Analytical Methods

Accepted Manuscript

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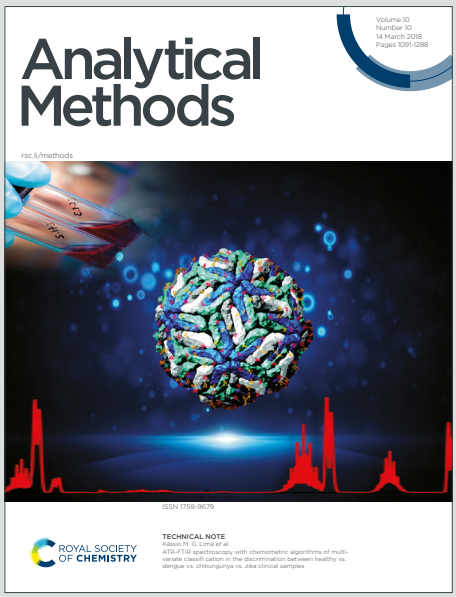

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DOI: 10.1039/D6AY00269B

Pheromone measurement using secondary electrospray ionization and portable membrane inlet mass spectrometry.

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Short Title: In situ pheromone monitoring.

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ABSTRACT

A secondary electrospray ionization high-resolution mass spectrometry (SESI-HRMS) system and a portable membrane inlet mass spectrometer (MIMS) have been used for the first time to detect and monitor insect sex pheromones, both qualitatively and quantitatively. Monitoring insect sex pheromones in the field is important because mating disruption works only when pheromone concentrations remain sufficiently high and spatially uniform. Measuring pheromone levels enables quick identification of coverage gaps, helping prevent pest resurgence and optimizing reapplication to reduce unnecessary costs and inputs. Compounds

tested include: (Z)-11-Hexadecenal, (Z)-11-Hexadecen-1-yl acetate, and (Z)-11-Hexadecen-1-ol. Gas-phase experiments were performed at concentrations ranging from low ppt to low ppm. For both methods, the results obtained showed excellent linearity within the examined concentration range, ppt limits of detection (LOD) for the SESI-HRMS system, and ppb limits of detection for the MIMS, low limits of quantification (LOQ) for both methods, and fast response (rise and fall) times. In addition, SESI-HRMS was tested for the direct analysis of real-life *Plutella xylostella* VOC samples, detecting the three key female pheromone components in female, but not male, headspace samples.

Keywords: *SESI-HRMS, portable MIMS, pheromones, agriculture*

1. INTRODUCTION

World food security depends largely on agriculture to supply calories and essential nutrients to a rapidly growing population [1]. However, agricultural production is increasingly constrained by a wide range of biotic and abiotic stressors, with insect pests remaining a persistent and significant threat to crop yield and quality. Herbivorous insects reduce yields, compromise quality, and increase post-harvest losses across nearly all major cropping systems, resulting in substantial economic damage each year [2–4].

Conventional reliance on broad-spectrum chemical insecticides has contributed to recurrent resistance in pest populations, harmed non-target organisms, including key pollinators and natural enemies, and raised serious environmental and human health concerns [5–7]. In response, integrated pest management (IPM) seeks sustainable, ecologically grounded alternatives. Among these, semiochemicals, particularly sex pheromones used for intraspecific communication, offer an environmentally sound complement to, or substitute for, conventional control measures. Pheromone-based techniques, especially mating disruption, exploit pest behavior to achieve species-specific control with minimal ecological disturbance.

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Mating disruption, which involves the release of synthetic sex pheromones to interfere with mate-finding, has become one of the most successful semiochemical-based strategies within IPM. By overwhelming male sensory systems or masking the chemical cues emitted by females, mating disruption reduces successful courtship and limits subsequent population growth. Its specificity, driven by the precise chemical composition of pheromone blends, enables targeted suppression of key pests while minimizing impacts on non-target organisms and natural enemies [8].

The effectiveness of mating disruption depends on maintaining a continuous and spatially uniform presence of species-specific pheromone across the treated area throughout the crop cycle. In practice, release rates vary with temperature, dispenser aging, wind conditions, crop canopy structure, and dispenser deployment density. If pheromone concentrations fall below efficient thresholds, localized mating may occur, and populations can rebound unless supplementary interventions, including additional pheromone applications, are implemented in time. Maintaining sufficient airborne pheromone concentrations is a key challenge, one that has driven innovations in application technologies, such as the use of unmanned aerial vehicles for precise and efficient dispenser deployment, particularly in tall or densely planted crops [9]. Field monitoring of pheromone levels is therefore essential to sustain disruption efficacy. Moreover, because pheromones represent a significant input cost, proactive monitoring of in-field concentrations can support more precise management, reducing unnecessary applications and associated expenses. As mating disruption becomes more widely adopted, there is a growing need for a portable system capable of in situ quantification of pheromone levels.

