Application of Tandem Mass Spectrometry In a Miniature Ion Trap MS: Measuring BTEX

Warren K. Mino, Jr.; Michael Spencer; James Wylde; David Rafferty

1st Detect Corporation, Houston, TX

ABSTRACT

- A miniaturized, light-weight, low-power consumption mass spectrometer capable of MS/MS has been developed for detecting volatile organic compounds in headspace.
- Two inlet systems have been engineered for headspace analysis with the miniaturized instrument.
- The instrument was able to detect the components of BTEX over a wide dynamic range (300 ppm - 30 ppb over membrane and 700 ppb - 25 pptr via the pre-concentrator inlet) with the enhanced selectivity of MS/MS.

INTRODUCTION

BTEX (benzene, toluene, ethylbenzene, and xylene) are volatile organic compounds (VOCs) that are abundant in petroleum-based products and industrial solvents. Environmental contamination from BTEX compounds poses a serious threat, as these compounds have toxic and carcinogenic effects. Thus, there is significant demand for a mobile instrument capable of on-site analyses. Furthermore, there is a need to reduce sample preparation complexity while maintaining analytical performance. To enable fast, direct detection of BTEX in the field, a miniature (7.5 in x 12.5 in x 9 in including pumping system), light-weight (17 lbs), low-power consumption (45 W with membrane/65 W with pre-concentrator) mass spectrometer capable of tandem MS, (MMS-1000, 1st Detect, Houston, TX) has been engineered to detect these compounds in ambient air. Two sample inlets are used for this application, a semi-permeable heated membrane inlet, and a novel pre-concentrator. The combination of inlets provide a larger dynamic range for chemical detection. The membrane inlet is suited for ppth to mid ppb range. The pre-concentrator is invoked when sample concentrations are sub ppb to single digit pptr. In addition to a wide dynamic range, both sample inlets can both be utilized in single MS and MS/MS modes of instrument operation.

METHODS

All mass spectrometric analyses were performed on the MMS-1000 mass spectrometer. Ionization was performed using electron ionization (EI) directly in the mass analyzer (cylindrical ion trap), and ions were detected with an electron multiplier. Data analyses were performed with the Conductor (1st Detect, Houston, TX) software package. Standard samples of each component were prepared as described in EPA method 8265[1] in section 7.11. For soil analysis, samples were prepared using EPA method 5021A[2] section 8.3.2. In short, approximately 2 g of soil was placed in a syringe for analysis. Blank spectra of the soil were recorded using both inlet systems. Samples of BTEX were added to the soil and the headspace was measured over time. Higher concentrations (high ppm – mid ppb) were sampled through the heated membrane inlet (Figure 1) and lower concentrations (< 10 ppb) through the pre-concentrator inlet (Figure 2). The pre-concentrator collects sample on a heater coated with a sorbent material inside a tube. After sample collection (10 seconds) the pre-concentrator is evacuated, followed by flash heating the sorbent, which releases the sample into the instrument for analysis.

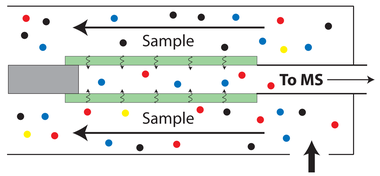


Figure 1. Illustration of the semipermeable membrane inlet for the MS. Sample is pulled over the passive membrane at 600 cc/min. The pressure differential between the sample (atm) and the vacuum chamber (~10-4) allows sample to cross the vacuum barrier without compromising the vacuum of the overall system.

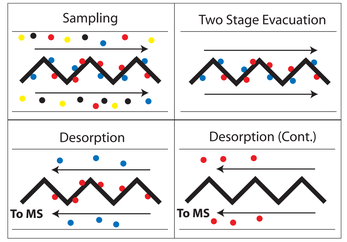


Figure 2. Illustration of the per-concentrator inlet system. Sample is collected on a sorbent for 10 s. The volume is evacuated is a two stage process to remove the background matrix. The sorbent is temperature ramped to desorb the compounds for detection. The temperature ramp yields chemical separation for deconvolution. Flow is indicated by arrows.

