. For example, a comparison of the detection limits

TABLE 1. SPME/IR Calibration Data for Gasoline-Range Organics and Calibration Standards Following 30-minute Extractions into Teflon PFA

	standard calibration data[a]			
	slope, (AU)/(mg/L)	intercept, AU	r^2	LDR,[b] mg/L
aviation gasoline	1.93×10^{-4}	2.22×10^{-4}	0.990	2.8−42
unleaded gasoline	2.62×10^{-4}	3.21×10^{-4}	0.994	2.0−30
lighter fuel	5.76×10^{-4}	4.19×10^{-4}	0.995	1.0−7.2
GRO-EPA mix	2.21×10^{-4}	2.00×10^{-4}	0.994	2.9−25
GRO-WISC mix	1.01×10^{-4}	1.69×10^{-4}	0.996	2.9−32

[a] Analytical absorbance band at 2966 cm^{-1}. [b] Tested linear dynamic range.

obtained by extracting solutions of 5 mg/L aviation gasoline in water for 30 and 60 min showed an improvement of a factor of 1.7.

Calibration information for the three gasoline-range fuels as obtained by 30-min SPME/IR into Teflon PFA is shown in Table 1. It should be noted that the linear ranges of calibration for the various fuels were limited by low water solubility at the high concentration levels.

In anticipation of using the SPME/IR method for determining "unknown" TGRO concentrations in natural water samples, two GRO mixtures were selected for testing as standards: Restek GRO-EPA mix and Restek GRO-WISC mix. These standards are sold for analyses based on GC/MS methods and not specifically for SPME techniques. Calibration data for standards prepared from these mixtures are presented in Table 1. It can be seen from this table that the response (slope of the calibration curve) of the GRO-EPA mixture is intermediate for the three GRO fuels examined in this study, while the response for the GRO-WISC mixture is smaller than any of them. This result implies that the GRO-EPA mixture would be the more appropriate standard mixture. Of course if the type of contaminant is known, then the calibration standard should be the same.

The slight variation in the response of the SPME/IR method for the various fuels and standards is principally due to the aromatic/aliphatic composition of the mixtures. That is, the absorbance data for the measurements were determined from the C−H stretching frequency which has both aliphatic and aromatic components. The GRO-WISC and GRO-EPA mixture contains approximately 22% and 39% aliphatic hydrocarbons, respectively. Gasoline, in contrast, is composed of approximately 60% aliphatic compounds. Overall, the SPME/IR data seems to indicate a lower response per unit concentration for hydrocarbon mixtures with a higher percentage of aromatic components. In fact, the response of the GRO-EPA standard is similar to that of the aviation gasoline (which has a higher aromatic content).

Detection Limits in SPME/IR. The detection limit is defined as the smallest amount of an analyte that can be detected with reasonable certainty by an analytical process. Various approaches of establishing a value that satisfy this definition have been discussed in the literature (*1, 7*−*10*). Standard methods for water analysis generally specify that the method detection limit (MDL) be determined as described by the U.S. Environmental Protection Agency (EPA) (*1, 7*). The MDL is therein defined as the constituent concentration that, when processed through the complete method, produces a signal with a 99% probability that it is different from the blank.

Another means of differentiating between analyte and blank distributions is known as the limit of quantitation (LOQ). It is described as the concentration level which produces a signal that can be reliably measured by the specified analytical method. The LOQ is defined as the constituent concentration that produces a signal equal to 10 standard deviations (*s*) above the reagent blank. An approximation of the LOQ is 2.5 times the MDL and provides a reasonable estimate of LOQ once the MDL has been determined.

TABLE 2. Detection Limits for Gasoline-Range Organics Following 30-minute Extractions into Teflon PFA

	actual MDL,[a] mg/L (%RSD)[b]	actual LOQ,[e] mg/L	predicted LOQ from MDL,[f] mg/L	predicted LOQ from spectral baseline noise,[g] mg/L
aviation gasoline	1.2 (6)[c]	4.2	3.1	2.9
unleaded gasoline	1.2 (11)[d]	4.0	3.1	2.6
lighter fuel	0.45 (9)[d]	0.99	1.1	0.78

[a] MDL defined as the constituent concentration that, when processed through the complete method, produces a signal with a 99% probability that is different from the blank. [b] Percent relative standard deviation. [c] %RSD obtained from 10 replicate extractions. [d] %RSD obtained from 12 replicate extractions. [e] Defined as the concentration that produces a signal equivalent to 10*s* above the blank. [f] An approximation of LOQ defined as 2.5 MDL. [g] The peak-to-peak baseline noise, defined as 5*s*, was determined for each spectrum. An LOQ was then calculated at 10*s* or twice the mean peak-to-peak noise.

