An In-Situ Ion Mobility Spectrometer Sensor System for Detecting Gaseous VOCs in Unsaturated Soils

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Abstract

Existing methods for the detection and measurement of volatile organic compounds (VOCs) in the vadose zone are often hampered by issues associated with ease of use, accuracy, and cost. As a result, there remains a need for inexpensive, minimally invasive, real-time instrumentation and sensor systems that can be used for characterizing or long-term monitoring of contaminated sites. A new sensor system to meet this need is under development at Boise State University, in collaboration with Washington State University.

A miniature Ion Mobility Spectrometer (IMS) has been fabricated from a machinable ceramic material and has been shown to have a resolving power comparable to a commercial IMS. The IMS system will be packaged in a probe housing for deployment using direct push methods and will be ultimately equipped with water content, temperature, and pressure sensors. The proposed system is designed for use in multi-probe arrays and features wireless transmission of data directly to the user. To our knowledge, an in-situ IMS for detection of subsurface gaseous VOCs has not been previously developed.

VOCs in Unsaturated Soils

If a VOC enters unsaturated soil as a result of a spill, it can be present in four different phases: gas (air), water, solid (soil), and as a free phase liquid. Partitioning

between the phases depends on the volatility, solubility, degree of saturation, amount of organic matter present, and temperature (Domenico and Schwartz, 1998). Compounds with large vapor pressures will volatize and move via diffusion in the gas or vapor phase. These vapors may escape to the atmosphere, dissolve in groundwater, or move into enclosed spaces such as basements, and impact indoor air quality. When a complete exposure pathway exists for vapor intrusion into structures, measurements of soil gas concentrations are needed to determine if the risk to human health warrants clean-up or other remedial action (EPA, 2002). Current methods for sampling and analyzing soil gas samples fall into two classes: passive sampling and active sampling. Passive sampling methods involve the shallow burial of a sorbent collector, which adsorbs the VOC from soil pore gas space as a result of diffusion (EPA, 1988). Passive sampling techniques require site-specific calibration for proper exposure time (typically 1-3 days) to ensure accurate results. Passive samplers are one-time use instruments, require offsite analysis and do not provide mass concentration data (Wong, 2003; EPA, 1988).

Active sampling involves the insertion of a sampling tube or probe into the soil. The gas sample is then extracted and brought to the surface for analysis, often using a field portable gas chromatograph (GC) for immediate results. However, these active sampling systems require the presence of a GC, a skilled technician, and all the systems and equipment needed for deployment and analysis. Thus, active sampling is typically expensive and labor intensive, which generally limits its use to short-term projects such as mapping contaminant plumes (EPA, 1988).

Limitations associated with existing methods led us to consider developing a new sensor system for collecting and analyzing soil gas samples in situ, based on ion mobility spectrometry.

IMS Sensor Applications and Theory

Ion Mobility Spectrometer (IMS) devices have been used in laboratory environments to analyze gaseous chemicals; more recently, these devices have been used in field applications to detect chemical warfare agents, explosives and narcotics. Ion mobility spectrometry is used to separate and quantify ions based on the drift of ions at ambient pressure under the influence of an electric field against a counter flowing neutral drift gas. Gas samples to be analyzed are introduced into the reaction chamber of the IMS system through a sample inlet by a carrier gas (typically nitrogen or air). In the reaction region the sample molecules are ionized and the resulting product ions (charged molecules) move under the influence of an applied electric field towards the ion gate which controls their entry into the drift region. When the ion gate is cycled, a given amount of the product ions is allowed to enter the drift region. The drift tube contains an electric field and a counter flowing drift gas which separates the ions according to their ion mobility. If a gaseous ion at atmospheric pressure is placed in a constant electric field, it will accelerate down the field until it collides with the neutral drift gas. Upon collision, the ion slows down, and, under the influence of the electric field, is accelerated again, resulting in another collision, and so forth. This chaotic sequential series of acceleration and collision at the molecular level translates into a constant ion velocity over macroscopic distances. As the ions

