SPECTROELECTROCHEMICAL SENSING OF CHLORINATED HYDROCARBONS FOR FIELD SCREENING AND IN SITU MONITORING APPLICATIONS

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ABSTRACT

The detection and identification of chlorinated hydrocarbon solvents (CHS) have been demonstrated by combining the principles of spectroscopy and electrochemistry. The successful observation of the CHS is highly dependent on the analysis procedure. The procedure is based on a photon induced electrochemical reaction which is detected by surface enhanced Raman spectroscopy (SERS) on electrodes. The results and methodology of the technique will be discussed.

INTRODUCTION

The importance of techniques to sense and monitor chlorinated hydrocarbon solvents (CHS) are becoming increasingly more important with the intensifying presence of groundwater contaminations. Our research and development effort is aimed at producing a commercial, low cost, field portable instrument for the field screening/in situ monitoring of contamination from chlorinated organic solvents based on spectroelectrochemical fiber optic probes. Some of the advantages of this technique for monitoring a contamination site are cost, small size of sampling probe, real-time analysis, the capability of sensing in adverse environments, and the ability of using a central detection facility. The technique has an advantage over current fiber optic chemical sensing methods for chlorinated organics in that the sensing only takes place when the electrochemical device is turned on. This should enable long term monitoring of a well to be accomplished with only one probe.

Our monitoring system for chlorinated organic solvents is based on the principle of combining spectroscopic, electrochemical and fiber optic techniques (Spectroelectrochemical Fiber Optic Sensing (SEFOS)). SEFOS is, in principle, a generic technique which can be adapted to many different sensing applications. With the SEFOS technique, we use electrochemical methods to reduce the chlorinated organic solvents into reactive intermediates. The reactive intermediates can then react with the "trapping" reagent and spectroscopic changes, such as surface enhanced Raman spectra, are used to sense the chlorinated organics at levels far below their detection means by electrochemical methods alone. Previous work (1) has shown the usefulness of using surface enhanced Raman spectroscopy (SERS) for the detection of groundwater contaminations and the technique has also been successfully applied to fiber optics (2). However, these past experiments have mainly been restricted to aromatic hydrocarbons.

In this manuscript we will discuss some of the fundamental aspects of using SERS for the examination of the following chlorinated hydrocarbons or organochlorides: carbon tetrachloride, 1,2-dichloroethane (DCE), chloroform and trichloroethylene (TCE). Our interest in these compounds stems from their existence in the groundwater at the Department of Energy hazardous waste sites.

EXPERIMENTAL

The Raman spectroscopy system for conducting the SERS experiments at EIC has been previously described (2). The system used at Oak Ridge National Laboratory (ORNL) is shown in Figure 1 and, with the use of an optical fiber for excitation, represents a first step toward a remote fieldable Raman system. Of note in the optical system is placement of the laser line pass filter (BP) after the optical fiber to remove interfering Raman scattering from the fiber itself

(3). Both research groups employed high-resolution spectrometers and diode array detectors for measuring Raman scattering from similar spectroelectrochemical cells. As shown in Figure 2A, each cell was fabricated from a 3 x 6 x 3 cm quartz cuvette with O-ring joints fused into three sides and the top. Electrodes were fed into the cell through O-ring joints and consisted of Pt counter, Ag/AgCl reference, and copper working electrode. The working electrode was placed about 2 mm from the (large) face of the cell between the two electrodes. This orientation minimized the path length of incident and scattered light through the sample solution and simplified alignment of the electrode in the optical system. For transport/concentration studies, a membrane could be sandwiched between the spectroelectrochemical cell and a second cuvette with matching O-ring joint fused into the bottom (Figure 2B).

The spectroelectrochemical procedures were first developed at EIC and then used at ORNL. Electrochemical roughening of polished copper electrodes, consisting of high purity 1.0 mm copper wire, was achieved with an oxidation/reduction cycle (ORC) from -0.6 to +0.2V in a 0.1M KCl electrolyte at 25 mV/sec. Saturated solutions of the chlorohydrocarbon solvents (CHS) in distilled water or 100 µg/ml solutions of CHS in 0.1M KCl were cycled several times under the same conditions and optimum SERS spectra were acquired at -0.2V on the cathodic sweep. All cycling occurred under laser illumination at 625 nm at EIC or 647 nm Krypton illumination at ORNL. The use of the slightly different wavelengths for illumination and Raman spectroscopy did not produce significantly different results at the two labs.

