In-Situ and Instantaneous Detection of Aerosolized Chemical Threats Using Chip-Scale Mass Spectrometry

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ABSTRACT

In-situ and instantaneous detection of aerosolized chemical matter is paramount to swiftly and accurately counter terrorism acts, industrial accidents, and environmental disasters. Aerosol chemical threats pose a significant danger due to the extended range of distance these nanometers (nm) to micrometers (µm) scale particulates can travel with the wind vector without dilution. Detect-ION is developing a versatile chemical threat detection platform that would collect, detect, and identify such aerosolized matter ranging in size from 20 nm to 20 µm. The detector platform, called "SPECTRAL," comprises three novel low-SWaP subsystems, namely an aerosol collection stage, a low-thermal-mass gas chromatograph, and a novel chip-scale mass spectrometer developed via prior IARPA funding, integrated into a battery operated ~10-L form factor. Detect-ION presents prototype development efforts, as well as the aerosol collection and detection performance for a broad range of chemical threat classes as defined by IARPA in the PICARD program.

Keywords: Aerosol Collection, PM 10, PM 2.5, PM 0.1, Chip-Scale Mass Spectrometer, Chemical Detection, Identification Algorithm.

1. INTRODUCTION

Non-volatile chemical compounds can persist in the atmosphere as aerosols in the size range of nanometers (nm) to micrometers (µm) range. In-situ collection and analysis of these compounds is paramount to swiftly and accurately detect acts of terrorism, industrial accidents, and environmental disasters. Detect-ION (DI) is developing a versatile chemical threat detection platform that collects, detects, and identifies aerosols of all sizes. The detector platform, called "**SPECTRAL**," comprises three novel low-SWaP subsystems, namely a miniature aerosol collector (**MAC**), a low-thermal-mass gas chromatograph (**LTM-GC**), and a chip-scale mass spectrometer (**µMS**) developed via prior IARPA funding.

The SPECTRAL system consists of three overall subsystems that function for collection, separation and detection. The collection subsystem, the MAC (**Figure 1**), is a versatile aerosol collector, leveraging DI's Glass Array Collector (**GLAC**) design (patent applied) [1], to provide efficient impaction with high surface area and rapid desorption for sharp injections into the GC stage. The following LTM-GC subassembly (**Figure 2**) provides low-SWAP gas chromatography with the versatility and performance of traditional oven-based GCs. DI's patent-pending, on-demand inline GC split design [2] delivers higher material content to be transferred to the µMS detector without compromising injection quality, using the first segment of the GC column as a column trap or secondary collector. The µMS subsystem (**Figure 3**) uses a microfabricated ion trap array and low-power electronics. The high-density array of chip-scale ion traps, when operated simultaneously, delivers low ppb-level limits of detection (LODs). The µMS deliver mass spectra from 40-210 m/z at a resolution of 1-1.3 amu using less than 3 W of power. The µMS mass spectra are electron impact (EI) NIST-compatible which allows the use of existing libraries for chemical identification. Several variants of the µMS were demonstrated for a broad range (>200) of volatile and semi-volatile organic compounds in prior government-sponsored efforts.

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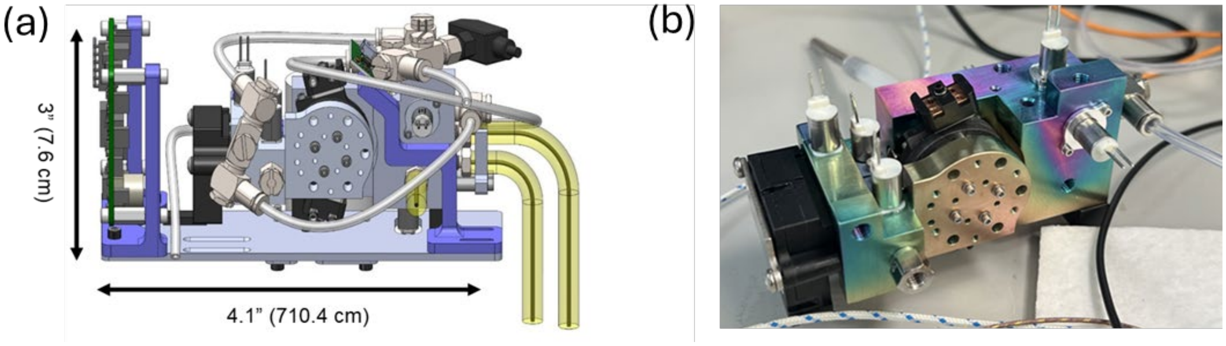