reach the ion collector (Faraday plate), a small current is generated. This current is recorded as a function of drift time; a microprocessor or other system is then used to identify each analyte and determine the concentration.
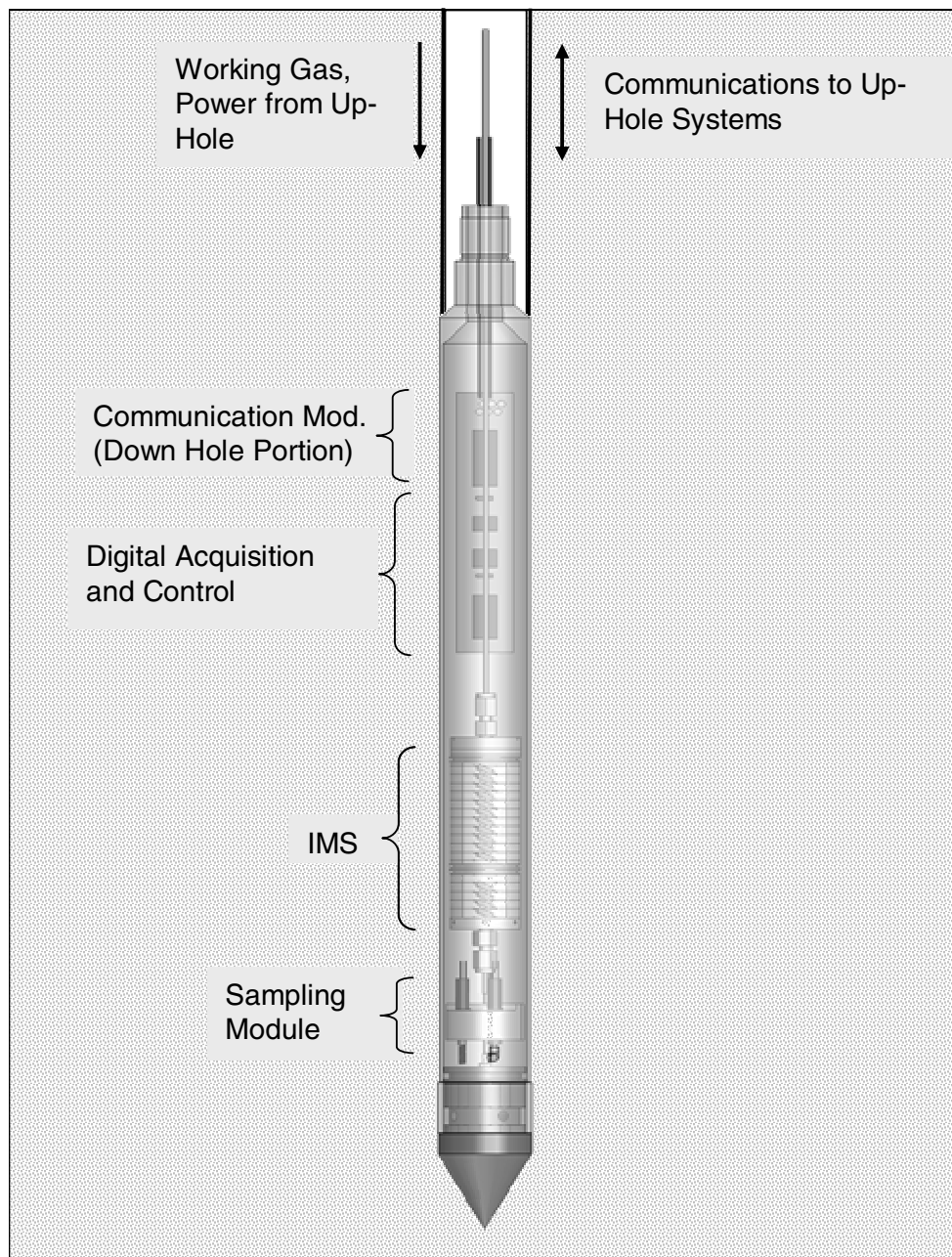
IMS Sensor System Overview