RESULTS AND DISCUSSION

Our results confirmed previous experiments (1) which indicated that carbon tetrachloride was not observable on Ag substrates. In addition, we were unable to observe the chlorinated hydrocarbons on Ag or Au substrates. However, when we examined the chlorinated hydrocarbons with a Cu electrode, we were able to observe the SERS spectra of carbon tetrachloride (Figure 3) as well as the SERS spectra of TCE, DCE and chloroform (Figure 4).

The best SERS spectra were obtained when the ORC cycle was stopped during the reduction step at the potential of zero charge for Cu(-0.2V) (4). The observation of the SERS spectra was also highly dependent on illumination during the cycling. Previous work by Thierry and Leygraf (5) has indicated the importance of illumination during the electrochemical roughening of Cu electrodes to produce Raman active sites.

The vibrational features in Figure 4 indicate that a reaction is occurring on the electrode surface (see Table 1 for vibrational assignments). From the spectra, it appears that ring formation is occurring due to an electrochemical and/or photochemical process. However, in our experiments no SERS spectra of the CHS were observed unless the electrode was illuminated during the reduction step and thus a strictly electrochemical reaction can be ruled out. This "photo" induced result indicates the possibility of a photoelectrochemical process. Copper oxides are known to be p-type semiconductors which eject electrons under illumination (Equation 1) (6). The band gaps for the two possible copper oxides are 2.0-2.6 eV (620-477 nm) for Cu_2O and 1.7 eV (730 nm) for CuO. These electrons can then electrochemically reduce the chlorinated hydrocarbon solvents.

$$Cu_2O + \lambda \rightarrow Cu_2O(h^+,e^-)$$

This electrochemical reduction is similar to a reaction scheme for the electrochemical reduction of chloroform which has been determined by Fritz and Kornrumpf (6) to be :

$$CHCl_3 + 2e^- \rightarrow CHCl_2^- + Cl^-$$

$$CHCl_2^- + CHCl_3 \rightarrow CH_2Cl_2 + CCl_3^-$$

$$CCl_3^- \rightarrow :CCl_2 + Cl^-$$

The formation of the dichlorocarbene during the electrochemical reduction process would tend to form a ring type structure (6). This ring type structure is indicated in our SERS spectra with the strong band at 1380 cm^{-1}.

A preliminary observation has indicated that the SERS spectrum is only observable for a finite amount of time. The result is either due to the degradation of the electrode or the sample. If the electrode was replaced with a new SERS surface and then placed in the same solution, the spectrum was still not observable. This indicates that the chlorinated hydrocarbons were being consumed during the experiments in the small volume (10 ml) of analyte. Confirmation of this result would indicate that the SERS on Cu surfaces is a method which is capable of both sensing and removing the chlorinated hydrocarbons from the solution.

To determine the cause of the disappearing SERS signal, a series of SERS/GC experiments which determined the TCE concentration before and after the SERS experiments were performed. Saturated samples of trichloroethylene (TCE) in 0.1M KCl and distilled H_20 were cycled in a sealed glass SERS cell to prevent the possibility of outgassing of the TCE. Samples of the saturated TCE solutions were collected both before and after the electrochemical cycling. These samples were analyzed on a Hewlett-Packard Model HP 5730A Gas Chromatograph. Chromatograms were recorded and the magnitudes of retention peaks were examined for the TCE peak in the experiments. Large spikes at the 45 second retention time were due to impurities in the distilled water. The chromatograms showed that a large amount of TCE was consumed during electrochemical cycling. Figure 5 represents a typical "before" and "after" chromatogram.

Analysis of "before" and "after" chromatograms showed an average consumption of 66% of the trichloroethylene during the electrochemical cycling and SERS experiments. This is consistent with our observation that a film was being formed on the roughened copper surface of our working electrode. The formation of a film also indicated the carbene may be originating a radical induced polymerization. Methods for determining the exact structure of the products formed during electrochemical cycling are currently under investigation.

CONCLUSION

The observation of a "photo" induced SERS process in the analysis of the chlorinated hydrocarbon solvents has future implications for environmental sensors. Previous to this work it was thought that the CHS type compounds were not observable by the SERS technique. Upon completetion of our fundamental experiments, future work will concentrate on the analytical applications of the process and the development of field portable Raman instrumentation.