A field-deployable monitoring device would offer several advantages: real-time verification of pheromone coverage to detect and correct gaps early; optimization of dispenser placement and re-application schedules; evidence-based calibration of release technologies under real environmental conditions; and support for predictive models linking environmental variables

to pheromone availability. Accurate in situ measurements would also help prevent excessive pheromone inputs, reduce programme costs, and promote more sustainable and resource-efficient IPM.

This paper explores how analytical technologies can be integrated into modern agricultural systems to monitor pheromone levels at multiple field locations, verifying their presence throughout the growing season. We argue that improving the practicality and accessibility of pheromone monitoring is critical to strengthening the resilience and sustainability of agricultural production amid increasing pest pressure and ongoing regulatory shifts away from conventional pesticides. We investigated two well-established mass spectrometry techniques for volatilomics: a benchtop secondary electrospray ionization coupled to high-resolution mass spectrometry (SESI-HRMS) [10-19] and a portable membrane inlet mass spectrometry (MIMS) system [20-26] for real-time detection and monitoring. SESI is a sensitive, non-invasive ambient ionization technique that enables direct analysis of volatile gas-phase compounds with little or no sample preparation, in real time. In SESI-MS, neutral analytes interact with charged electrospray droplets and ionize before MS detection. When coupled with HRMS, SESI-HRMS provides high sensitivity, accurate mass information, and robust compound confirmation. Because of its benchtop configuration, SESI-HRMS is well-suited for analyzing samples collected in sampling bags, gas canisters, or thermal desorption tubes and subsequently transported from the field to the laboratory. In contrast, MIMS uses a semi-permeable membrane to transfer volatile analytes from the gas phase into the mass spectrometer's vacuum region, enabling rapid measurements with minimal sample handling. Portable MIMS systems can be readily transported to the field and are therefore attractive for on-site pheromone monitoring. Compared with established approaches such as GC-MS, trap-based laboratory analysis, or nanosensors, SESI-HRMS and MIMS offer real-time or near-real-time monitoring capabilities. SESI-HRMS is used as a high-specificity reference for compound

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confirmation and performance benchmarking, while portable MIMS is evaluated as the candidate field-deployable monitoring system. Both systems exhibited low detection limits (LOD) and limits of quantification (LOQ) (ppt/ppb levels), and fast chemical analysis (within a few seconds). Even though gas nanosensors are promising and efficient tools for pheromone sensing in pest management [27], to our knowledge, this study is the first to demonstrate gas-phase detection and monitoring of insect sex pheromones at concentrations ranging from low ppt to low ppm using high-resolution MS and a portable MIMS system.

2. EXPERIMENTAL SECTION

2.1 Motivation. This work focuses on the qualitative detection and quantification of insect sex pheromones using a benchtop high-resolution MS and a lightweight portable MS system (11 kg). Target compounds that were selected to be investigated in this work and their relevant physical properties are presented in Table 1.

2.2 Reagents. Analytical standard solutions of (Z)-11-Hexadecenal, (Z)-11-Hexadecen-1-yl acetate, and (Z)-11-Hexadecen-1-ol were purchased from Bedoukian Research Inc., Danbury, CT 06810, USA. All chemicals were provided in liquid form and stored in the fridge at 4 °C until their use. The electrospray solution was prepared from Optima LC-MS grade water purchased from Fisher Scientific, and formic acid (99.5 % purity) was obtained from VWR Chemicals.

Table 1. Summary of the pheromones analyzed by the SESI-HRMS and the MIMS system.

Compound	Formula	CAS Number	Molecular weight	Vapor pressure (kPa) at 25°C
(Z)-11-Hexadecenal	$C_{16}H_{30}O$	53939-28-9	238.4088	6.4×10^{-5}

(Z)-11-Hexadecen-1-yl acetate	$C_{18}H_{34}O_2$	34010-21-4	282.4614	5.20×10^{-5}
(Z)-11-Hexadecen-1-ol	$C_{16}H_{32}O$	56683-54-6	240.4247	7.87×10^{-6}

2.3 Experimental Setup.

SESI-HRMS system: On-line analysis of the generated gas standards was performed using a commercial SESI source (Fossil Ion Tech, Spain) coupled to a Q Exactive Plus Orbitrap mass spectrometer (Thermo Fisher, Germany). Gas samples were introduced via a custom-made adaptor attached to the SESI sampling line, which was continuously heated to 130 °C, while the ionization chamber was maintained at 90 °C. The electrospray solution was 0.1% aqueous formic acid delivered through a nano-electrospray capillary (20 µm i.d., 365 µm o.d.; Fossil Ion Tech, Spain) under 0.8 bar overpressure; charged droplets interacted with the gas-phase sample in the ionization chamber to enable charge transfer prior to MS analysis. Sheath and auxiliary gases were set to 15 psi and 2 a.u., respectively; the spray voltage was +3.5 kV; and the inlet capillary temperature was 250 °C. The Orbitrap was operated with an AGC target of 10^6, a maximum injection time of 500 ms, an m/z range of 50–500, and a resolving power of 140,000.