In this project, we have designed and fabricated a miniaturized IMS for use in unsaturated soils. The sensor system is comprised of many subsystems that reside either down-hole in the probe housing or up-hole on the surface. Figure 1 shows a block diagram of the system and Figure 2 shows the sensor system in its probe housing.
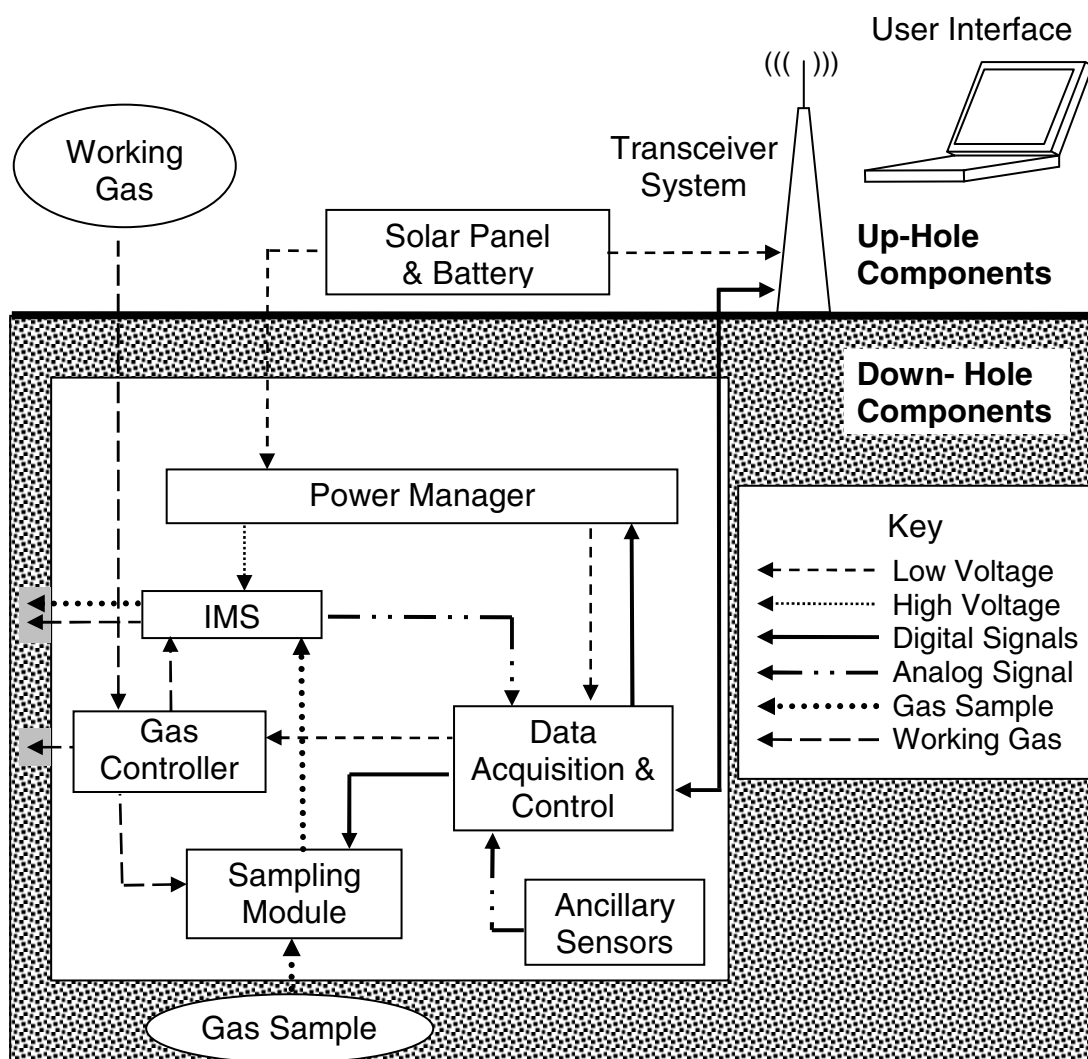
Figure 1. Block Diagram of the IMS Sensor System.

