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Octadecylthiol-Modified Surface-Enhanced Raman Spectroscopy Substrates: A New Method for the Detection of Aromatic Compounds

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■ A method for detection of aromatic organics in groundwater has been tested. It was found that use of surface-enhanced Raman scattering and an octadecylthiol coating on roughened silver produced a system which could partition the organics out of water into the strongly Raman enhanced region near the silver surface. The selectivity of the method was illustrated with the three isomers of xylene. Sensitivity was tested with benzene and naphthalene. The detection limits are 7.5 and 2.3 ppm for benzene and naphthalene, respectively. It was found that the calibrations followed a Langmuir-type isotherm at low solution concentrations.

Introduction

There is a subset of the large number of common organic compounds which appears to be ubiquitous to hazardous waste sites. These include primarily aromatic compounds (benzene, toluene, ethylbenzene, and xylenes) and halogenated organics (1, 2). These compounds are reported at concentrations exceeding 10 ppm in groundwater near these sites. Current monitoring methods for waste sites involve the removal of samples and laboratory analysis. In the case of volatile organics, there can be considerable loss of sample during and after sample collection through aeration and biodegradation (3). We have been examining methods for in-situ detection of groundwater components with fiber optic probes. In this report we will discuss a new method for detection of organic compounds in water.

In-situ analysis is difficult due to the inability to pre-concentrate the sample and separate the sample into component groups to avoid interferences. For example, Chudyk et al. have shown that it is possible to detect fluorescence from aromatic compounds in landfill leachates (4). However, the use of UV excitation (266 nm) is not compatible with long lengths of optical fibers and requires expensive pulsed laser systems. Moreover, the absorption and fluorescence spectra of these compounds are all very similar and it would be impossible to resolve individual components in a complex mixture. The problem of resolution was overcome with resonance Raman spectroscopy. Several publications have illustrated the possibility of resonance Raman excitation for groundwater contaminants (5-7). The problems of UV excitation still exist as well as problems with large background fluorescence from the water sample. Some phenolic compounds have been detected with reasonable detection limits and near-UV excitation from Ar⁺ lasers (7). The use of visible excitation was demonstrated by Schwab and McCreery (8, 9). They have shown that careful fiber optic probe construction can lead to very large collection efficiencies. A detection limit

of 2 ppm was found for benzene in carbon tetrachloride (9). This system performed well in pure solvents which do not fluoresce and when the solvent could act as an internal standard. The Schwab and McCreery approach works well at ppm level concentrations of strongly scattering analytes. However, since it cannot perform a pre-concentration of the sample, a definite detection limit exists. More recently, approaches have been tested which concentrate the analyte at the surface and this is followed by Raman analysis. Surface-enhanced Raman spectroscopy (SERS) has been tested by Carrabba et al. for the detection of polar organics which adsorb to electrodes (10, 11). The advantage of the SERS is that the silver surface quenches background fluorescence, making it possible to detect hazardous materials in natural samples. More recently, Bello et al. avoided electrochemistry by looking at SERS spectroscopy of organic acids and compounds which will strongly adsorb to a silver substrate (12, 13).

We have been examining SERS as an in-situ technique (14-16). Unlike previous workers, we have been modifying the SERS substrate with analyte specific coatings. This has a twofold purpose. First, the pre-concentration step of the analysis is chemically controlled at the fiber surface with affinity coatings. Second, the coating material possesses Raman bands which can be used as an internal standard for accurate calibration of the sensor. This is important for in-situ analysis since small changes in the fiber or laser power will lead to inaccuracies in the absolute intensity of the Raman signal from the analyte.

Our coatings allow us to increase the local concentration of analyte at the surface. Previously we examined coatings for metal ions and pH. These coatings are composed of chemically derivatized indicators. One problem one meets in using SERS for groundwater analysis is the stability of the indicator and the SERS substrate. We have overcome this problem with coatings composed of indicators derivatized with disulfide functionalities. The disulfide group reacts with the silver surface and prevents its deterioration under extreme conditions. For example, we have tested our probes from pH 2 to 11 and have not found any loss of signal due to surface deterioration. As well as protecting the surface, the silver thiolate bond anchors the indicator to the surface. We observed that the SERS substrate/indicator system is stable for a couple of months in aqueous solutions (this is the longest period of time which the substrates have been tested).

