Development of Multi-Membrane Near-Infrared Diode Mass Spectrometer for Field Analysis of Aromatic Hydrocarbons

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Abstract. Membrane Inlet Mass Spectrometry (MIMS) is a technique that incorporates a semi-permeable membrane selective for differing organic molecules and chemistries. This eliminates the need for time-consuming sample preparation and facilitates near instantaneous analysis. This study will examine how the front end of MIMS incorporates three dual inlet ports, allowing for differing MIMS materials and selectivity for specific environments. Polydimethylsiloxane (PDMS) membranes have proven to be selective of benzene, toluene, and xylene (BTX) as well as aromatic hydrocarbons that are common in petroleum products while remaining selective against the aliphatic chains. PDMS has proven to be a successful choice of membrane with high permeability in atmospheric environments. In addition, polycyclic

aromatic hydrocarbons (PAHs) such as acenaphthene, acenaphthylene, naphthalene, and fluorene have recently been detected to the 5 ppb level in a nitrogen atmosphere with our current configuration. This preliminary work provides proof of concept using near-infrared laser diodes that act upon the membrane to increase its permeability and provide higher sensitivity of aromatic samples.

Keywords: Membrane inlet, Laser diode, Aromatic hydrocarbons

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Introduction

Membrane inlet mass spectrometry (MIMS) provides simple, rapid, and selective means of analysis in liquid, atmospheric, and solid environments. The use of a semi-permeable membrane as a chemical or matrix separator allows for molecules to selectively permeate into the mass spectrometer [1]. This method requires minimal sample preparation and obtains meaningful analytical results at up to part-per-trillion levels [2–5]. This paper addresses the development of a multi-membrane inlet front end and an incorporated method of improving analytical signal using near infrared (NIR) laser diodes as a means of increasing sample permeability and desorption from the membrane in a portable system.

This usage of a selectively permeable membrane is especially advantageous and has been used in other projects because it allows for an almost immediate analysis with little sample preparation [6–9]. Owing to the pressure conditions of mass spectrometry being so extreme, it is difficult to design

a membrane—preferably planar—that can withstand the difference in pressure. For this reason, the tubular design is currently the most common option. Studies have shown that a flow-over membrane design, where the analyte is merely directed over the membrane, is 100 times less efficient than a flow-through design, in which the analyte is directed through a membrane [10]. This research further suggests that tubular membrane designs in which the analyte flows through the tubing and diffuses out of the membrane walls have faster permeation rates than do similar tubular designs in which the analyte flows over the tubing and into the membrane walls [10].

During the past few decades, other advancements in volatile compound and gas analysis with the MIMS technique include the development of portable time-of-flight mass spectrometers for environmental analysis [11]. The viability of environmental atmospheric monitoring using MIMS sampling has also been examined [3, 12]. Other work has yielded manipulated front-end designs specifically to analyze volatile organic compounds [7]. Other methods offer the viability of MIMS for the detection of volatile organic compounds (VOCs), sulfur containing compounds, and presence of carbon dioxide in

Figure 1. The developed multi-membrane inlet front end designs. Mounted diodes will act upon the tube they are focused upon. Each pair of feed-throughs (inlet and outlet) allows for ‘flow through’ membranes selective of various chemistries to be installed

the atmosphere [13]. Broadening these techniques will allow the proposed design to incorporate the ability to monitor the civic atmosphere.

Progress has been made in water quality analysis using MIMS. The method has been used to quickly and accurately detect nitrogen, oxygen, and argon in water, with high throughput systems that provided real-time data for analysis of ever-changing environmental factors [14]. Other methods that have applied the MIMS technique to GC/MS provide excellent results in detecting benzene, toluene, ethylbenzene, and xylene in water samples [15, 16]. In 2007, Bell et al. developed and proved the utility of MIMS for analysis in seawater [17]. In addition, research has been performed regarding the permeability of membranes in varying salinity, which will lead to determination of an appropriate membrane for a range of ionic concentrations [18]. Petroleum products have been measured to ppm levels in aqueous environments via MIMS [19]. Other investigations have been conducted to examine the properties of MIMS for use in water quality monitoring [20–23].

As MIMS instrumentation and techniques for sample introduction have been well established, further research into selective membrane materials and increasing permeability are other

opportunities of interest. Membrane materials have been characterized for water and atmospheric analysis [18, 24]. Materials beyond PDMS, such as those with nanocrystallines, are of further interest. Thermal methods have increased the temperature of the membrane inlet with increased analyte perviousness increasing resolution [25, 26]. Developed CO₂ laser desorption methods have augmented the analyte release from the membrane on the vacuum side of instrumentation [27]. Continued advancement in methods to increase permeability will maximize use of existing membrane materials and aid in characterizing new developed materials ever broadening the MIMS field.

The developed system allows for three different membranes to be installed. Each membrane can be selective for certain chemistry and analytes can be directed through each. The incorporated NIR diode advancement for increasing analytical signal allows the system to remain portable while allowing for the emitted laser to aid in membrane permeability. The results of the experiments detailed below are indicative of a system that is highly selective of VOCs and PAHs. The ability of enhanced data acquisition, while remaining portable and rugged, serves to increase this platform’s use in various locations for environmental monitoring.

