DETECTION OF VOCS IN AIR USING MICROELECTRODE SENSORS

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ABSTRACT

The use of microelectrode sensors to detect volatile organic compounds (VOCs) in air is demonstrated. In general, VOCs that easily oxidize to form protons gave a larger electrochemical response. The use of voltammetry for speciation and the effect of electrode size on the electrochemical response are discussed.

We demonstrate that surface enhanced Raman spectroscopy (SERS) can be used to monitor the electrochemical reactions in-situ and discuss its applicability in identifying the electroactive species.

INTRODUCTION

Many techniques have been employed in the detection and identification of volatile organic compounds (VOCs). Commonly used techniques for environmental monitoring include GC/MS, Dräger tubes, flame (FIDs) and photo-ionization detectors (PIDs), and Surface acoustic wave (SAW) devices. The FIDs, PIDs, and SAW devices, although reusable and exhibiting good response times and sensitivity, are very poor at speciation.

Dräger tubes make use of colorimetric chemical determination reactions. As such, they exhibit good selectivity and sensitivity; however they are not reusable. Of the technologies discussed, GC/MS exhibits the best selectivity and sensitivity. However, it requires the use of sophisticated instrumentation and cannot be used for continuous monitoring.

An ideal VOC detector would be one that could rapidly detect contaminants as well as identify and quantify those contaminants. One technology which has the capability of meeting these criteria is electrochemical detection using microelectrode sensors. Ultramicroelectrodes (UMEs) can be made from any electrode material (Au, Pt, C, etc.) in any geometrical arrangement (disks, rings, bands, etc.) and can be assembled into arrays. The choice of electrode material, size, and geometry depends on the application. The unconventional properties of UMEs make them attractive as sensitive electrochemical sensors and detectors in a variety of media. In UMEs the characteristic dimension that is given by the geometry of the electrode must be very small. Reducing that characteristic dimension results in very small currents, decreased Ohmic losses due to the diminished current, reduced capacitive charging currents, and an increase in mass transport to and from the electrode. As a consequence of reduced capacitive charging currents and increased mass transport rates, UMEs exhibit excellent signal-to-noise (S/N) characteristics. Furthermore, the electrode potential can be changed rapidly permitting voltammetric measurements on a sub-microsecond timescale and measurements in highly resistive domains. The reduced iR effect is particularly important because it allows measurements to be made on nonpolar solvents in the presence of appropriate support electrolytes, polar solvents, and mixtures of polar and nonpolar solvents in the absence of purposely added support electrolytes, low-temperature glasses and eutectics, and the gas phase.

The use of UMEs for the analysis of electroactive species in the gas phase was demonstrated first by Pons et al. In these initial investigations, it was shown that the sensitivity of the device was dependent upon the electrochemical properties of the analyte and on the properties of the surface separating the inner UME from the outer auxiliary electrode. Species selectivity of these microelectrode detectors arises from differences in the redox potentials of the analyte. Either constant potential or voltammetric techniques may be used. Because there is an interest in developing new technologies for environmental monitoring, we began investigating the feasibility of using these microelectrode sensors to detect and identify VOCs in the air under ambient conditions. In particular, we examined the effect of electrode material and size on the magnitude of the electrochemical response as well as the possibility of using the voltammetric response for speciation. We explored chemical modification of the sensors and the use of arrays of microelectrode sensors for speciation. We also demonstrated the use of surface enhanced Raman spectroscopy (SERS) to monitor the electrochemical reactions in situ and discuss the applicability of SERS in species identification.

ELECTROCHEMICAL RESPONSE OF MICROELECTRODE SENSORS TO VOCS IN THE GAS PHASE

Figure 1 shows a schematic of the microelectrode sensor used in this investigation to detect VOCs in the gas phase. The inner working electrode consists of a metal wire that is epoxied inside the outer auxiliary electrode. The electrochemical response of a C/Au microelectrode assembly to acetonitrile in air is summarized in Figure 2. Similar results were obtained for other microelectrode
sensors and other VOCs. Voltammetric curves (Figure 2a) were obtained for acetonitrile as it evaporates. In air, a linear response is observed as a function of applied potential. The background current is on the order of 1 pA. Within minutes after an aliquot of acetonitrile was injected inside the sample chamber, an increase in current flow was observed. As the concentration of acetonitrile in air increases, the voltammograms begin to exhibit more curvature. Static and dynamic exposure tests yield the results shown in Figures 2b and c, respectively. The results summarized in Figure 2 indicate that the response of these sensors to an electroactive material in the gas phase is reversible. The sensors can be used in either a flowing stream or in a quiescent environment and can be used to monitor contaminants in air.

Our results indicate that the electrochemical response is greatly dependent upon the electrode material as well as the analyte. The largest electrochemical response is observed for compounds containing oxygen and nitrogen atoms, such as ethanol, acetonitrile, and 2-butanone. These materials are polar and have fairly large dipole moments and dielectric constants.