In this report we have replaced the ion indicators with a coating which will adsorb hydrophobic organics from solution, octadecylthiol. Octadecylthiol is known to self-assemble on metal surfaces and form compact layers (17). It will be shown that the coating can adsorb molecules from

an aqueous solution and concentrate them at the surface.

Experimental Section

The octadecylthiol (98%) was purchased from Aldrich and used without further purification. The analytes were reagent grade. The SERS substrates were prepared from 2-mm-thick silver foil (99.9%, Aldrich). The foil was etched in rapidly stirred 30% nitric acid and rinsed with deionized water. This has been shown to produce strongly enhancing substrates (18). The foil was dried and immersed in a 14 mM ethanolic solution of octadecylthiol for at least 24 h. This leads to a coating that is resistant to strongly basic and acidic solutions and protects the silver. The SERS spectra show an all-trans configuration for the C-C backbone, indicating that the layer has self-assembled (17).

Solutions of the analytes were prepared by dilution from saturated solutions. The concentration of the saturated solution was determined with UV/visible spectroscopy. The extinction coefficients used are benzene, $\log \epsilon_{256} = 2.4$; naphthalene, $\log \epsilon_{275} = 3.75$; *o*-xylene $\log \epsilon_{265} = 2.3$; *p*-xylene $\log \epsilon_{267} = 2.7$; and *m*-xylene, $\log \epsilon_{269} = 2.3$ (19). The UV/visible spectra were obtained with a Perkin-Elmer Lambda-9 spectrometer in sealed FUV cuvettes. Calibration curves were obtained with standard solutions from the saturated solution. The spectra were obtained with a SERS substrate rigidly fixed in a cuvette filled with the analyte solution. Calibration curves were made by removing one analyte solution and adding another from the fixed sample. Care was taken such that the calibration was formed from the same spot on the substrate. It has been observed that small variations in the peak intensities occur at different areas on the sample. Excitation at one spot most closely resembles the real situation of illumination of a fiber tip. The analytes appeared to have reached equilibrium with the surface layer within the time scale of our experiments. This was usually on the order of 1 min or less.

The SERS spectra were obtained with a Spectra Physics 2025 Kr⁺ laser operating at 647 nm. The detection system was a Photometrics CCD9000 spectroscopic system. The CCD temperature was held at -102 °C. We found that optimal signal to noise ratio was obtained for a binning of 30 pixels/group. The total number of pixels used was 250. Integration times were maintained at 200 s while the calibration curves were being formed. The detector was mounted on a ISA HR-320 spectrograph with 1200 g/mm ion etched grating blazed for 650 nm. The slit width was set at 20 μ m. The laser power was set at 50 mW, and sample illumination was with a line focus produced by a 50-mm cylindrical lens (Melles Griot). The Raman was collected with a F1.8 Minolta camera lens and a ~4:1 magnification for *f*-number matching with the spectrograph.

Results and Discussion

It is our desire to demonstrate two aspects of our prototype sensor: selectivity and sensitivity. Selectivity will be discussed first and illustrated through the resolution of the three isomers of xylene. Sensitivity was tested for benzene and naphthalene. These were chosen for their different solubility properties in water and the octadecylthiol coating. Correlation of our results with octanol/water partition coefficients indicates that some materials can be detected at sub-ppb levels. The analytes used in this study are illustrated in Figure 1.

Octadecylthiol Coatings. Figure 2A shows a SERS spectrum of octadecylthiol on a roughened silver substrate. The spectral region shown is large enough to include the

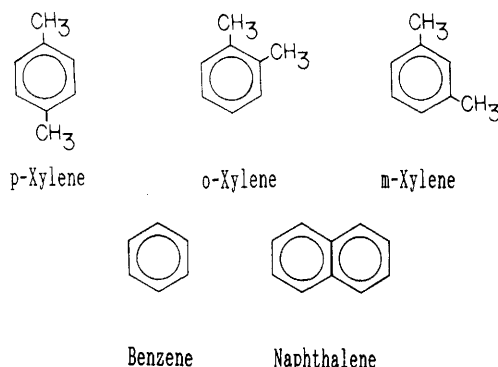


Figure 1. Structures of the analytes examined in this work.