Figure 1. (a) A screenshot of the CAD model of the MAC 1.0 subsystem showing the valve manifold and the latching valves used to enable a versatile set of pneumatics required for MAC sampling, desorption and cleaning. (b) A photo of the first prototype MAC-1.0 showing the GLAC (*built in black PEEK*) sandwiched between two valve blocks. The valve blocks were machined in aluminum and all internal surfaces exposed to the chemical stream were passivated using SilcoNert®2000 to minimize chemical memory effects.

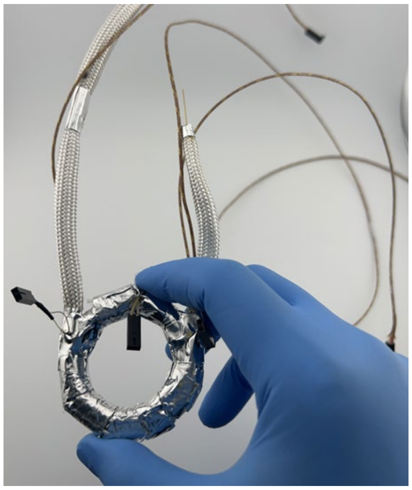

Figure 2. A prototype of the 10-m LTM-GC that delivers high-speed gas chromatography needed to separate individual constituent chemicals from a complex chemical mixture before delivering the gas bolus to the µMS for chemical detection.

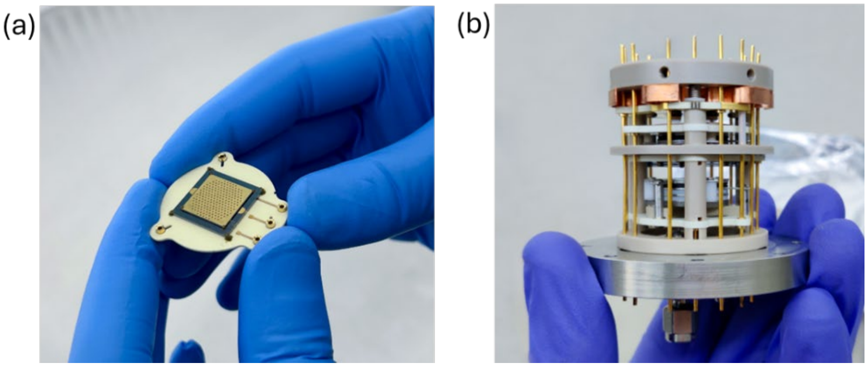

Figure 3. (a) A µ-ion trap array installed on a Roger-4350 PCB substrate for vacuum integration. (b) A fully integrated µMS mounted onto a custom miniature vacuum flange before being integrated with vacuum pumps for pump down and system testing.