Figure 2. Electrochemical response of a C/Au disk microelectrode sensor to acetonitrile in the gas phase at room temperature. Diameter of the C working electrode is 7 μm.

(A) A 25 μl aliquot of acetonitrile was injected into a glass flask. The evaporation of acetonitrile was monitored electrochemically by sweeping the voltage from 0 to 8 V at a sweep rate of 100 mv s⁻¹.

(B) Results of a static exposure test. The voltage was held constant at 3V. An arrow indicates the time of injection of a 2 μl sample of acetonitrile.

(C) Dynamic response as a function of time for acetonitrile vapor. The potential was held constant at 8 V and the Ar flow rate was 10.9 mL min⁻¹. The UME assembly is repeatedly exposed to analyte vapor and then to pure argon yielding the differential response shown. The solid arrows indicate when the C/Au assembly is exposed to argon bubbling through acetonitrile. The open arrows indicate purging with pure argon.
In contrast the electrochemical response of the aromatic VOCs is very small while that for the chlorinated hydrocarbons falls between these two extremes. Anodic oxidation of organic substances has been thoroughly investigated using voltammetric techniques in aprotic solvents. Aromatic hydrocarbons and their derivatives undergo oxidation to form radical cations which lose a proton rapidly to give the free radical. It was shown that substitution can increase the stability of aromatic cation radicals and that molecules capable of greater charge delocalization produce the more stable radicals. The anodic oxidation of aliphatic hydrocarbons generally proceeds by the transfer of two electrons and the loss of one proton to give a carbenium ion:

\[ \text{RH} = \text{R}^+ + \text{H}^+ + 2e^- \]

These observations indicate that the ease of oxidation leading to the formation of protons directly correlates with the magnitude of the electrochemical response.

**EFFECT OF ELECTRODE SIZE ON THE ELECTROCHEMICAL RESPONSE**

Figures 3a and b summarize static and dynamic exposure tests respectively, for methylene chloride and Ag/Au disk microelectrode sensors. The results indicate that the magnitude of the electrochemical response increases with increased electrode size as does the S/N ratio. Although the background current of the larger electrodes is slightly greater than the 25 µm diameter Ag disk microelectrode sensor, the background current for the larger sensors is still below 1 pA. The increase in size of the inner electrode does not dramatically affect the shape of the voltammograms. Since the magnitude of the response is proportional to the diameter of the inner electrode of the sensor and not its area, the electrochemical reactions occur at the electrode perimeters. These results also indicate that current flows over the surface of the insulating ring separating the two electrodes. Consequently, the insulator surface can be viewed as the selective layer. Modification of this insulating surface will affect the magnitude of the electrochemical response as well as the selectivity of the sensor.

Figure 3. Static and dynamic exposure tests for methylene chloride and Ag/Au microelectrode sensors as a function of working electrode diameter.
(A) Static exposure tests using 25, 125, and 500 µm diameter Ag disk electrodes in the sensors. The applied potential is 8 V.
(B) Dynamic exposure tests using 25 and 500 µm diameter Ag disk electrodes in the sensors. The applied potential is 8 V and the flow rate is 9 mL min⁻¹.
IDENTIFICATION OF THE ELECTROCHEMICALLY ACTIVE SPECIES

The microelectrode sensors used in this investigation proved to be very sensitive. However, an environmental monitoring device not only requires detection of a material but also identification.

Linear sweep voltammetry could allow speciation. The shape of the current/voltage reflects the specific set of events associated with the charge transfer reaction taking place under selected experimental conditions. The overall current-voltage relationship is complex and differs for various conditions. It is affected by the chemical nature and concentration of the electroactive species, by the chemical nature of the electrode material, and by the mode of transport. Figure 4 shows voltammograms obtained for ethanol in the gas phase using Pt, Pd, C, Ag, Au, Ni, and Cu microelectrode sensors. Although voltammograms can be obtained for these materials in the gas phase, their utility in species identification is questionable for an environmental monitoring device. The voltammograms for acetonitrile obtained as a function of time using a C/Au assembly (Figure 2a) indicate that the response is instantaneous. However, with time, as more acetonitrile molecules enter the gas phase, the voltammograms begin to exhibit more curvature, until they achieve their characteristic shape. In addition to concentration issues, mixtures present an obvious difficulty in using voltammetry for speciation in an environmental monitoring device.

![Image](image_url)

Figure 4. Voltammograms obtained for ethanol in the gas phase. The auxiliary electrode is Au. The working electrodes of the sensors are 25 µm diameter Ni, Au, Pt, Pd, and Ag disks; 7 µm diameter C disk; and 50 µm diameter Cu disk. Voltammograms were obtained at a sweep rate of 100 mV s⁻¹.