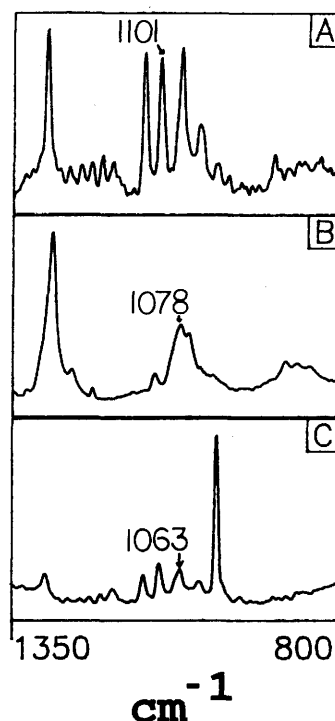


Figure 2. (A) SERS spectrum of an octadecylthiol layer on a roughened silver surface. The triplet of bands between 1050 and 1150 cm^{-1} correspond to C-C stretches. The center band at 1101 cm^{-1} will be used as an internal reference throughout this work. (B) Raman spectrum of liquid octadecylthiol. Of interest is the change in the C-C region. The new bands correspond to a gauche configuration. (C) SERS spectrum of benzene absorbed into an octadecylthiol monolayer on silver. Of significance in this spectrum is the shoulder, which appears on the 1063- cm^{-1} trans C-C stretch. The shoulder corresponds to the formation of a gauche component to the structure of the monolayer upon introduction of benzene.

characteristic frequencies of most aromatic hydrocarbons. This region contains the strong C-C stretches of octadecylthiol and the methylene twist at 1294 cm^{-1} . The C-C stretches correspond to an all-trans configuration of the layer. The layer is therefore considered self-assembled (19). Figure 2B is a spectrum of liquid octadecylthiol. In the liquid phase the preferred conformation is gauche. The band at 1078 cm^{-1} corresponds to a gauche conformation. We have found that when benzene intercalates into the monolayer, a small amount of gauche orientation appears as a shoulder on the 1063- cm^{-1} band. This can be seen in Figure 2C. Changes in the spectrum upon exposure to benzene were observed in other regions of the spectrum. In particular, the methylene bending region and C-H stretching region both indicate that the surface monolayer has become "liquified" in the presence of benzene. Since we intended to use the octadecylthiol monolayer as our

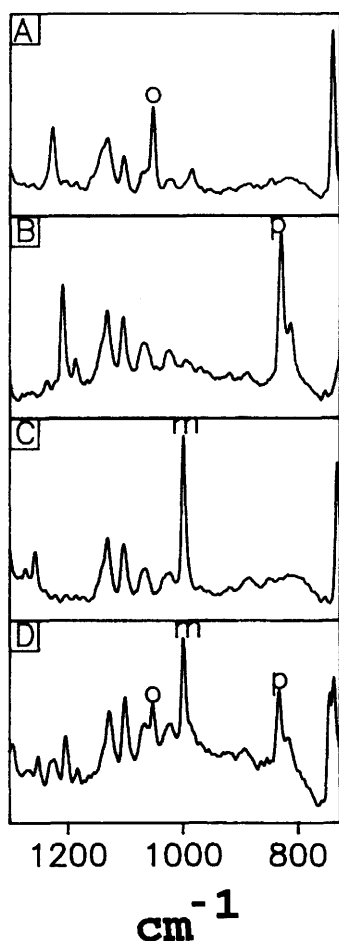


Figure 3. (A) SERS spectrum of *o*-xylene partitioned into an octadecylthiol layer on a silver surface. The band labeled "o" is a peak characteristic of *o*-xylene at 1055 cm^{-1} . (B) SERS spectrum of *p*-xylene partitioned into an octadecylthiol layer on a silver surface. The band labeled "p" is a characteristic band of *p*-xylene at 830 cm^{-1} . (C) SERS spectrum of *m*-xylene partitioned into an octadecylthiol layer on a silver surface. The band labeled "m" is a characteristic band of *p*-xylene at 1000 cm^{-1} . (D) SERS spectrum of a mixture of *p*-, *o*-, and *m*-xylene partitioned into an octadecylthiol layer on a silver surface. The characteristic bands are labeled.