RESULTS

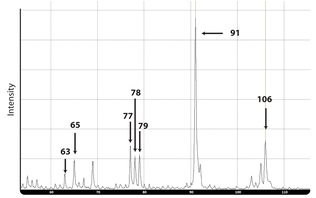


Figure 3. Mass Spectrum of xylene recorded on the MMS-1000. The most dominant peak is 91 which is the neutral loss of a methyl group. The molecular ion, m/z 106 is also observed.

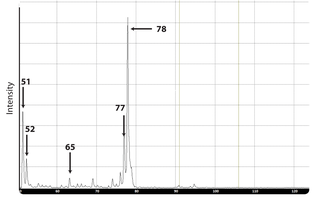


Figure 5. Mass Spectrum of benzene recorded on the MMS-1000. The most dominant peak is 78 which is the molecular ion. Loss of a hydrogen is also observed for the m/z 77 peak.

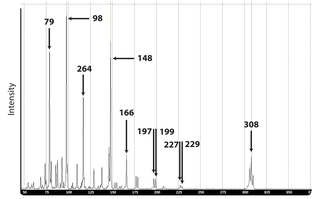


Figure 7. Mass Spectrum of 1,2-dibromotetrafluorobenzene recorded on the MMS-1000. The most dominant peaks are the 79, 98, and 148. The molecular ion, m/z 308 is also observed.

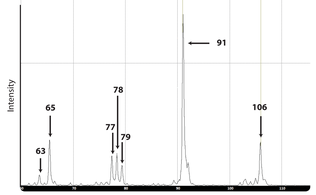


Figure 4. Mass Spectrum of ethylbenzene recorded on the MMS-1000. The most dominant peak is 91 which is the loss of a methyl group from the molecular ion. The molecular ion, m/z 106 is also observed.

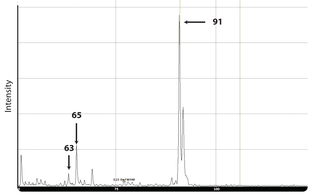


Figure 6. Mass Spectrum of toluene recorded on the MMS-1000. The most dominant peak is 91 which is the loss of a hydrogen from the molecular ion. The molecular ion, m/z 92 is also observed.

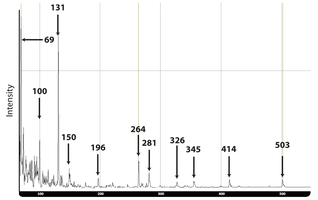
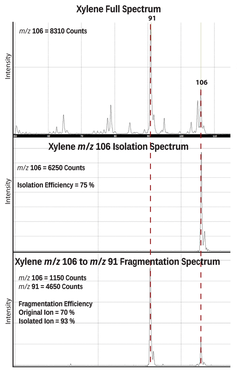


Figure 8. Mass Spectrum of perfluorotributylamine recorded on the MMS-1000. The most dominant peaks are the 69 and 131. The largest mass recorded was 503. This spectrum illustrates the mass range capability of the MMS-1000.

RESULTS (Cont.)



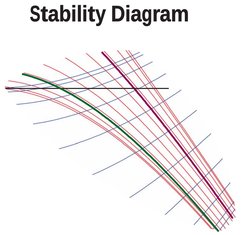


Figure 9. Mass Spectra of xylene recorded on the MMS-1000. Top Spectrum: Full scan mass spectrum. Middle Spectrum: Isolation mass spectrum of the molecular xylene ion. Bottom Spectrum: Fragmentation spectrum of the molecular ion to the 91 ion via neutral loss of a methyl group. The stability diagram is shown for reference. The user identifies which peak to isolate and fragment via a mouse selection in the software. The isolation window is user defined and set to 3 amu. The fragmentation tickle voltage is user defined and set to 20 % of the maximum excitation voltage. Overall fragmentation efficiency was 70% from the original ion.