The current EPA-recommended procedures for determining the method detection limit, and the limit of quantitation are, however, tedious and time-consuming. In previous work from this lab, detection limits for the Parafilm solid phase extractions were defined as that concentration which produces an absorbance equivalent to twice the peak-to-peak baseline noise (*3*). This definition, which is related to that developed by the International Union of Pure and Applied Chemistry (IUPAC) (*8*−*10*), presents a simple means of predicting an LOQ directly from the spectral data. This definition is based on the assumption that, providing interferences are minimal, the baseline noise near the analytical band is nearly equivalent to the blank noise in the region of the analyte absorbance. Since many individual spectral points comprise the baseline noise (e.g., 20−50), the baseline level is a good statistical representation of the blank level. In this section, we examine the relationship of this definition to the other, more standard, definitions of detection limits (i.e., the MDL and the LOQ).

Method detection limits of the three test fuels were determined for the Teflon PFA solid-phase extractions using described EPA-recommended procedures at fuel concentrations that provided signal-to-noise ratios in the range of 3−5. Twelve replicate extractions were performed for both the unleaded gasoline and the lighter fuel. The standard deviations of the analyzed concentrations were then multiplied by 2.718 to obtain the MDL. This multiplier was the value of *t* selected from a table of the one-sided *t* distribution for 11 degrees of freedom at the 99% confidence level. Twelve replicate extractions were also performed for the aviation gasoline, but the standard deviation was taken from only 10 of the analyzed concentrations because of known, nonrandom errors in the handling of two samples. A *t*-value of 2.821 was therefore selected as the multiplier.

Quantitation limits for the three fuels were obtained from the absorbance data used to determine each MDL. A standard deviation of absorbance values from the replicate extractions was multiplied by 10, and a concentration was then calculated. Estimates for LOQ were also obtained from the spectral data. Peak-to-peak baseline noise, defined as 5*s* (*11*), was measured for each absorbance spectrum in a clear spectral region near the analyte absorbance (generally between 2800 and 2500 cm^{-1}). The mean value of the measured noise was then multiplied by 2, to obtain 10*s*, and an analyte concentration was calculated.

A comparison of these various techniques for determining the limits of this method is shown in Table 2. The LOQ

TABLE 3. Analytical and Physical Data for Two Wastewater Samples

wastewater sample	dilution	concentration, mg/L (%RSD)[a] SPME/IR gasoline[b]	SPME/IR GRO-EPA[c]	SPME/IR GRO-WISC[d]	purge and trap/GC	total solids, g/L	turbidity, NTU
"A"	undiluted	3.6 (10)	4.9 (10)	9.8 (10)	3.5 (2)	2.39	56
	(1:2)	3.6 (10)	4.9 (10)	9.9 (10)			
"B"	undiluted	<loq[e]	<loq	<loq	5.7 (2)	3.24	50
	(1:2)	4.3 (16)	5.7 (16)	11.7 (16)			

[a] Percent relative standard deviation data from three replicate, 30-min extractions into Teflon PFA. [b] Values calculated using gasoline calibration curve data. [c] Values calculated using GRO-EPA calibration curve data. [d] Values calculated using GRO-WISC calibration curve data. [e] Less than the limit of quantitation.

determined for each fuel from the extraction procedure (actual LOQ in Table 2) is slightly greater than the LOQ predicted from the spectral noise. This result is expected since the standard deviation of the absorbance data includes error for the total extraction procedure and will, therefore, be slightly greater than the standard deviation of the measured spectral noise. However, this study does show that the process of estimating the LOQ from spectral noise adjacent to an analytical band is a good approximation of the EPA-recommended value for LOQ estimated from the MDL. Differences between the two methods range from 21% to 35% (for this work).

Overall, the detection limits for the gasoline-range fuels determined by SPME/IR at 30 min are quite good for such a simple procedure and are similar to those obtained by the infrared partition method using Freon or hexane. Additionally, these detection limits are low enough to meet drinking water standards for toluene and xylenes as specified by the EPA (*12*). Precision data for each of the SPME/IR determinations of the three fuels, expressed as percent relative standard deviation (%RSD), was calculated from the replicate analyses used to determine the method detection limit. These values are quite good (6−11%) for these volatile analytes. The precision of the method is, of course, affected by analyte volatility loss which can potentially occur at several steps during the procedure. For example, evaporative loss of analyte from the Teflon PFA occurs as soon as the film is removed from the water matrix. Previous research with Parafilm showed that this loss is accelerated as the film is heated by the IR beam of the spectrometer (*3*). Of course, each step has been designed to minimize these losses. Nevertheless, it should be noted that the attainable precision of this method depends somewhat on the alacrity of the operator.