MIMS system: Experiments were conducted using a portable membrane inlet quadrupole mass spectrometer (MIMS-QMS; Q-Technologies Ltd., Liverpool, UK). The system comprised a membrane-inlet sampling probe that enables gas-phase analytes to permeate the membrane into the vacuum chamber for ionization and analysis, a triple-filter QMS, a vacuum system to maintain stable low pressure while providing sufficient pumping of permeated molecules, and a laptop for data acquisition and interpretation. Spectra were acquired across the full mass range with 10 points per unit mass, averaged over 20 scans per measurement, and then compared against reference spectra using the NIST Chemistry WebBook.

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The triple-filter QMS included an electron impact (EI) ion source, a quadrupole mass analyzer, and a detector. The EI source employed a twin Thoria filament assembly operated at ~1.68 mA electron emission current. The analyzer consisted of a 25 mm pre-filter, a 125 mm main filter, and a 25 mm post-filter (6.3 mm rod diameter), providing unit mass resolution over m/z 1-300 (peak-to-valley ratio 10%) with a sensitivity of 1×10^{-4} A/mbar. Detection was performed using a Channeltron electron multiplier. The QMS was housed in a stainless-steel chamber evacuated by a TURBOLAB 80 system (Oerlikon Leybold Vacuum Ltd., UK) comprising an oil-free DIVAC 0.8 T diaphragm pump (to ~1×10^{-2} Torr) and a TURBOVAC SL 80 H turbomolecular pump (base pressure ~7.5×10^{-8} Torr), with pressure monitored by a digital Pirani/cold-cathode gauge (MRT 100; Pfeiffer Vacuum Ltd., UK). During testing with the portable MIMS system, a flat polydimethylsiloxane (PDMS) membrane probe connected to the vacuum valve was used to sample the prepared standard gases. The sampling system consisted of 10 cm of stainless-steel tubing and a PDMS membrane sheet supported at one end by a 6.35 mm Swagelok stainless-steel vacuum fitting union. The non-sterile PDMS sheeting (Technical Products, Inc., Georgia, USA) was 0.12 mm thick with a 33.2 mm² sampling area, and measurements were conducted at ambient temperature without any analyte enrichment (e.g., carrier gas).

2.4 Sample Preparation. The linearity of the SESI-HRMS and MIMS systems during online monitoring of the target VOCs was assessed using gas standards generated with an in-house vapor generator [11, 28]. The vapor generator operates by controlled evaporation of a liquid analyte (concentrated or diluted in a solvent at a standard concentration), followed by its diffusion in a carrier gas stream (in our case, medical air, Linde Gas Schweiz, CH). The generator is an automated, modular system comprising (a) a mixing chamber, (b) three individually temperature-controlled evaporation chambers into which liquid analytes are introduced via a septum-sealed side injection port, (c) four mass flow controllers, and (d) an

automation platform controlled through LabVIEW software, enabling production of single- or multi-component gas standards in either periodic or dynamic modes.

The mixing and evaporation chambers were manufactured from grade 303 stainless steel. The cylindrical mixing chamber (80 mm length, 20 mm i.d., 25 mm o.d.) features 6.35 mm Swagelok stainless-steel fitting unions as inlet and outlet ports and three 3.18 mm Swagelok fittings on its periphery for connection to up to three evaporation chambers (single- or multi-analyte configurations). Each evaporation chamber is cylindrical (12 mm i.d., 20 mm internal length, 30 mm o.d.) and includes a 3.18 mm Swagelok fitting union on the top, a peripheral Swagelok union tee with one port connected to a mass flow controller and the other sealed with a thermoresistant septum (Sigma Aldrich) for liquid analyte introduction, and a heating-cartridge inlet on the opposite side (RS Components International). The heater is regulated by a temperature controller with a type K sensor, with the temperature settable from 0 to 150 °C in 0.1 °C increments and monitored continuously by a thermocouple. During measurements, all evaporation chambers were maintained at 20 °C, and analytes were loaded using a Hamilton syringe. Carrier-gas flows through all chambers were controlled by GE50A mass flow controllers (MKS Instruments UK Ltd., United Kingdom), with the controller connected to the mixing chamber operating over 0.5–10 L/min and those connected to the evaporation chambers over 0.1–10 mL/min; the controllers were driven by an automation platform running custom LabVIEW software to enable simultaneous control and programmed sequences of time steps and gas flows, and all controllers were calibrated for N_2 with the inlet pressure held constant at 1.5 bar.