Since voltammetry is of limited utility, another means of speciation needs to be found. One approach is to chemically modify the sensors so that they will respond to a particular compound or class of compounds. This approach has been applied with various degrees of success to surface acoustic wave, SAW, devices. A second approach is to package a number of these microelectrode sensors into one device. In this approach, multiple micro-

electrode sensors at different bias voltages will yield a pattern characteristic of a compound upon exposure. Neural networks or cluster-seeking routines can then be utilized to identify the components of a mixture. The usefulness of this latter approach has been demonstrated by Stetter et al. However, as the number of VOC species increases, the accuracy of this approach in identifying those VOCs decreases. When used in conjunction with a chromatograph, this approach works well for speciation.

Another approach is to combine the specificity of spectroscopy with the sensitivity of electrochemistry. For organic compounds, Raman spectroscopy is ideal for the purpose of speciation. Virtually all organic molecules display a characteristic Raman emission. Besides specificity, simultaneous multicomponent analysis is possible in Raman spectroscopy due to the high resolution of Raman spectra. Raman scattering from molecules adsorbed on such noble metals as silver, copper, and gold can be enhanced by as much as 10⁶ to 10⁷. The phenomenon, surface enhanced Raman spectroscopy (SERS) requires a roughened surface. Both alkanethiols and dialkyl disulfides react with Ag and Au to form self-assembled monolayers, SAMs. The alkyl group is attached to the surface by a metal thiolate bond. Carron et al. showed that octadecylthiol coated Ag SERS substrates can be used to detect both aromatic compounds and chlorinated hydrocarbons in ground water. The coating also protects the SERS substrates from oxidation and fouling from atmospheric materials. This increases the lifetime of the SERS substrate from minutes or hours to months. The coating itself has a characteristic SERS spectrum and can be used for calibration purposes. Since the electrochemical reactions occur at the electrode perimeters in the gas phase, the electrochemical response of the microelectrode sensor can be measured while simultaneously obtaining SERS spectra of the surface of the working electrode.

Both static exposure and dynamic exposure tests were conducted using Au/4-chlorothiophenol microelectrode sensors. Figure 5 shows the current/time curves obtained during the dynamic exposure test. The letters along the current/time curve indicate when a SERS spectrum was obtained. The 650-800 cm⁻¹ spectral region of these spectra is shown. Although the 4-chlorothiophenol spectrum has a vibrational peak at 703 cm⁻¹, it does not interfere with the detection of the methylene chloride peak at 715 cm⁻¹. The results summarized in Figure 5 show that the increase/decrease of current flow upon exposure of the microelectrode sensor to methylene chloride directly corresponds with the intensity of the methylene chloride peak in the SERS spectra. This indicates that the electroactive species is methylene chloride. These experiments demonstrate that in situ spectroelectrochemical measurements of these thiol modified microelectrode sensors upon exposure to VOCs are feasible. It is possible to use the spectra to identify the electroactive species and spectra can be obtained when the sensor is operated in both a flowing stream and in a quiescent environment.
CONCLUSIONS

It has been shown that microelectrode sensors can be used to detect VOCs in air under ambient conditions. In the presence of VOCs, the electrode assemblies exhibit a good response time, are reversible, and can be used in either a flowing stream or in a quiescent environment. Although the microelectrode sensors used in this investigation were fairly large, it has been shown that microlithographic techniques can be used to prepare these sensors on chips, thereby significantly reducing their dimensions. The magnitude of the electrochemical response is dependent upon the electrode material and is related to the molecule's ease of oxidation leading to the formation of protons. It was found that VOCs with high dielectric constants and net dipole moments generally gave a larger electrochemical response. Since explosive materials and drugs contain polar functional groups, these sensors can be used for their detection as well. Voltammograms of the VOCs can be obtained in the gas phase. The shape of the voltammogram is dependent upon the chemical nature of the electroactive species as well as the electrode substrate. However, the possibility of mixtures reduces the utility of voltammetry for speciation in a device used for environmental monitoring.

In the gas phase, the electrochemical reactions occur at the perimeters of the electrodes making up the assembly. Therefore, the critical dimension is the spacing between the inner and outer electrodes of the assembly, which must be small. Larger diameter wires can be used provided this spacing is kept small, preferably under 100 µm. The advantages of using larger diameter wires in these microelectrode sensors are an increase in sensitivity and better signal-to-noise ratios.

The microelectrode sensors used in this investigation proved to be very sensitive. However, an environmental monitoring device not only requires detection of a material but also identification. Since voltammetry is of limited utility, another means of speciation needs to be found. One approach is to chemically modify the sensors so that they respond to a particular compound or class of compounds. A second approach is to package a number of these microelectrode sensors into one device. In this approach, multiple microelectrode sensors at different bias voltages will yield a pattern characteristic of a compound upon exposure. Neural networks or cluster-seeking routines can then be utilized to identify the components of a mixture. Another approach combines spectroscopy with electrochemistry. The microelectrode sensors are used to continuously monitor the environment. When an increase in current flow between the two electrodes of the sensor occurs, spectroscopic techniques are used to identify the electroactive species. In this investigation, the use of SERS to monitor the working electrode surface in situ during anodic oxidation has been demonstrated.
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REFERENCES