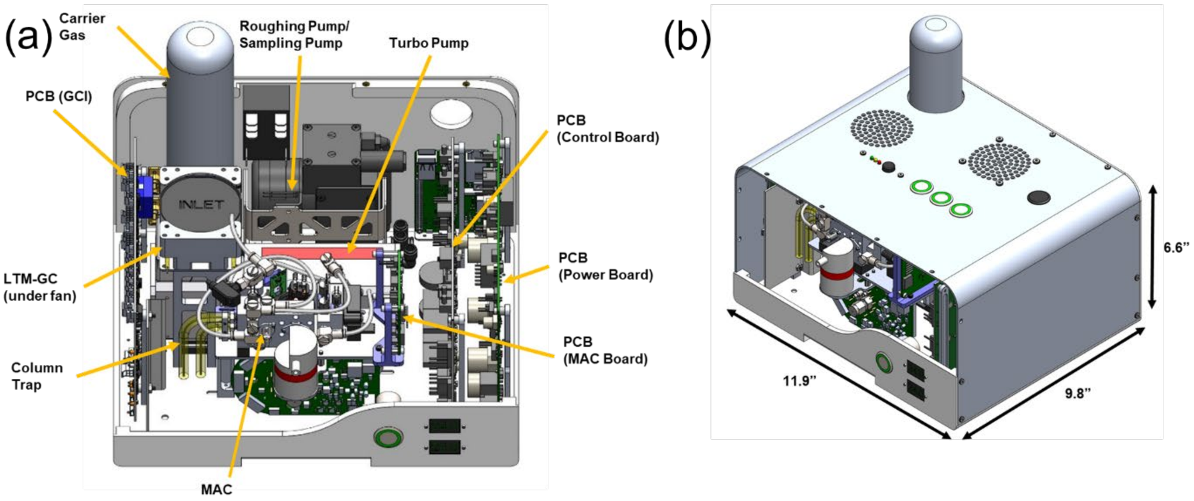

Figure 4. CAD model of the fully integrated SPECTRAL 1.0 platform (7.5 kg, 12 L) comprising of all three subsystems.

2. METHODOLOGY

To evaluate SPECTRAL 1.0, a versatile flow-through aerosol generation testbed was developed, as shown in **Figure 5**. Using a CH Technologies Blaustein Atomizer (BLAM) and a Sono-Tek Atomizer (Sono-Tek), aerosols in a size range between 10 nm and 7 µm can be reliably generated (**Figure 6**). The aerosols are characterized using TSI's Aerodynamic Particle Sizer (APS 3321) and TSI's Scanning Mobility Particle Sizer (SMPS 3938) which measure fine and ultrafine particulates, respectively.

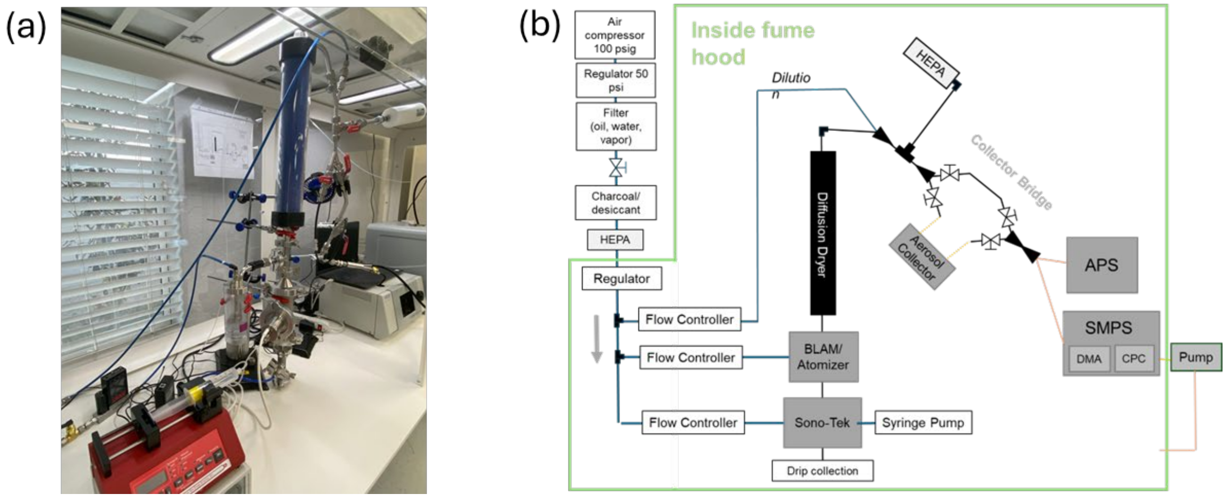

Figure 5. (a) Flow-Through Aerosol Generation and Characterization Testbed. (b) Schematics of the fluidics of the Aerosol Testbed.