ACKNOWLEDGMENT

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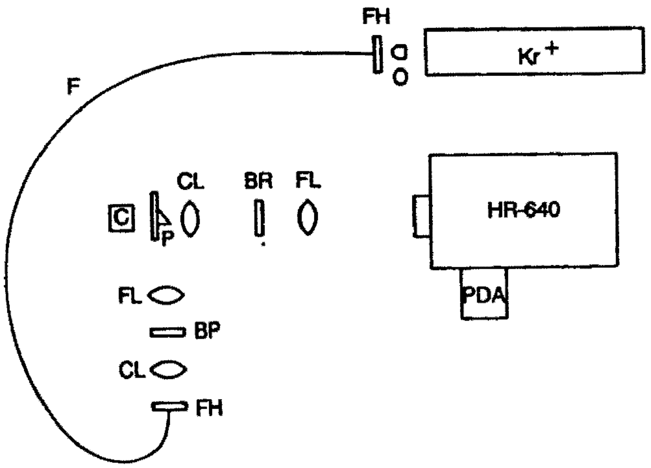

Figure 1. Experimental setup for "photo" induced SERS experiments at ORNL. F = optical fiber, O - microscope objective, CL- collimating lens, FL = focusing lens, P = right angle prism, BP = laser line pass filter, BR = laser line rejection filter, C = spectroelectrochemical cell.

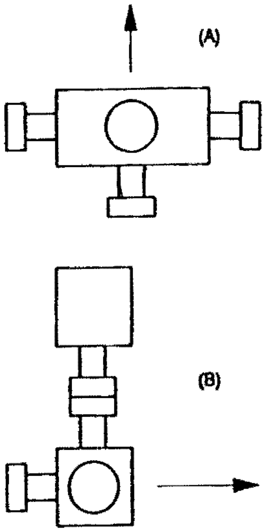

Figure 2. Diagram of spectroelectrochemical cell. (A) Top view showing 3 electrode ports and O-ring joint opening in the top of the cell. (B) side view showing sample reservoir attached to the top for membrane concentration/transport studies. Only 2 of the 3 electrode ports are visible. In both diagrams the arrows point along the optical axis as shown in Figure 1.

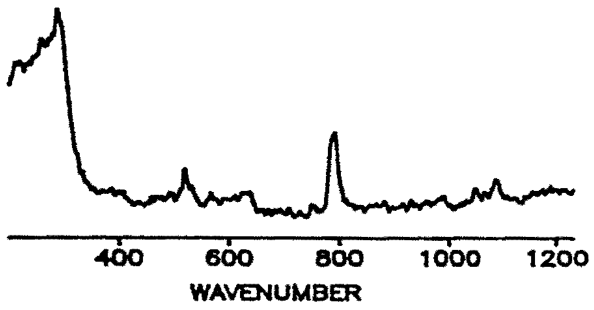

Figure 3. The SER spectrum of a saturated solution in water on a Cu electrode of carbon tetrachloride. The spectrum has been smoothed for clarity.

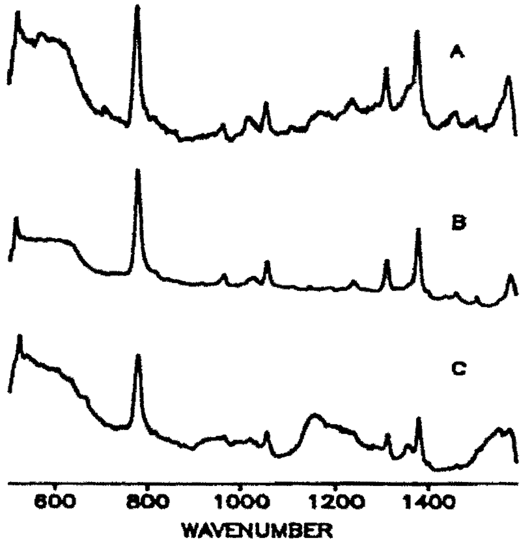

Figure 4. The SER spectra of saturated solutions in water on a Cu electrode of (A) trichloroethylene, (B) 1,2,-dichloroethane and (C) chloroform.