Liquid stock solutions of the tested pheromones were prepared, and for each pheromone, 40 µL of its respective stock solution was introduced into a pre-purged chamber. Three measurements were then performed using different flow programs shown previously by our group [11]. Specifically, an increasing (1, 2, 4, 6, 8, and 10 mL/min), random 1 (2, 6, 8, 10, 1,

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4 mL/min), and random 2 (10, 6, 4, 8, 1, 2 mL/min) N_2 flow programs were applied through the evaporation chamber, while the N_2 flow through the mixing chamber remained constant at 10 L/min. Each step lasted 120 s, whereas the initial and final steps, representing the background N_2 flow through the mixing chamber, were each maintained for 360 s. The final gas-phase concentration of each pheromone was calculated using the ideal gas law.

2.5 Headspace VOC sampling. A laboratory colony of *Plutella xylostella*, originating from wild populations, was established at the Chemical Ecology and Natural Products Laboratory of NCSR "Demokritos", Athens, Greece. Larvae were reared on fresh cabbage leaves. All life stages were kept at a 16:8 (L:D) photoperiod, at 25 ± 1 °C and 60 ± 5% relative humidity. Insects were sexed at the pupal stage and kept separate.

Experiments were conducted in a dark room under low red-light illumination (3 -5 lux), sufficient to allow handling while minimizing visual disturbance to the insects. Lab conditions were maintained at 25 ± 1 °C and 60 ± 5% relative humidity throughout the sampling period. Two hours prior to testing, moths were transferred to two identical cylindrical chambers (200mL) covered with perforated lids, one containing 10 adult, two-day-old, virgin *Plutella xylostella* females and the other containing 10 adult males and left in the same conditions to acclimate. Using separate chambers enabled sex-specific characterization of the headspace volatile profiles. Volatile organic compound sampling was carried out using a Markes International ACTI-VOC low-flow sampling pump connected sequentially to the lid of each chamber via 30 cm of inert Teflon tubing. Headspace air was drawn from each chamber at a constant flow rate of 100 mL min^{-1}. The pump outlet was connected to a 1 L Supel™-Inert Multi-Layer Foil gas sampling bag to collect the gas phase from each chamber for subsequent analysis. To account for background volatile compounds in the experimental lab environment, a blank sample was collected from ambient air in the dark room under the same sampling

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conditions. Samples were analysed using SESI-HRMS. Figure 1 shows a schematic representation of the experimental setup.

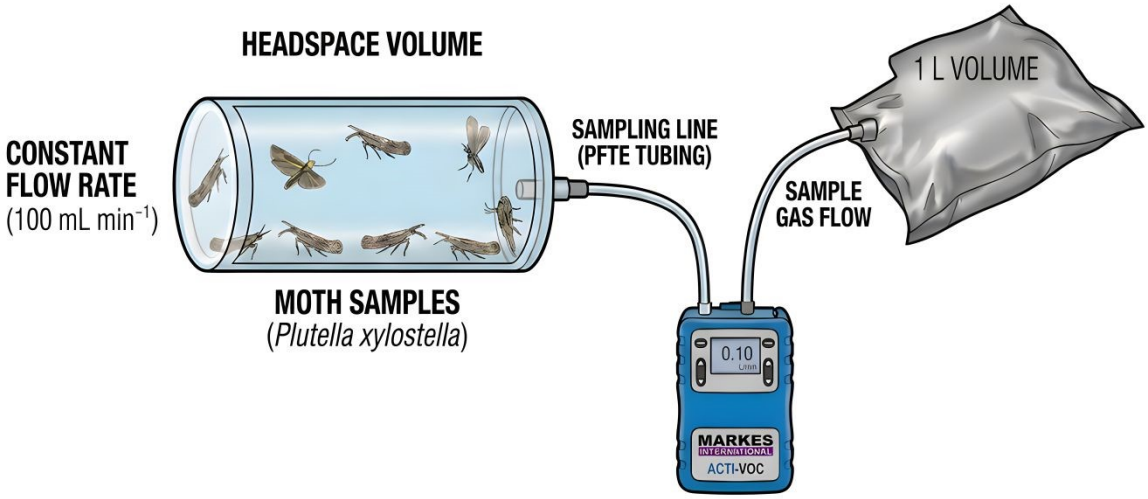

Figure 1. Schematic representation of the experimental setup.