Once deployed, the IMS sensor probe will be connected to an "up-hole" system comprised of an electrical power source, a serial port for local data collection and/or device configuration, and a transceiver system to provide off-site data analysis. The transceiver will use either satellite or land wireless infrastructures to allow data collection and analysis by users in one or more global locations through a web interface.

Figure 2. Layout of the IMS Sensor System in Probe Housing.

Our IMS sensor system is designed to provide real-time monitoring and in-situ identification and concentration values of target VOCs without the need for time consuming, off-site analysis. This sensor provides a method for long-term monitoring of sites and eliminates the need for expensive equipment and labor at a site associated with current active sampling methods. More information on the specific modules of the IMS sensor system under development is provided below.

IMS Sensor

The heart of the sensor system is the IMS sensor, which is compact enough to fit within the probe housing, yet offers the resolving power needed to accurately identify a variety of VOCs. The current dimensions of the IMS are an outer diameter of 3. 8 cm and a length ranging from 12 to 16 cm. Our IMS is composed of a reaction region with a Ni^{63} ionization source and a drift tube constructed of an alternating series of metal and insulating rings. The insulating rings were fabricated out of a machinable glass material called Macor (Dow Corning, Corning, NY). The conducting rings are connected with voltage divider network such that an electric field is created through the center of the tube. A Faraday plate at the end of the drift tube collects the ions that travel down the drift tube to generate a current that is sensed by the data acquisition and control module.

Gas Controller and Sampling Module

The gas controller moves gas samples extracted from the unsaturated soil through the sampling module and provides the counter-flowing drift gas to the IMS. We anticipate using nitrogen or air as the working gas for both of these functions. A venturi pump is used to generate a small vacuum to pull gaseous samples through a porous metal filter into the probe housing and introduce them into the IMS reaction region. The volume of soil impacted during sampling (i.e., the support volume for the measurement) will depend on the intrinsic permeability, degree of saturation and porosity of the soil. An increase in the intrinsic permeability results in an increase in the support volume. Conversely, an increase in degree of saturation will result in a decrease in the relative permeability to the gas phase and decrease in the support volume for a given sampling interval. Finally, an increase in the porosity (not accounting for a change in the intrinsic permeability) will also decrease the support volume. Work is currently underway to determine the working range of the sampling module with respect to these variables for different soil types.

Data Acquisition and Control (DAC) Module

This subsystem serves both the data sensing and harvesting roles. First, this subsystem amplifies the nano-ampere (nA) level current of the Faraday plate with a gain of ~1 Volt per nA. Then it digitizes the data and reduces noise prior to processing the data. This subsystem also controls other down-hole subsystems, such as the gas sampling module, gas controller, and power module, and exports the digital

data for subsequent communication from the down-hole probe location to the up-hole support system.

Communication Module

The two major communication pathways in the sensor system beyond the device interaction within the probe housing are:

- Communication between the down-hole (probe) system and up-hole system using the industry standard protocols.
- Communication between the up-hole sensor systems to the Internet using a satellite or other wireless communications infrastructure. The satellite communications link from the probe to the Internet has been simulated using existing tools by our industry partner, TenXsys (Eagle, Idaho), using a data source to the satellite in place of an actual sensor transmitter.