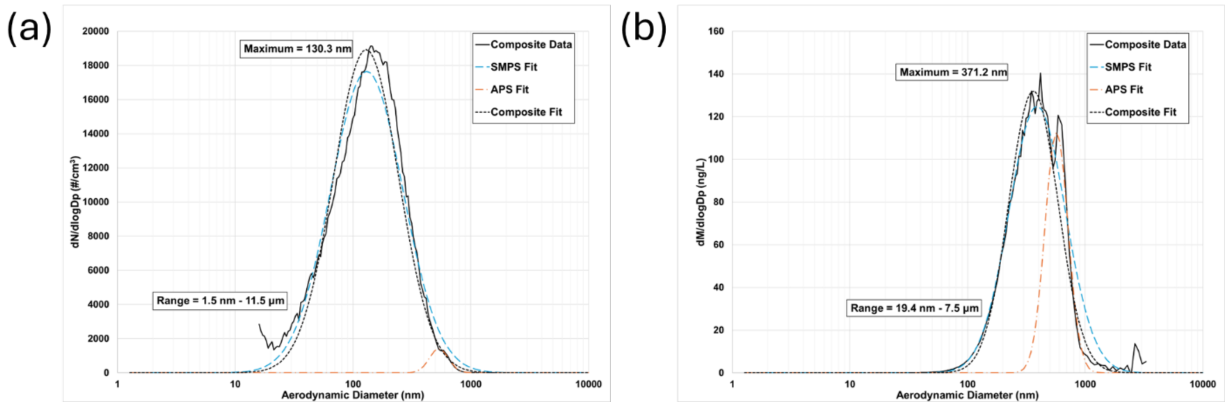

Figure 6. Size distribution of caffeine particles. (a) Particle count (dN/dlogDp) over particle diameter; (b) Mass distribution (dM/dlogDp) over diameter. Particles were generated by a combination of Sono-Tek and BLAM aerosolizers and characterized with merged data from the APS and SMPS particle sizers. The caffeine particle distribution is mostly in the ultrafine range (measured by the SMPS instrument), but the larger particles have much more mass, which is indicated by the APS Fit differences between (a) and (b).

The aerosol testbed includes a collector bridge that enables effective determination of collection efficiencies as a function of particle size. To establish the ground truth, the collection and the desorption efficiencies for different aerosol collectors and a variety of aerosols are determined by collecting aerosol samples on commercial sorbent tubes (Tenax® TA) that are subsequently analyzed on a Shimadzu QP2020NXNC GC-MS coupled with a Shimadzu TD-30 Thermal Desorption System.

Collecting aerosols directly from the testbed provides a reliable baseline for comparison. Collecting the aerosols after passing through the collector allows for the calculation of the collection efficiency while thermally desorbing collected material onto the sorbent tubes enables precise calculation of the desorption efficiency.

3. DATA

Using the Aerosol Testbed, individual subsystems and the integrated system are challenged with a uniform aerosol generation of different aerosolized compound to measure both the collection and desorption efficiencies of the GLAC from the use of particle counters and TD-GC-MS methods. For example, GLAC's collection efficiency based on TD-GC-MS measurements is 89% and the desorption efficiency is 80% resulting in an overall efficiency of 72% for caffeine (CAS No. 58-08-2).

Aerosols in the ultrafine range, such as tributyl phosphate (CAS No. 126-73-8) (**Figure 7**) were shown to have an efficient collection on the GLAC, based on the proximity to the maxima of the dashed black trace to that of the generated aerosol (blue trace). The APS and SMPS particulate data show an 81% and 85% collection efficiency by mass, respectively. A minor reconfiguration of the aerosol test bed by replacing the silica desiccant of the diffusion dryer with activated charcoal, permits the generation of aerosols from non-aqueous solvents, such as methyl undecanoate (CAS No. 1731-86-8) in methanol (**Figure 8**) where the MAC subsystem containing the GLAC where the APS and SMPS show a 69% and 85% collection efficiency by mass, respectively. Caffeine is at the upper end of the particle size distribution of the aerosols and for caffeine, the GLAC has a 96% and 95% collection efficiency by mass on the APS and SMPS, respectively (**Figure 9**).