3. RESULTS AND DISCUSSION

3.1 Pheromone Experiments using SESI-HRMS. This experimental series was done to investigate the mass spectrometric detection and monitoring of insect pheromones in the gaseous phase using a SESI-HRMS and a portable MIMS system. Representative SESI-HRMS mass spectra for the pheromones investigated, corresponding to 100 ppb, are presented in Figure 2. Table 2 lists the theoretical and measured m/z values for the positive ion mode, along with the calculated mass error in ppm. Mass error was determined by subtracting the theoretical exact mass from the measured mass, and the result was expressed in parts per million (ppm) to provide a standardized measure of mass accuracy.

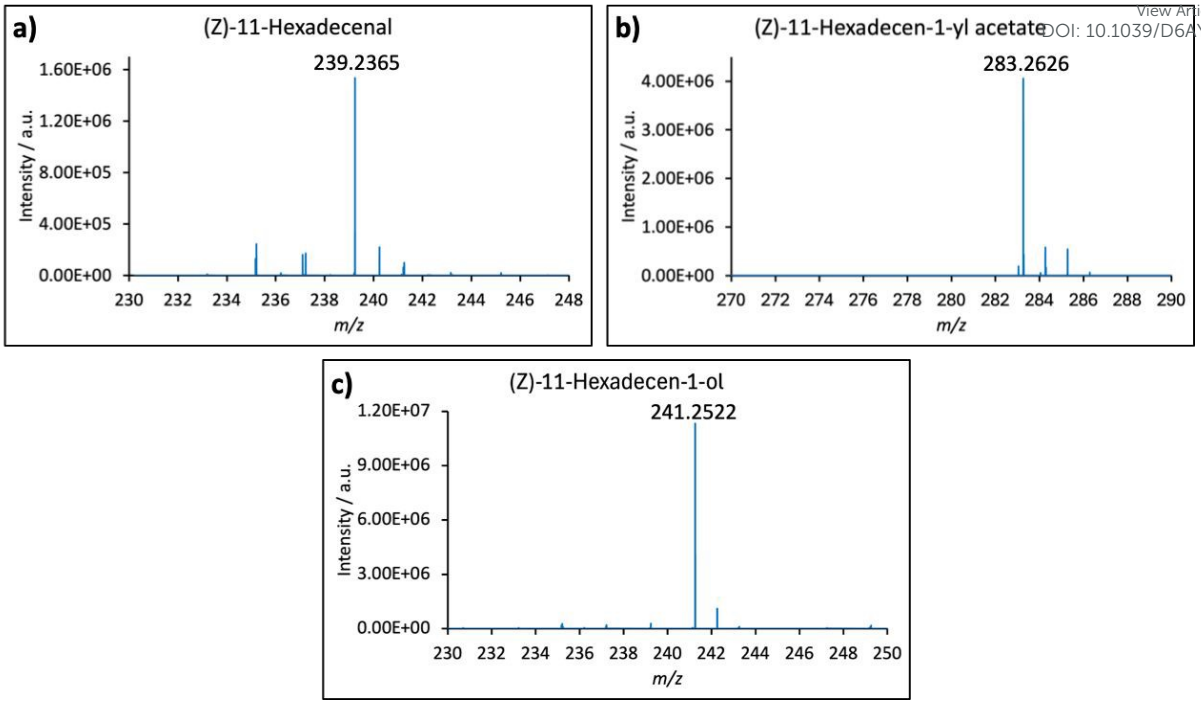

Figure 2. Representative experimental mass spectra at 100 ppb for a) (Z)-11-Hexadecenal, b) (Z)-11-Hexadecen-1-yl acetate, and c) (Z)-11-Hexadecen-1-ol, acquired with our SESI-HRMS system. The measured *m/z* value of the protonated pheromone is shown in each subfigure.

Table 2. Summary of the theoretical and measured m/z of the pheromones measured in the positive ion mode with a resolution of 140,000.

Compound	Exact m/z $[M+H]^+$	Measured m/z $[M+H]^+$	Mass Error (ppm)
(Z)-11-Hexadecenal	239.2369	239.2365	-1.67
(Z)-11-Hexadecen-1-yl acetate	283.2631	283.2626	-1.77
(Z)-11-Hexadecen-1-ol	241.2525	241.2522	-1.24

Experiments were conducted in triplicate under dry conditions (0% RH) [11]. Gaseous standards were prepared as described in Section 2.4. Gas standards of the selected pheromones

were prepared for online monitoring at the following concentration levels: blank, 0.25 ppb, 0.5 ppb, 1ppb, 10 ppb, 50 ppb, 100 ppb, 250 ppb, 500 ppb, 750 ppb, and 1000 ppb. The signal intensities corresponding to the protonated pheromones were plotted against the gas-phase concentrations and used to generate the calibration curves shown in Figure 3. Calibration curves of our SESI-HRMS system for the target pheromones over the concentration range from 0.25 ppb to 1000 ppb exhibited very good linearity with R^2 values in the range from 0.9995 to 0.9998.