internal standard, it is desirable to choose a band which is intense and which does not change as increasing amounts of analyte are adsorbed into the film. The 1101-cm^{-1} peak appears best suited for our internal standard. The spectrum in Figure 2C is benzene adsorbed into the octadecylthiol layer from the vapor phase. We found excellent partitioning of the analytes from the vapor phase as well as aqueous solutions.

Selectivity. Figure 3 shows the SERS spectra of *o*-, *m*-, and *p*-xylene intercalated into an octadecylthiolate film on a silver substrate. Figure 3A is a spectrum of *o*-xylene partitioned from a saturated aqueous solution. The concentration was measured to be 199 ppm. *o*-Xylene contains a characteristic peak at 1055 cm^{-1} which is labeled o. This band is due to an a_1 ring mode which is characteristic of ortho-disubstituted benzenes (20). Figure 3B is a SERS spectrum of *p*-xylene partitioned from a saturated aqueous solution. The concentration of *p*-xylene was measured to be 142 ppm. A peak which is characteristic of *p*-xylene at 830 cm^{-1} has been labeled as p. This corresponds to an a_g ring mode which is characteristic of para-substituted benzenes (20). Figure 3C is a SERS spectrum of intercalated *m*-xylene from a saturated aqueous solution. *m*-Xylene was intercalated from a saturated aqueous solution at 178 ppm. *m*-Xylene contains a characteristic peak at

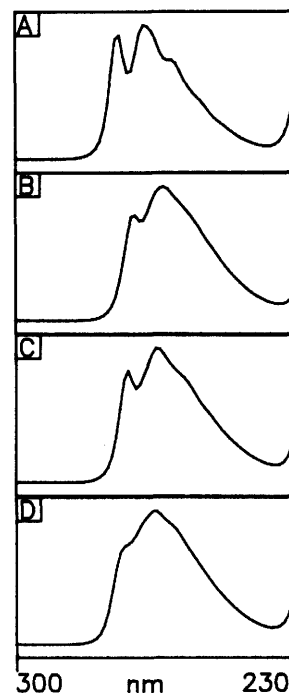


Figure 4. (A) UV spectrum of a saturated aqueous solution of *p*-xylene. (B) UV spectrum of a saturated aqueous solution of *m*-xylene. (C) UV spectrum of a saturated aqueous solution of *o*-xylene. (D) UV spectrum of a saturated aqueous solution formed from a 1:1:1 mixture of the three isomers of xylene.

1000 cm^{-1} . This band is an a_1 mode that is equivalent to the strong ring breathing mode of benzene (20). Figure 3D is a spectrum of a 1:1:1 mixture of the isomers intercalated into the surface monolayer. *o*- and *m*-xylene also contain characteristic peaks in this spectral region at 740 and 730 cm^{-1} , respectively. However, it can be seen in the mixture spectrum that significant overlap exists, and it would be difficult to quantify each species.

Chudyick et al. attempted to measure aromatics in groundwater with fluorescence spectroscopy (4). Figure 4 shows the absorption spectra for *o*-, *m*-, and *p*-xylene and for a 1:1:1 mixture. It can be seen that the similarity of the absorption spectra would make it impossible to specifically analyze for a single isomer of xylene. Furthermore, virtually all aromatic compounds have absorptions in this region. In Raman spectroscopy, distinction between these compounds arises from two sources. First is the symmetry of the molecule. *o*- and *m*-xylene have C_{2v} symmetry, and *p*-xylene has D_{2h} symmetry. Vibrational spectroscopies are very sensitive to symmetry, and this leads to the large difference between the para and the two C_{2v} isomers. The second factor which leads to selectivity is the neighbor effect. The center of mass must be conserved during the vibrations. In ortho substitutions this leads to very strong dissymmetry in the potential energy distributions of the C-C and C-H components of the ring modes. Meta substitution is more symmetrical across the rings and leads to spectra which more closely resemble benzene.