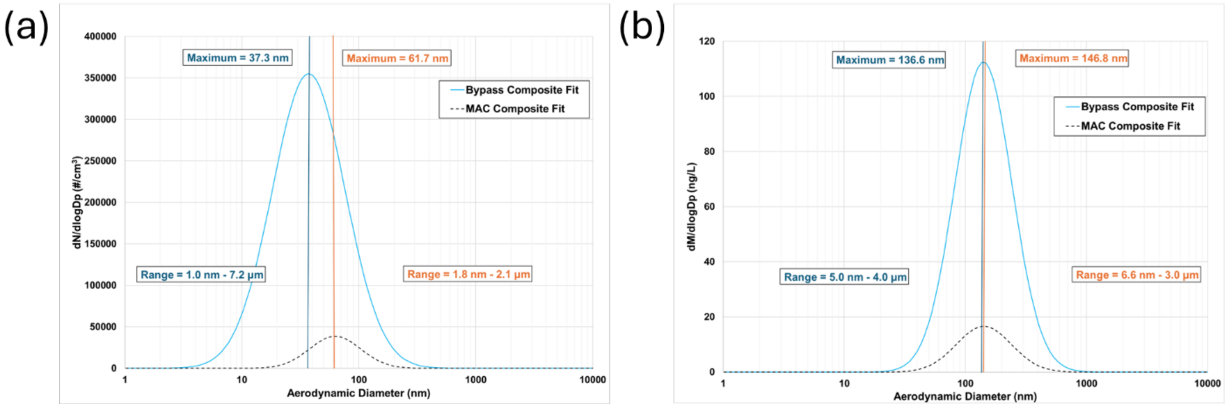

Figure 7. GLAC has an 81% and 85% collection efficiency by mass, for tributyl phosphate aerosols by the APS and SMPS, respectively. The graph shows merged APS/SMPS data of the particle size distribution of the aerosol (*solid, blue trace*) and the aerosol that passed through the GLAC (*dashed, black trace*) by particulate counts (a) and particulate mass (b).

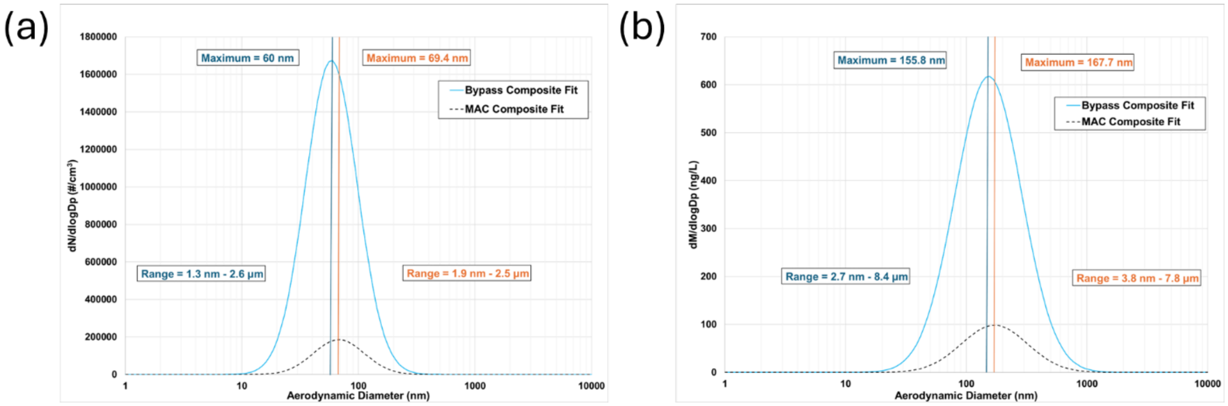

Figure 8. GLAC has a 69% and 85% collection efficiency of methyl undecanoate aerosols generated from a methanol solution. The plots show the particle size distribution of the aerosol (*solid, blue trace*) and the aerosol that passed through (*dashed, black trace*) the GLAC by particulate counts (a) and particulate mass (b).