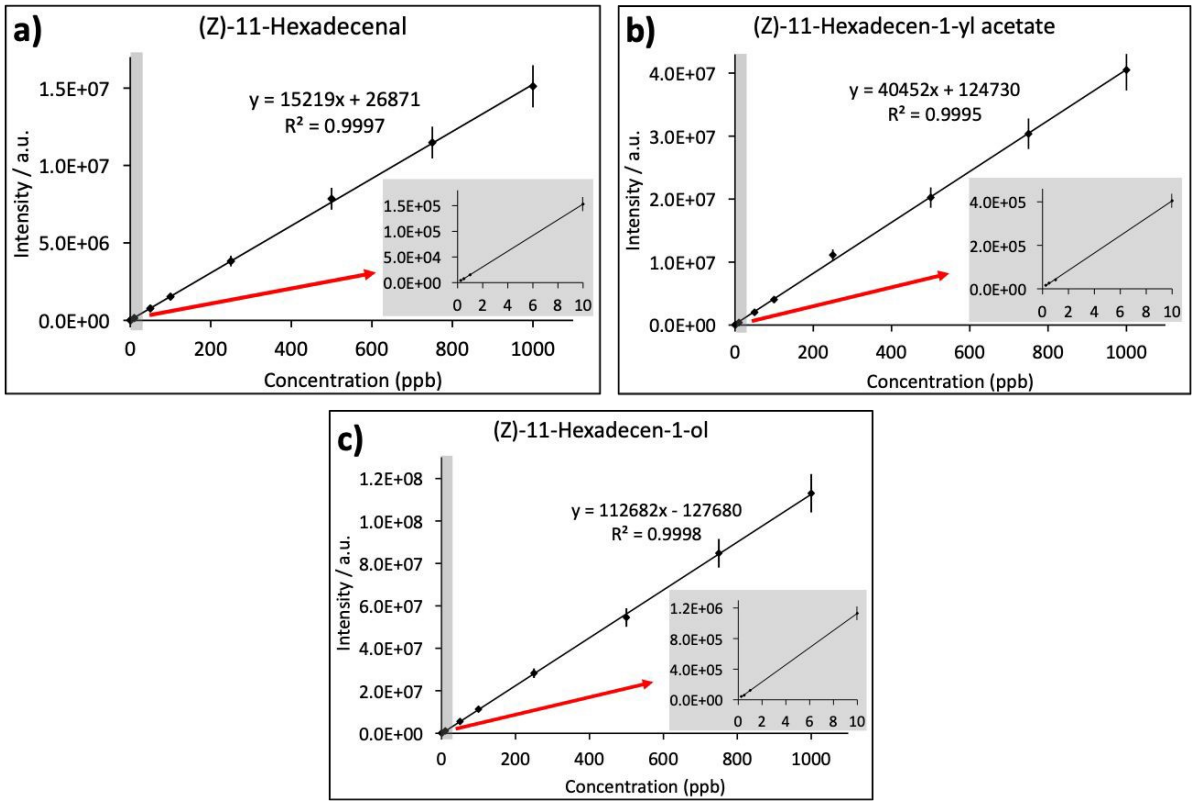

Figure 3. Calibration curves for a) (Z)-11-Hexadecenal, b) (Z)-11-Hexadecen-1-yl acetate, and c) (Z)-11-Hexadecen-1-ol, obtained from the SESI-HRMS system. Data points represent the average of three independent experiments, and error bars show the standard error, calculated as 9%. Graph insets provide an expanded view of the 0-10 ppb concentration range.

The performance of the SESI-HRMS system was evaluated using the following analytical criteria: a) linear dynamic range within the examined concentration range, b) LODs, and c)

LOQs under dry conditions. LOQs were approximated by multiplying each LOD by 3.33. Table 3 summarizes the results. Overall, the calculated LODs and LOQs are in the low ppt range.

Table 3. Summary of the analytical characteristics (R^2, LOD, LOQ values) obtained for the examined pheromones in the positive ion mode using a Q-Exactive Plus Orbitrap.