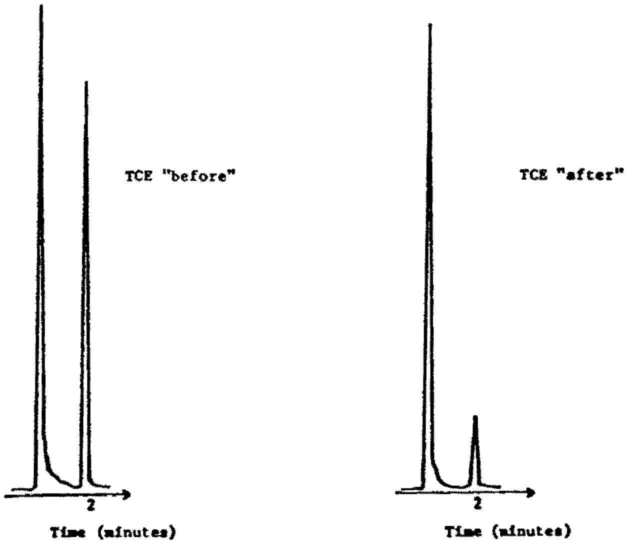

Figure 5. Gas chromatograms of TCE solution before and after the SERS experiment. Retention time for the TCE peak was 2 minutes.

Table 1

Major Raman/SERS Peak Positions (cm^{-1}) and Vibrational Assignment for the Chlorinated Hydrocarbon Solvents

CCl_4		$CHCl_3$		DCE		TCE		Vibrational Assignment
Raman	SERS	Raman	SERS	Raman	SERS	Raman	SERS	
227 s	220 w							Cu-C ?
	261 w							Cu-C ?
	288 w							Cu-C ?
319 s								"chain expansion"
462 s								symmetric CCl_4 str.
	521 w		526 m		521 m		524 m	CCl str., Cu-C stretch?
						628 s		CCl str. - secondary CA
		689 s	670 w	656 s				CCl str. - primary CA symmetric CCl_3 str.
				674 m				CCl str. - primary CA
762 w								CCl str. - primary CA
787 w	791 m	760 m	783 s	755 s	782 s	780 m	781 s	CCl str. - primary CA
				882 w		842 w	862 w	CC skeletal str.
				944 w	965 w	930 w	963 w	CC skeletal str., ring "breathing"
			1021 w		1024 w		1018 w	in-plane CH deformation, CC str., ring "breathing"
	1051 w		1056 m	1055 w	1058 m		1055 m	CC str., ring "breathing"
	1089 w				1101 w		1105 w	CC str., ring "breathing"
			1151 w		1148 w		1167 w	ring "breathing" - cyclopropane type
		1218 w		1209 w				CH_2 twist and rock
			1234 w		1239 w	1247 m	1237 w	CH_2 twist and rock, in-plane CH deformation
			1313 m	1306 w	1312 m		1312 m	CH_2 in-phase twist, CH_2 twist and rock, in-plane CH deformation
			1352 m				1358 m	CH deformation
			1381 s		1379 s		1379 s	ring str.,
				1433 w				CH_2 deformation
			1465 w		1464 w		1463 w	CH_2 deformation
					1509 w		1505 w	symmetric C=C str. - cyclo
			1550 w					C=C str. - cyclobutene
			1581 w		1582 m	1585 s	1580 s	C=C str. CA, 3 or C=C couple str. - polyene

s - strong intensity, m - moderate intensity, w - weak intensity
CA = Chloroalkane, str. = stretch

DISCUSSION

ARTHUR D'SILVA: In the E.I.C. experiments at what wavelength did you measure the fluorescence?

MICHAEL CARRABBA: We're looking at the complete spectrum, in this case a very simple proof of concept. We weren't trying to develop a highly skilled system as the Livermore people have developed, or as the people at GEO-Centers. We're proving the concept here. We just monitored the intensity under the total fluorescence band.

ARTHUR D'SILVA: What is the excitation wavelength?

MICHAEL CARRABBA: The excitation wavelength was 514 nanometers. We added an argon-ion laser. We believe we could use just about any of the wavelengths from 488 up to about possibly 600, but we really didn't try the 600.

EDWARD POZIOMEK: In the experiment where you described the photon induced reaction, did you utilize a base?

MICHAEL CARRABBA: In the electrochemical experiment you don't need the base. We use it as our bench mark, and then put the electrodes in. I believe we don't need the base, and that's probably the important point.

EDWARD POZIOMEK: If you had the opportunity to solve a technology barrier, which one would you go after first in this area to move it faster?

MICHAEL CARRABBA: The implication of the dichlorocarbene, going after a double bond, could be quite lucrative in the future. And we believe we can make probe systems that have been coded right onto an optical fiber and a very simple sensor. That's where I think we'd pursue it at this point. Basically we'd use some particular dyes that when the dichlorocarbene attacks the double bond it breaks the conjugation and the fluorescence disappears or new fluorescence appears. That's the direction that we're working on right now.

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