The large differences observed are not unique to methyl-substituted benzenes. Halogenated benzenes and phenols will have similar characteristic frequencies. In the case of halogenated compounds, the shifts are related to the mass of the halogen. The bands used to characterize these substituted benzenes are called x-sensitive vibrations because of their characteristic changes with substitution (21).

One problem that could occur in the determination of mixture components is competitive saturation of the monolayer. In the case of the xylenes, one can see from Figure 2D that no one xylene has saturated the monolayer.

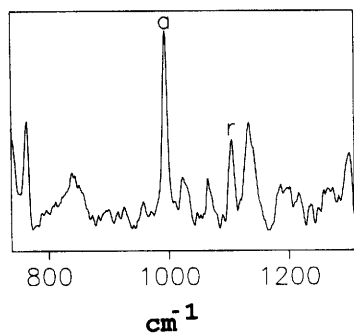


Figure 5. SERS spectrum of benzene partitioned into an octadecylthiol monolayer on silver. The band labeled "a" corresponds to the strong a_{1g} totally symmetric stretch of benzene at 991 cm^{-1} , and the band labeled "r" is the 1101-cm^{-1} C-C stretch of the monolayer.

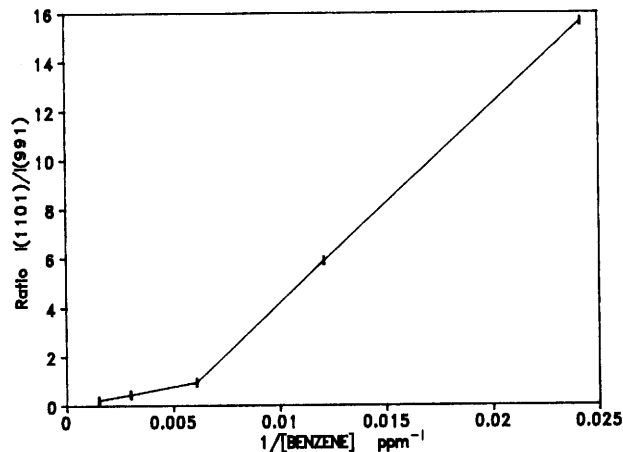


Figure 6. Calibration curve for benzene in octadecylthiol on silver. The low-concentration portion of the calibration fits a line: $I_{1101}/I_{991} = 812 \times 1/[\text{benzene ppm}] - 4.0$. The R^2 is 0.999 936, the standard error of the slope is 3.7, and the standard error of the intercept is 0.055.

It appears from benzene vapor-phase studies that the saturation level of the films is well above that reached from the relatively low aqueous concentrations. The concentrations in the mixture relative to those from saturated solutions are 45% *m*-, 25% *o*-, and 30% *p*-xylene.

Sensitivity. To test the sensitivity of our technique we have chosen benzene and naphthalene as analytes. The solubility of benzene in water at 25°C was found to be 661 ppm. We prepared a saturated solution of benzene in water and made standard dilutions from this solution. The SERS spectrum of benzene adsorbed into an octadecylthiol monolayer from an aqueous solution is shown in Figure 5. The strong peak labeled "a" (for analyte) is the ring breathing mode of benzene at 991 cm^{-1} . Also shown is the reference peak, "r", at 1101 cm^{-1} . It was found that the best fit was obtained for a Langmuir-type isotherm. The plot shown in Figure 6 is therefore plotted as $1/\text{ratio}$ versus $1/\text{concentration}$. The R^2 value for the linear low concentration portion of this plot is 0.999 94. The 991-cm^{-1} peak is approximately 15 pixels wide. A 15-point Savitsky-Golay smooth was used to improve our signal to noise ratio. It was found that larger smoothing produced significant decreases in the signals. When we calculate the detection limit based on the smoothed data, we find a detection limit of 3 times the standard deviation of the background to be 7.5 ppm. At this point the error in the reference peak is insignificant. At higher concentrations where the intensity of the benzene peak is larger than the reference, the precision of the calculation will be determined by the reference.