Compound	R^2	LOD (ppt)	LOQ (ppt)
(Z)-11-Hexadecenal	0.9997	1.90	6.33
(Z)-11-Hexadecen-1-yl acetate	0.9995	4.44	14.79
(Z)-11-Hexadecen-1-ol	0.9998	2.23	7.43

3.2 Pheromone Experiments using MIMS.

To test the MIMS system's response at different concentration levels, gas standards of the selected pheromones were prepared for online monitoring at the following concentrations: blank, 50 ppb, 100 ppb, 250 ppb, 500 ppb, 750 ppb, and 1000 ppb, as described in section 2.4. The experimental mass spectra of the tested pheromones matched the reference spectra from the NIST 23 mass spectral library. Characteristically, the match factor for (Z)-11-Hexadecenal, (Z)-11-Hexadecen-1-yl acetate, and (Z)-11-Hexadecen-1-ol was 98%, 99%, and 98%, respectively. Experiments conducted across three replicates were reproducible, with a relative standard error of 7.8%. Table 4 summarizes the LODs determined from the calibration curves, the rise and fall times, and the linear regression R^2 values for the examined concentration range. LOD estimates were based on signal current values obtained from the 50 ppb samples. They were calculated from the experimentally obtained signal current values for the most abundant mass fragment of each compound and counted as three times the baseline. Rise time is the duration required for the peak signal intensity to reach 90% of its maximum value. Fall

response time is the time required for the membrane and, later, the system to purge and for the signal intensities of the monitored mass fragments to return to baseline.

Table 4. Summary of the PDMS membrane rise and fall times, R^2 values, and LOD for the target compounds that were examined using our MIMS system.

compound name	characteristic mass fragments (*m/z*)	rise time (sec)	fall time (sec)	R^2	LOD (ppb)
(Z)-11-Hexadecenal	55, 69, 67, 81, 83, 238	12	22	0.9915	0.94
(Z)-11-Hexadecen-1-yl acetate	55, 82, 43, 96, 81, 222, 282	27	49	0.9992	2.31
(Z)-11-Hexadecen-1-ol	55, 82, 41, 67, 69, 96, 222	19	28	0.9942	1.02

3.3 Headspace VOC Sampling of *Plutella xylostella*

Figure 4 shows the representative mass spectra obtained from female and male *Plutella xylostella*. The spectra indicate the presence of all three target pheromone compounds ((Z)-11-hexadecenal, (Z)-11-hexadecen-1-yl acetate, and (Z)-11-hexadecen-1-ol) in the female population, whereas these compounds were not detected in males. In addition, the relative abundance ratio of the detected pheromones was consistent with values previously reported in the literature [29, 30].

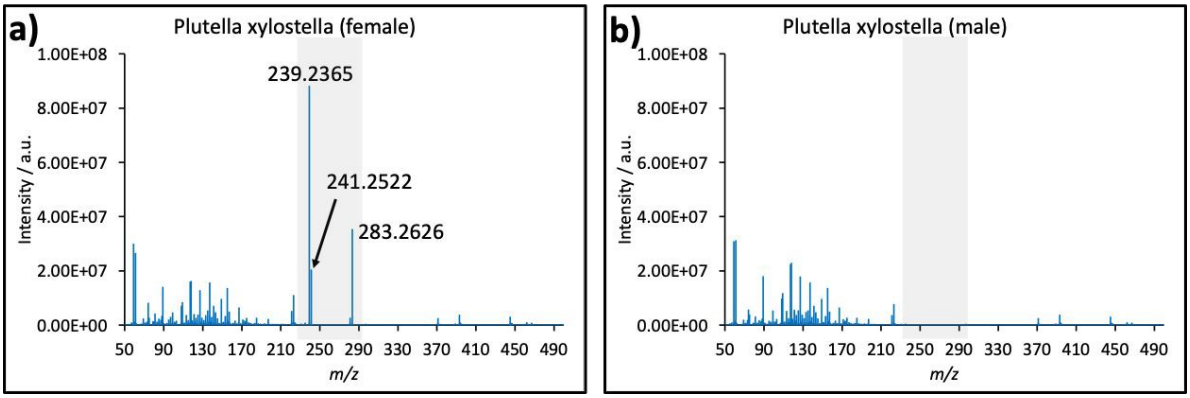

Figure 4. a) Representative positive-ion mode mass spectrum of female *Plutella xylostella* obtained using the SESI-HRMS system; and b) representative positive-ion mode mass spectrum of male *P. xylostella* obtained using the SESI-HRMS system. The three target pheromone components ((Z)-11-hexadecenal, (Z)-11-hexadecen-1-yl acetate, and (Z)-11-hexadecen-1-ol) were detected in the female headspace, whereas they were not detected in the male headspace under the same experimental conditions.