User Interface

The use of the Internet enables simple, flexible and intuitive data collection. Internet-based communication allows access by users across the globe. Also, no proprietary software is needed on the user's PC to access the data. An example of how the user interface may look is shown in Figure 3 below.
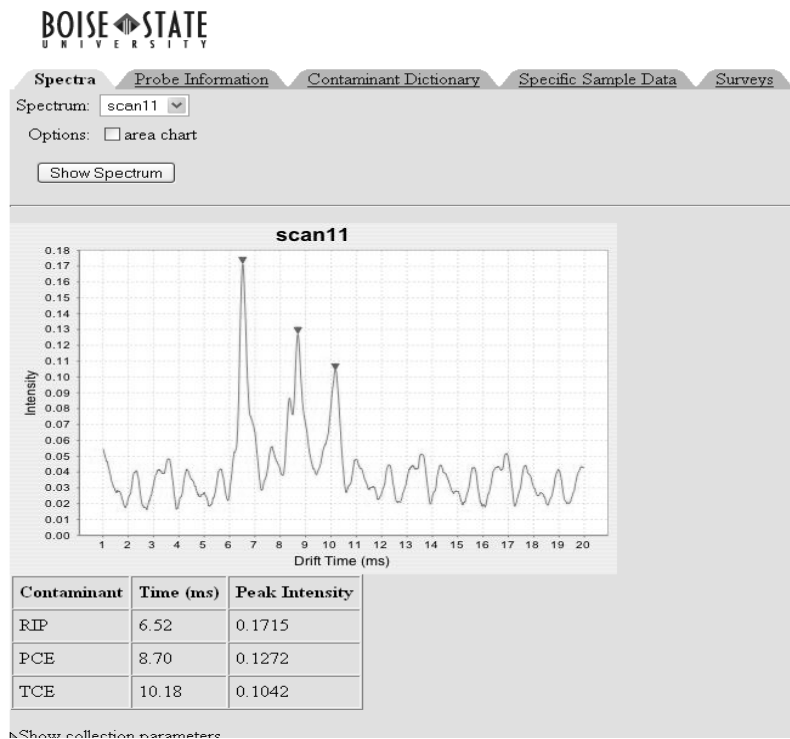

Figure 3. Example User Interface for the IMS Sensor System created by TenXsys (Eagle, Idaho).

Experimental Results

Two sets of experiments were conducted to evaluate the IMS prototype components. Additional experiments were carried out by the Washington State University team to characterize the IMS sensor itself for sensitivity and selectivity to various VOCs. These experiments verified the functionality of the IMS device, DAC, sampling module and high voltage power modules. The following sections describe the experimental results in more detail.

<u>IMS Sensitivity</u>

The IMS prototype's ability to detect target VOCs was evaluated using a reference laboratory amplifier, power supply and data acquisition system. Figure 4 shows the experimental setup for these tests.
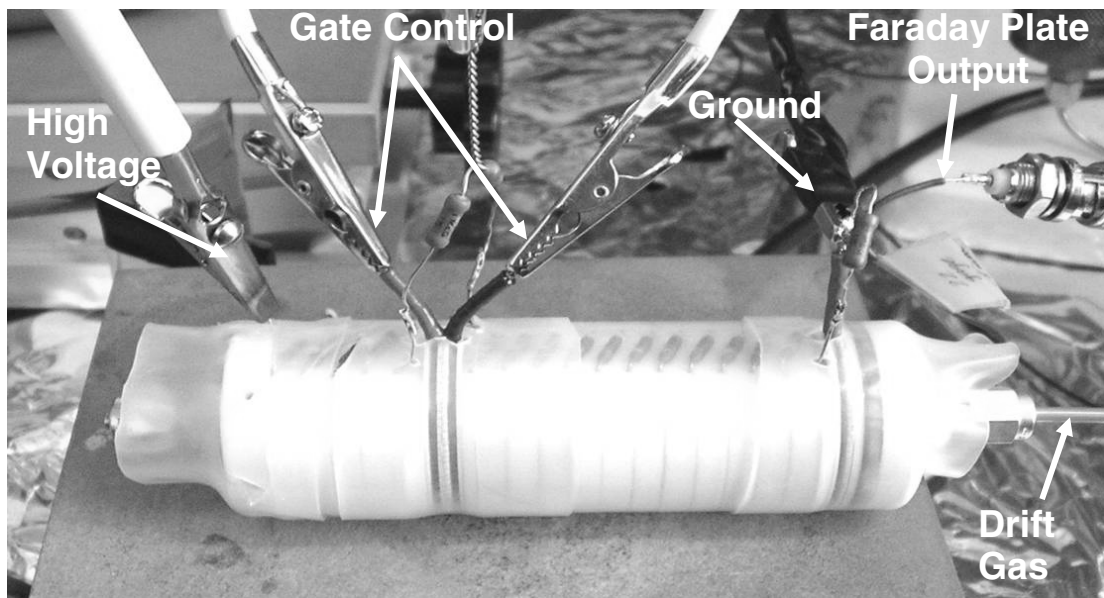
Figure 4. IMS Test Setup.