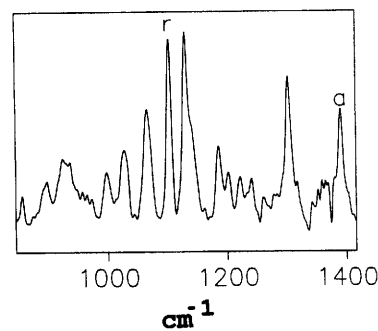


Figure 7. SERS spectrum of naphthalene partitioned into an octadecylthiol monolayer on silver. The band labeled "a" corresponds to the strong a_g totally symmetric stretch of naphthalene at 1385 cm^{-1} , and the band labeled "r" is the 1101-cm^{-1} C-C stretch of the monolayer.

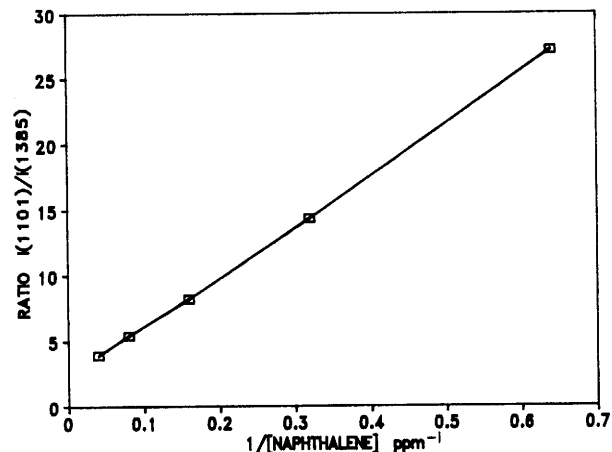


Figure 8. Calibration curve for naphthalene in an octadecylthiol monolayer on silver. The curve fits a line: $I_{1101}/I_{1385} = 38.8 \times 1/[\text{naphthalene ppm}] + 2.16$. The R^2 is 0.999 484, the standard error of the slope is 0.509, and the standard error of the intercept is 0.248.

Naphthalene is known to have a higher octanol/water partition coefficient than benzene (22). With the assumption that our coating mimics octanol, we anticipate better detection limits for naphthalene. Figure 7 shows a spectrum of naphthalene adsorbed into an octadecylthiol layer from a saturated aqueous solution. The concentration of naphthalene in the saturated aqueous solution was found to be 25 ppm. The peak labeled "a" (for analyte) at 1385 cm^{-1} is the strong a_g mode of naphthalene. The peak labeled "r" is our usual 1101-cm^{-1} octadecylthiol peak. Due to the low solubility of naphthalene in water, it appears that all points fit a Langmuir-type isotherm. A linearized Langmuir-type plot is shown in Figure 8. An R^2 value of 0.9995 was found for this plot. The detection limit was 2.3 ppm.

Conclusion

We have demonstrated that it is possible to detect aromatic organic compounds with SERS. The technique showed very good selectivity in detecting the isomers of xylene. Sensitivity was tested with benzene and naphthalene. The detection limits for benzene and naphthalene were 7.5 and 2.3 ppm, respectively. These values are below concentrations reported for leachates at contaminated sites. The octanol/water partition coefficient for naphthalene is 17 times higher than that for benzene. Our detection limit did not scale this due to the lower Raman cross section for naphthalene. However, the octanol/water partition coefficients for polychlorinated biphenyls and polycyclic aromatic hydrocarbons are over 3 orders of magnitude larger than that for naphthalene. On this basis,

we predict detection limits to be less than 10 ppb for these compounds.

When coupled with optical fibers, this technique should provide a method of analysis for real-time in-situ monitoring of contaminated sites. The ability of our surfaces to partition organics out of the vapor phase will make them excellent tools for vadose zone monitoring. Future work will be directed at improving our detection limits. These will include increasing the chain length of the alkyl coatings and chemically altering the coating to make it better match the analyte. Finally, it is expected that high-power diode lasers will become commercially available and could be used to improve our detection limit by as much as a factor of 50.

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Registry No. *p*-Xylene, 106-42-3; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; benzene, 71-43-2; naphthalene, 91-20-3; water, 7732-18-5; octadecylthiol, 2885-00-9.

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