3.4 Field-Realistic Pheromone Concentrations and Deployment Benchmarks

To contextualize our analytical performance under realistic deployment conditions, we converted representative pheromone release rates used in mating-disruption programs into expected in-air concentrations using a fixed, steady-state "single-cell" air-circulation model referenced in European Commission guidance for semiochemicals [31]. Assuming a release rate of 1.5 mg/dispenser/day and 500 dispensers/ha (750 mg/ha/day; 31.25 mg/ha/h), at 1 atm, 25 °C, and a 5 m mixing height over a 1 ha field, the predicted steady-state airborne mass concentration is approximately 20,800 ng/m³. Under the same conditions, this corresponds to volume-based mixing ratios in the low-ppb range for key compounds, including approximately 2.14 ppb for (Z)-11-hexadecenal, 1.80 ppb for (Z)-11-hexadecen-1-yl acetate, and 2.12 ppb for (Z)-11-hexadecen-1-ol. These estimates place expected field-relevant pheromone levels within the quantification regime demonstrated in this work, supporting portable MIMS as a practical on-site screening tool with low-ppb LOD, and rapid response, while SESI-HRMS provides higher sensitivity and specificity for confirmation and detailed characterization. Both systems together are advancing a realistic pathway toward field-deployable pheromone monitoring. While behavioral thresholds vary across species, this study focuses on determining the identification thresholds of our methods. These findings will support our ultimate goal, which is to monitor pheromone levels in mate-disruption-treated fields during an upcoming study.

4. CONCLUSIONS

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We report, for the first time, the use of SESI-HRMS and a portable MIMS system for the qualitative and quantitative analysis of insect sex pheromones, demonstrating that both platforms can deliver rapid, sensitive detection with minimal sample handling. By benchmarking key analytical criteria (LOD/LOQ) for individual pheromone compounds, we show that SESI-HRMS operated under dry conditions achieves ultra-trace performance in the low ppt range, while the portable MIMS achieves robust detection in the low ppb range, performance levels well aligned with many practical monitoring needs. Importantly, both methods provided real-time (SESI-HRMS) and near-real-time (MIMS) responses (on the order of seconds) and required little to no sample pre-treatment.

Beyond sensitivity, the results highlight a complementary relationship between the two technologies. SESI-HRMS offers outstanding trace-level capability and chemical specificity, suitable for detailed characterization and confirmation, whereas the portable MIMS system provides operational flexibility and field-deployability with a favorable speed–sensitivity balance. Taken together, these attributes suggest a practical analytical toolkit that can be adapted to different monitoring contexts, ranging from laboratory-based method development and mechanistic studies to mobile, on-site screening. SESI-HRMS enabled sex-specific headspace VOC profiling of real-life *Plutella xylostella* samples, successfully detecting the three key female pheromone components ((Z)-11-hexadecenal, (Z)-11-hexadecen-1-yl acetate, and (Z)-11-hexadecen-1-ol) in headspace samples, while these compounds were not detected in males under the same experimental conditions.

These findings have direct implications for pheromone research and applied entomology. The ability to detect and monitor pheromone signatures rapidly can accelerate investigations into emission dynamics, pheromone release from dispensers, and temporal variability relevant to insect behavior and mating disruption strategies. Moreover, the demonstrated low-prep, fast-

response workflow points to potential for higher-throughput measurements and for integration into automated or semi-automated monitoring schemes.

Future work will focus on translating this performance into real-world deployment under complex environmental conditions. Key next steps include evaluating matrix effects (humidity, temperature, wind, background volatile organic compounds load/matrix effects), assessing long-term signal stability, and validating selectivity against co-emitted or ambient interferents. Finally, field trials, both near controlled pheromone sources and in operational trapping or mating-disruption settings, will be critical for establishing practical in situ detection limits and defining the most effective roles for SESI-HRMS and portable MIMS within integrated pest monitoring frameworks.

DATA AVAILABILITY STATEMENT

The original data used in this publication are made available in a curated data archive at ETH Zürich (https://www.research-collection. ethz.ch) under the DOI: http://hdl.handle.net/20.500.11850/795918

AUTHOR CONTRIBUTION

SG performed the experiments and analysed the data. SG, DR, and MK interpreted the compiled results. SG prepared the manuscript. All authors contributed to the discussion and revision of the paper.

ACKNOWLEDGEMENT

The research leading to these results has received funding from the NutriExhalomics project (grant agreement No. 15668). The authors gratefully acknowledge Marco Zesiger and Christian

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DOI: 10.1039/D6AY00269B

Marro from the mechanical workshop of the Department of Chemistry and Applied Biosciences for the technical support of this work.

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DATA AVAILABILITY STATEMENT

The original data used in this publication are made available in a curated data archive at ETH Zürich (https://www.research-collection. ethz.ch) under the DOI: http://hdl.handle.net/20.500.11850/795918