<u>System Level Measurement</u>

The IMS system was also tested to evaluate the behavior of the DAC module, power supply, sampling, and other modules. All modules were successfully integrated as a system and were demonstrated to perform the following tasks:

- Withdraw contaminant samples in controlled volumes and introduce the samples to the IMS.
- Provide and control the different high voltages needed by the ion gate and drift tube.
- Ionize the sample and control the drift event.
- Amplify and digitize current generated by the ionized sample.

- Provide data processing and storage of the current waveform.
- Provide automated control of the system through the DAC.

The IMS was able to identify the following compounds when introduced separately:

- Tetrachloroethylene (PCE)
- Trichloroethylene (TCE)
- Isobutyl methyl ketone (MIBK)
- Tert-butyl methyl ether (MTBE)

It was also able to identify the following compounds in mixtures:

- TCE and PCE
- MIBK and MTBE

       A representative set of spectra that show that TCE and PCE can be detected by the IMS is presented in Figure 5. Preliminary results suggest that the detection limits will be in the ppm_v range. Optimization of the system may lead to detection limits in the ppb_v range. Thus, we expect the resolving power of the IMS to be comparable to commercial IMS systems.
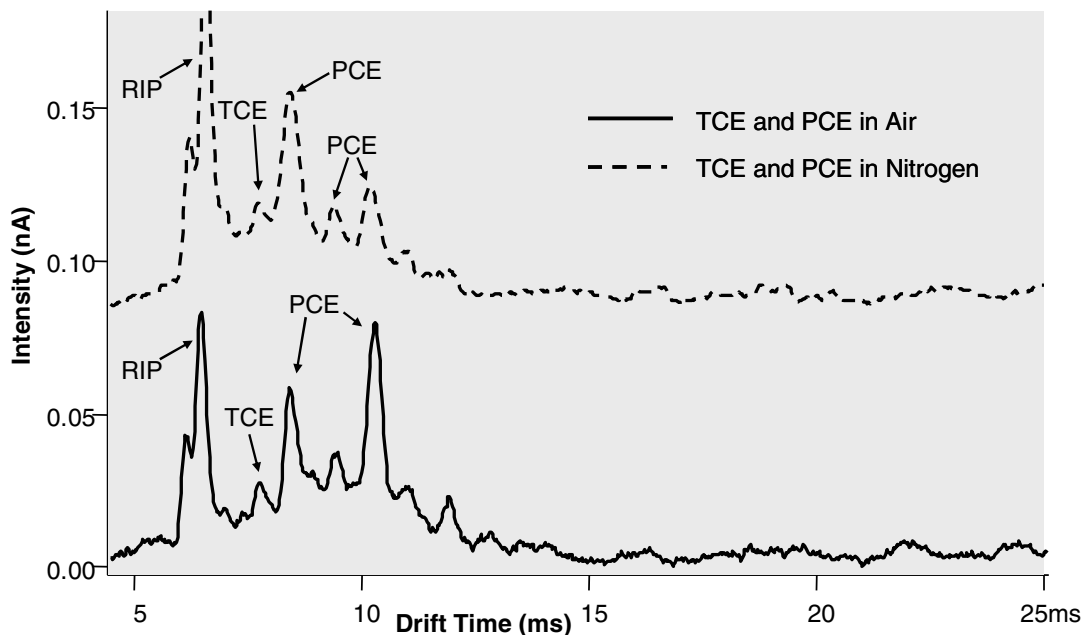
Figure 5. Preliminary Spectra of TCE and PCE from the IMS.