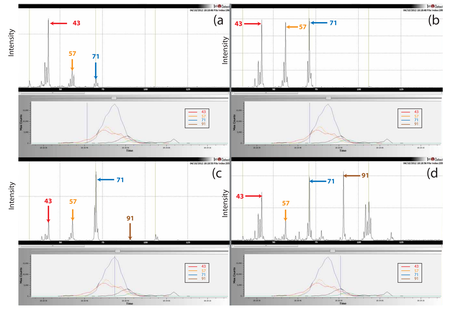


Figure 10. Using the pre-concentrator for chemical separation. Sequence is shown from a through d. A sample matrix containing C3 - C5 (propane, butane, pentane) and ethyl benzene at a concentration of 500 ppb was made. The figure illustrates as the temperature of the pre-concentrator is ramped over time, the relative intensities change for each chemical, as smaller to larger chemicals are desorbed. The software can monitor a user defined number of peaks and is shown to monitor 4 peaks in the chromatograph. The heavier molecules are released from the pre-concentrator at higher temperatures, creating chemical separation and deconvolution of a complex sample.

RESULTS (Cont.)

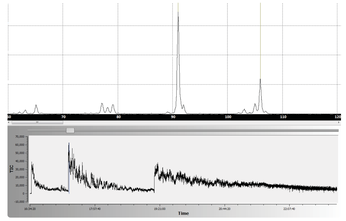


Figure 11. Response of the instrument to 2 g of soil contaminated with 10 uL of xylenes via the membrane inlet. The headspace of the soil was measured by the instrument in a parking lot. The temperature was 71 °F with 0 % humidity and wind gust of 13 mph from the SSW, Signal was detect for 7 hours after contamination.

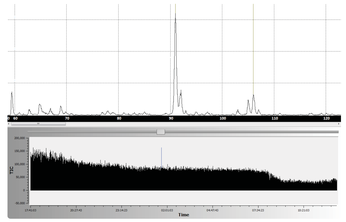


Figure 12. Response of the instrument to 2 g of soil contaminated with 10 uL of xylenes via the pre-concentrator inlet. The headspace of the soil was measured overnight in a warehouse. The soil samples had detectable xylene for >14 days

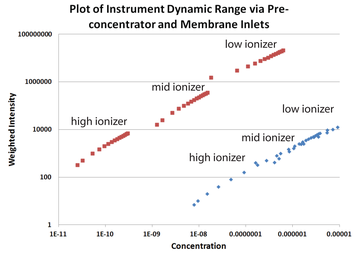


Figure 13. Plot of the Instrument dynamic range. The membrane exhibits a dynamic range of 300 ppm to 30 ppb and the pre-concentrator showed a dynamic range from 700 ppb to 25 pptr, which gives the instrument a dynamic range that spans over 10^7. Furthermore, the gain of the pre-concentrator is shown to be 10^4 over the membrane inlet.

SUMMARY

A miniaturized, light-weight, low-power consumption mass spectrometer has been developed for field deployable on-site analysis. Specifically, the instrument was used to analyze the components of BTEX in static headspace with no sample preparation required. The instrument is capable of detecting a wide dynamic range of concentrations and has a mass range suitable for most VOC applications. The instrument is capable of unit resolution and has a mass range of 50 - 420 m/z; however, as shown in the perfluorotributylamine spectrum the mass range can be extended up to 600 m/z. In addition to the mass range and dynamic range of the instrument, the instrument is also capable of MS/MS analyses. The overall fragmentation efficiency was ~90 % of the isolated ion and significantly enhances the selectivity of the instrument. Furthermore, the pre-concentrator can be invoked for additional concentration gains as well as chemical separation increasing the overall selectivity of the instrument.

ACKNOWLEDGEMENTS

This material is based upon work supported by the Dugway Proving Ground under Contract No. W911S6-10-C-0012. Any opinions, findings and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the Dugway Proving Ground. The authors would like to thank the Texas emerging technology fund (TETF) for the support of this work. The authors would also like to acknowledge the support of the Defense Threat Reduction Agency, Joint Science and Technology Office - Chemical and Biological Defense Program for their support of the work presented here.

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