Application to Natural Water Samples. Table 3 presents the results of analysis for TGRO in two petroleum wastewater samples by SPME/IR and purge-and-trap/gas chromatography. Sample B was obtained from a holding tank, and sample A was taken from the outlet line of a processing unit that included air stripping. Both samples were used without pretreatment, and, thus, both samples had a high amount of dissolved/suspended solids (as shown in Table 3). The SPME/IR analyzed concentrations were determined using both the GRO-EPA mix and the GRO-WISC mix standards as well as a gasoline standard.

Purge-and-trap/GC analyses provided the definitive concentrations for both wastewater samples, and Figure 5 shows typical chromatograms. This technique is considered to be a standard method for the analysis of volatile compounds in aqueous solutions and was, therefore, chosen to provide reference results. The validity of using this technique with the wastewater samples was verified by collecting the waste solutions after purging and then extracting any remaining analytes with dichloromethane. Gas chromatographic analysis of the nonpurgable components revealed concentrations of 80 and 70 μg/L (total extractable organics) for samples A and B, respectively, which account for less than 3% of the TGRO values obtained.

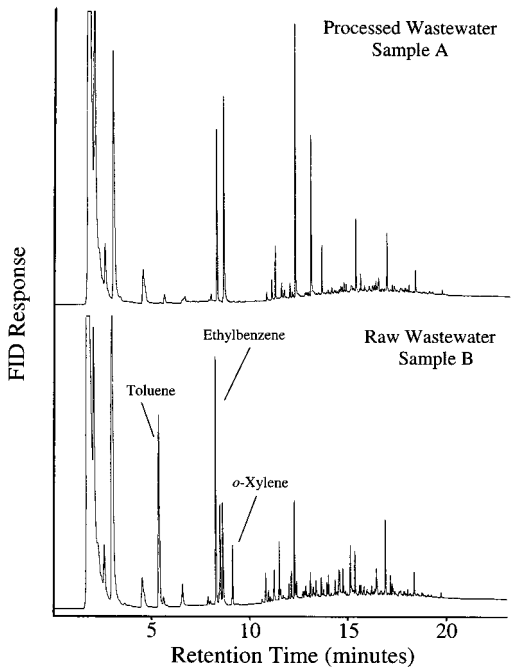

FIGURE 5. Purge-and-trap/gas chromatograms of two petroleum wastewater samples. A 25-mL aliquot of the processed wastewater sample A was diluted to 50 mL with distilled water prior to analysis. The raw wastewater sample B was diluted from 35 to 100 mL with distilled water.

A comparison of the purge-and-trap results and the SPME/IR results shown in Table 3 reveal two features. First, as discussed above, the determination of sample concentrations by SPME/IR is somewhat dependent upon which calibration standard is used. The TGRO concentration of sample A, as determined from the gasoline calibration curve, most closely correlates with the purge-and-trap/GC analyses. These results suggest that the response of the processed wastewater sample more closely resembles gasoline. The raw wastewater sample B (diluted, as explained in the proceeding section), however, is more closely matched to the GRO-EPA mix calibration. This is reasonable since the air stripping process would eliminate aromatic compounds and volatile short-chain aliphatic hydrocarbons. However, it should be noted that calibration standards prepared from either the gasoline or the GRO-EPA mixture would provide results reasonable with the purge-and-trap analytical method. Of course for true unknowns, inspection of the spectral profile will provide some information about the component mixture. For example as shown in Figure 4, the 2932 cm^{-1} aliphatic-methylene stretching absorbance is larger for mixtures that contain a higher proportion of aliphatic hydrocarbons.

A comparison of the purge-and-trap results and the SPME/IR results shown in Table 3 also shows that, while the SPME/IR TGRO results for undiluted sample A agreed with the purge-and-trap results, the SPME/IR concentrations for undiluted aliquots from the raw wastewater sample (B) were significantly lower than the purge-and-trap/GC results. However, a 1:2 dilution of this sample in distilled water provided results comparable to the GC method (no change was observed in the concentration of TGRO for sample A upon dilution). We believe sample dilution provided a means of releasing compounds into the water that had adsorbed/absorbed onto the solids in the wastewater samples. Thus for natural water samples with an extremely large amount of dissolved or suspended particles (as evidenced by their turbidity), sample dilution will be necessary with this procedure in order to minimize matrix effects. This requirement is similar to that used in the standard purge-and-trap method.

The relative standard deviations (RSDs) obtained for the SPME/IR analyses of the natural water samples are in the range of 10−16%. This degree of precision is acceptable for these types of volatile samples. It should be noted that these RSDs are higher than those obtained by the purge-and-trap analyses. However, the purge-and-trap technique uses an internal standard which significantly improves the precision.

Acknowledgments

The authors would like to thank the United States Environmental Protection Agency, Grant no. R 825343-01-0, for providing financial support for this work.

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Received for review July 28, 1998. Revised manuscript received December 4, 1998. Accepted December 15, 1998.

ES980777G