Figure 2. Obtained benzene (78.11), toluene and xylenes fragment (92.14), xylenes (106.16), and associated fragments spectrum through the multi-membrane inlet front end

Figure 3. Detectable spectrum of 50 ppb sample of PAHs, naphthalene (128.17), acenaphthylene (152.19), acenaphthene (154.21), fluorene (166.22), and anthracene (178.23)

Figure 4. Detectable levels of benzene (78.11) in hydraulic fracturing fluid

Methods

Instrument Design, Front End Construction, and NIR Laser Diode System

The advancement of the MIMS system is centered on the recently developed Gas Analysis System in conjunction with Inficon (Syracuse, NY). The rack-mountable portable system contains a Transpector MPH Residual Gas Analyzer (RGA), which contains a quadrupole mass analyzer and a Faraday cup/electron multiplier means of detection. The in-house built Multi-Membrane Inlet front end is constructed on 2.75" CF flange. Each set of feed through is designed to accommodate 0.012" to 0.025" inner diameter membrane tubes with gas-tight plugs inserted for when the instrument is not in use. Membranes for this experimental analysis was 0.020" Dow Corning Silastic (60-011-02; Helixmark, Carpinteria, CA, USA). A small diaphragm pump (W311-11; Parker Hannifin, Mayfield Heights, OH, USA) provides suction for air and liquid sample flow through. Vacuum is maintained by a Pfeiffer (Asslar Hesse, Germany) MVP020-3 DC diaphragm pump in conjunction with a Pfeiffer SplitFlow 80 turbomolecular pump.

The MIMS front end, Figure 1, is further adapted with a NIR laser diode system. This technique used 1310 nm laser diodes (ML725B8F; Thorlabs, Newtown, NJ, USA) focused with a 3.0 mm diameter sphere sapphire lens (R5000106974-14086; Edmund Optics, Nether Poppleton, York, UK). The diode-lens arrangement is placed approximately 1.43 mm from

the membrane within the vacuum chamber. Diodes were controlled with external power supply and circuitry based upon a 555 timer to provide an approximately 80% duty cycle at 100 Hz emission frequency.

The system can also be outfitted with typical fiber optic, broadband IR diodes, ranging from 1100 to 1700 nm.

The ruggedized and portable MIMS system is secured in a rack-mountable case. It is easily transportable and provides considerable opportunity to accelerate the deployment of a portable mass spectrometer. Identifying unknown chemical species at their sources and the spatial distribution therein is a realistic step forward in portable systems. This pursuit of laboratory-quality instrumentation and associated 'on demand' analytical results drives this type of innovative technology forward. Combined with minimal sample preparation, ease of operation, and on site testing, this portable system seeks to advance the field of portable mass spectrometry.

Results and Discussion

Initial qualification of the inlet system began with samples of VOCs, benzene, toluene, and xylenes, prepared in nitrogen atmosphere in tedlar bags. The spectrum obtained is shown in Figure 2, with the resultant peaks showing outstanding selectivity and permeability of the three chemical compounds. The intention here is to confirm a proper seal of the membrane attachment on the fitting and confirm the choice of Silastic membrane material as selective. The tedlar bag itself was then connected to one inlet of a pair in the multi-membrane inlet front end. The small diaphragm pump was then connected on the paired outlet and suction was applied to provide constant flow through of the sample.

Recognizing the need for greater breadth of samples to be detected in atmospheric environments, a 50 ppb PAH sample was prepared in the same manner. Figure 3 shows the resultant spectrum with high precursor ion resolution. PAHs provide superb means of determining the ability to sample and as a test analyte for exploratory methods used to increase permeability as minimal fragmentation occurs. Once more, it is important that the sample is allowed to constantly flow through the membrane material with the aid of the diaphragm pump.

Owing to the prevalence of shale oil hydraulic fracturing, there is a continued need for methods to monitor environmental

Figure 5. Spectra obtained of normal sampling mode and while the diodes were active: (a) shows the increased resolution of benzene, toluene, and xylenes analytes during multiple sample analysis; (b) shows the initial benefit for naphthalene

effects of the process. Samples of proprietary hydraulic fracking fluid were obtained and exposed to the membrane inlet system. Detectable levels of benzene are observed in Figure 4. This instrumentation could be further developed to monitor constituents of methods used in the efforts to recover unconventional oil deposits.

Improvements to the MIMS system began with development of a NIR diode laser modification to the front end. The objective was to increase permeability and to aid in desorption of the analyte from the membrane material while remaining portable. Laser diodes that require minimal power supply proved to be a keen method. The diodes are focused upon the membrane material, Figure 1, and frequency modulated to pulse while sampling. Laboratory tests of single molecule analytes show an order of magnitude increase in parent ion detection in a 50 ppb atmospheric sampling of naphthalene shown in Figure 5a. While actual sampling will often involve multiple analytes detected at once, a 50 ppb sample of benzene, toluene, and xylene was prepared in nitrogen. The analysis shows increased resolution but unfortunately not as equally high of a gain in spectrum intensity, Figure 5b. However, the overall system still provided meaningful increases in analytical results.

Conclusion

The developed MIMS system with Silastic membranes provides excellent analytical separation of VOCs and PAHs from the atmosphere. Furthermore, the ability to mount various membranes allows for utilization of differing chemistries, and, as such, selectivity will enable quantification in a wide variety of environments. The advancement in using NIR diodes as a means of increasing permeability allows for an order of magnitude improvement when monitoring single analyte chemistries, while providing meaningful improvement when sampling has multiple contaminants.

Further investigation of this system will include various frequencies of diode operation and include other wavelengths. This could provide wavelength-membrane combinations that are increasingly effective in improving MIMS resolution. The more immediate goal of this research is to mount the platform on a vehicle to act as a portable test bed. This mobile analysis vehicle could be outfitted with multiple portable instruments with an extensive range of analytical options. With the increasing prevalence of hybrid vehicles, one such option is to use battery-only drive capabilities while in the field. Removing internal combustion exhaust from the mobile platform while sampling would provide a system clear of any interferences.

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