       Figure 6 shows results of the end to end measurement of the IMS sensor system for a mixture of PCE and TCE. This measurement demonstrates the accuracy of the IMS sensor system in the time domain, but also reflects undesirable rounding of the peaks relative to the laboratory DAC system. We have identified the major

contributors to this problem as inadequate amplifier bandwidth and a noise reduction algorithm that is providing a low-pass filtration of the signal. As bandwidth is increased and an improved noise reduction algorithm is implemented in the DAC, less substantial rounding of the output should be possible. Overall, these experiments successfully validated the IMS sensor hardware as a platform for taking the technology forward for subsurface use.

Next Steps

The next major step is to redeploy these subsystems in the probe housing for in-situ measurement. This will require:

- Design and construction of the probe housing.
- Addition of pressure and temperature sensors to enable normalization of the ion mobility measurement.
- Construction and testing of a smaller sampling module and gas controller (designs are already completed).
- Completion of the down-hole to up-hole serial bus.
- Design and completion of the up-hole system power supply (battery, solar panels and controller).
- Completion of the up-hole system gas supply system.
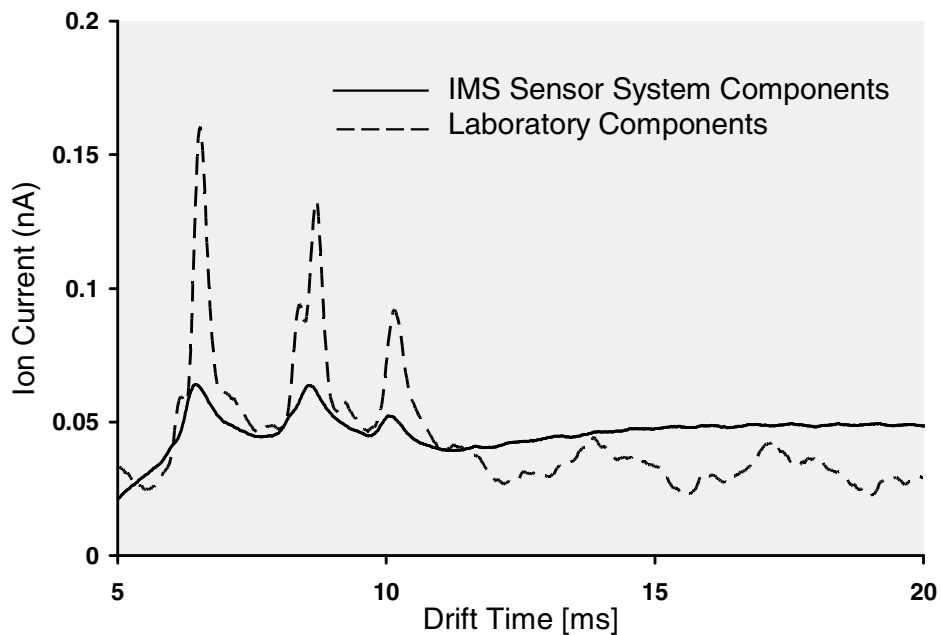
Figure 6. IMS Sensor System Measurement Relative to Lab System

In addition, refinements are expected to take place concurrently with the probe-based sensor in the following areas:

- Continued characterization and optimization of the IMS to achieve higher resolution.
- Investigation of the effects of interferences on IMS performance.
- Work to reduce noise and increase bandwidth of the DAC amplifier.
- Development of improved algorithms to enhance data processing in the DAC module.

Conclusions

We have designed, fabricated, and tested a miniaturized ion mobility spectrometer in the laboratory for use in unsaturated soils to detect gaseous VOCs. Preliminary experimental results suggest that this IMS will be able to detect PCE and TCE, and MTBE and MIBK in mixtures, with detection limits expected to be in the ppm_v range. Optimization of the system may lead to ppb_v-level detection limits. Additional characterization work is needed to determine the effects of interferents and verify the ability of the IMS to detect other VOCs of interest.

Acknowledgements

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