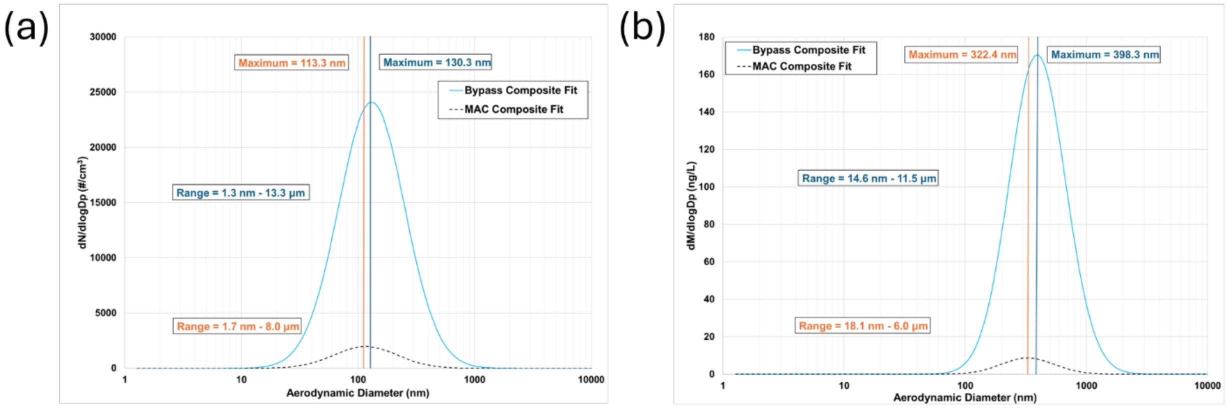

Figure 9. Caffeine forms aerosols that are at the upper end of the aerosol size distributions, and the GLAC has a 96% and 95% collection efficiency by mass of caffeine as measured by the APS and SMPS, respectively. The plots show the particle size distribution of the aerosol (*solid, blue trace*) and the aerosol that passed through (*dashed, black trace*) the GLAC by particulate counts (a) and particulate mass (b).

The SPECTRAL system can detect a wide variety of organic aerosols, currently up to a volatility that translates to a gas chromatographic retention index of 2400. The low internal dead volume (0.3 mL) of the GLAC in combination with short paths inside the heated MAC enables rapid thermal desorption of collected aerosols onto the LTM-GC for optimal chromatography (**Figure 10**), while the µMS delivers NIST-compatible EI-MS mass spectral signatures (**Figure 11**) and enables high-confidence chemical identification.

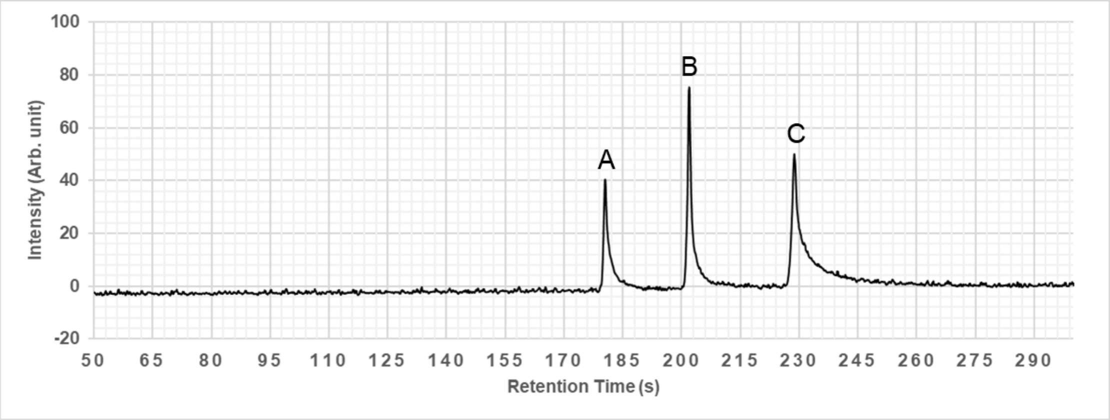

Figure 10. A partial ion chromatogram showing response of the GC-MS stage of the SPECTRAL 1.0 system, connected to a Shimadzu liquid injector, for 20 ng each (A) 4,6-Dinitro-m-xylene; CAS No. 616-72-8; (B) Phenanthrene; CAS No. 85-01-8, and (C) Eicosane; CAS No. 112-95-8. [GC method: Shimadzu injector 250 ºC, 50 cm hydroguard 0.320 mm ID, oven 250 ºC isotherm, split ratio 5, carrier gas: helium 50 kPa (7.25 psi) constant pressure, transfer line in air and column connector heated to 220 ºC, MXT-5 (10 m x 0.25mm x 0.25 µm), µMS vacuum chamber 61 ºC, vacuum feedthrough 160 ºC.]

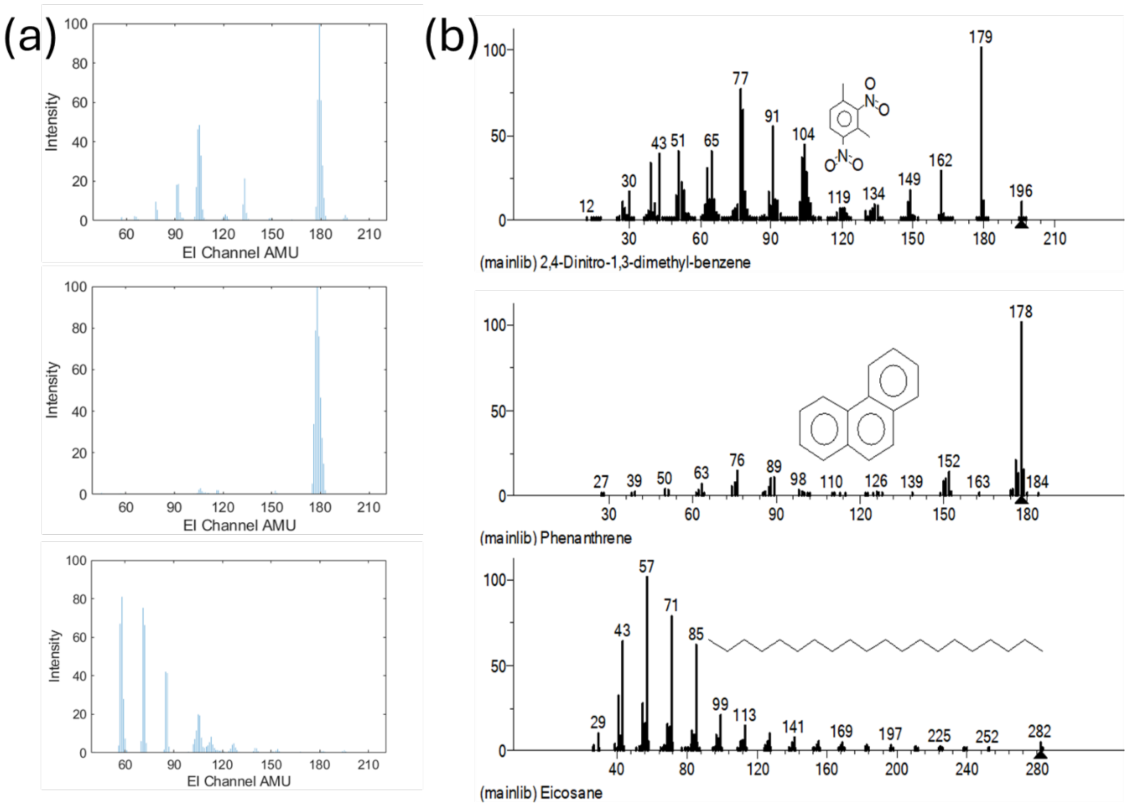

Figure 11. (a) Mass spectra generated by the µMS as shown in blue. (b) NIST mass spectral signatures [3] in black shows close the similarity between the two spectra for all the three chemical examples. Such similarities have been observed for most chemicals that the SPECTRAL µMS has been evaluated for.

4. RESULTS

The tests conducted on SPECTRAL 1.0 thus far demonstrate that SPECTRAL development is projected to address most of the PICARD program metrics. Building up on the lessons learned in SPECTRAL 1.0 testing, Detect-ION is currently advancing to SPECTRAL 2.0 design optimization with emphasis on a lower energy consumption MAC subsystem and higher temperature capability of gas interfaces to minimize cold spots across the three stages of the SPECTRAL system. In addition, Detect-ION has collected sensor responses for a 75 chemical list and is currently developing an aerosol threat library and automated identification algorithm based on GC retention index and mass spectra.

Aerosol measurement tests of the GLAC across aerosols with varying chemical and physical properties demonstrate a high collection efficiency, including that of ultrafine aerosols, likely due to the high surface area and circuitous path of the particles through the micro-pores of the GLAC plates (**Figures 7-9**). The integrated GLAC can also efficiently desorb collected aerosols into the SPECTRAL GC-µMS aided by very low thermal mass, ultra-low internal dead volume and efficient thermal isolation from the rest of the MAC assembly.

5. CONCLUSIONS

SPECTRAL's combined efficiency across the collection, desorption, and detection stages allows < 1 ng of LOD with a sampling duration as short as 2 min. The overall system latency for this sampling method is < 15 min, which includes embedded smart cleaning. Additionally, the mass spectral output of the SPECTRAL µMS is compatible with the NIST mass spectral library, thereby facilitating high-confidence chemical identification. Therefore, SPECTRAL can be applied to collect trace-level chemical threat signatures in a dynamic threat environment to meet IARPA's key mission requirements.

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