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Modular and reconfigurable gas chromatography / differential mobility spectrometry (GC/DMS) package for detection of volatile organic compounds (VOCs)

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Abstract

Due to the versatility of present day microcontroller boards and open source development environments, new analytical chemistry devices can now be built outside of large industry and instead within smaller individual groups. While there are a wide range of commercial devices available for detecting and identifying volatile organic compounds (VOCs), most of these devices use their own proprietary software and complex custom electronics, making modifications or reconfiguration of the systems challenging. The development of microprocessors for general use, such as the Arduino prototyping platform, now enables custom chemical analysis instrumentation. We have created an example system using commercially available parts, centered around on differential mobility spectrometer (DMS) device. The Modular Reconfigurable Gas Chromatography - Differential Mobility Spectrometry package (MR-GC-DMS) has swappable components allowing it to be quickly reconfigured for specific application purposes as well as broad, generic use. The MR-GC-DMS has a custom user-friendly graphical user interface (GUI) and precisely tuned proportional-integral-derivative controller (PID) feedback control system managing individual temperature-sensitive components. Accurate temperature control programmed into the microcontroller greatly increases repeatability and system performance. Together, this open-source platform enables researchers to quickly combine DMS devices in customized configurations for new chemical sensing applications.

Keywords

differential mobility spectrometry (DMS); volatile organic compounds (VOCs); reconfigurable electronics

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INTRODUCTION:

The detection of chemicals in open air environments has been an important for decades, especially rapid detection of toxic chemicals. Historically, animals have sometimes been used as “detectors” given their acute sense of smell for certain chemicals, which can be more suitable to trace detection than the human olfactory system. Presently, canines are successfully used by security forces for a rapid detection of illegal drugs, explosives and other contraband [1–3]. Those animals are also being successfully deployed for disease detection in agriculture settings [4]. While animal detection can be very useful in field applications [5], it also requires tremendous time commitments from human handlers and is not always scalable for widespread, persistent monitoring. As chemical sensors advance, we can now consider hardware/software solutions to routine and ubiquitous monitoring of our environments.

At present, there are a variety of chemical sensing modalities for trace environmental detection, with some commercially available. Quantitative abundance measures are frequently needed for a specific application, or chemical detection is required in the ambient gas phase. One notable category of detection methods for these gas phase detection strategies is Ion Mobility Spectrometry (IMS) [6–8], and these techniques are widely employed today in multiple industries, such as: space exploration [9], the food and beverage industry [10–12], metabolomics for health diagnostics [13, 14] and fuel applications [15]. Used widely since the 1970’s, the technique uses ion mobility in an electric field as the basis of chemical separation and detection. Over the last 60+ years, IMS has evolved into many sub-categories of related configurations that each operate a little differently. In 2011, there was an estimate that ~40% of all IMS devices in existence are available commercially, and it was speculated that a large number of systems are custom built in research facilities for a specific purpose [16]. Easily and rapidly reconfigurable systems can help accelerate the pace of discovery and application development.

One sub-category of IMS is particularly interesting for field use: the differential mobility spectrometer (DMS) [17–21]. This instrument works on the principle of non-linear mobility of ions in the presence of a high strength electric field. VOCs are first ionized and then travel via a carrier gas to a channel with 2 parallel electrodes on the top and bottom. A voltage is applied to the electrodes resulting in an electric field that forms perpendicular to the flow of ions. An RF waveform sets up alternating high- and low-strength electric fields across the drift channel at megahertz frequencies. Ions oscillate between the plates and move towards one due to non-linear ion mobility at high field strengths. The non-linear mobility behavior of ions can be attributed to elastic scattering and collision, resonant charge transfer, and clustering/declustering of ions [22]. A linear DC compensation voltage is superimposed onto the RF waveform, and this allows the instrument to effectively ‘tune’ which ion mobility is allowed to pass through the channel. The abundances of the specified ion(s) are measured by a pair of amperometric detectors at the channel exit. These detectors can be biased to quantify either positively- or negatively-charged ions, which broadens the application range for these devices. DMS instruments have been used in many industries [18, 23, 24].

Frequently, a gas chromatography (GC) column is added before the DMS to allow for pre-separation of ions prior to separation and detection [17]. These GC-DMS devices are versatile in terms of their practical applications, and have used to detect infectious diseases in citrus trees [25, 26]. This same device configuration was also previously used for air quality monitoring within buildings and also at a traffic intersection [27], as well as for biological and chemical agent detection [28–33].

The performance of a DMS device can be affected by humidity, temperature, pressure and the RF waveform used [34–37]. When comparing data sets acquired from these hybrid GC/DMS systems, a slight difference in any of the many variables mentioned above can shift otherwise similar data in time and/or the compensation voltage dimensions. Furthermore, adding a GC column requires additional control parameters. The effect of multiple disturbances can also be cumulative, and lead to more uncertainty in the data due to the propagation of errors within the system. While there are numerical signal processing approaches for aligning different data sets for more accurate comparison [38, 39], it is also possible to reduce data variability by precise control of each module within the GC-DMS instrument system.

The GC-DMS system concept and configuration is not new, and advanced commercial prototypes have been produced (Sionex Corporation). However, the hardware, electronics, control circuitry and user interfaces for those prototypes are quite complex and custom created for industrial scale manufacturing of identical units that does not allow users to easily tailor it. With the availability of commercial off-the-shelf (COTS) microcontrollers and custom low-volume printed circuit board (PCB) manufacturing, we now have the ability to assemble an inexpensive and high-functioning modular GC-DMS platform and a customizable open source Graphical User Interface (GUI) for individual research groups. This paper offers an inside look into the design, construction and test operation requirements of a Modular Reconfigurable - Gas Chromatography - Differential Mobility Spectrometry package (MR-GC-DMS).

MATERIALS AND METHODS:

System Overview:

The MR-GC-DMS system was designed for portable use and rapid reconfiguration and is roughly the size of a large shoe-box (Figure 1; 18 in × 13 in × 8 in). COTS components were chosen for optimal system performance while still being flexible for end-user applications. From end-to-end, the system contains modules and parts to effectively introduce an ambient gas phase chemical sample into the tool, control all of the instrumentation for analysis, and record the results. More detailed information on the design and construction follows, but a brief overall description is provided below.

The purpose of the MR-GC-DMS device is to detect and identify VOCs in trace concentrations. The device uses a pre-concentrator to trap VOCs for a designated sampling time, and then later expel them in a greater concentration for chemical analysis. After evacuating the pre-concentrator, the VOCs are pushed by helium through the GC column and then to the DMS. The GC column is sandwiched at its inlet and outlet between two

guard columns. The guard columns are the same diameter as the GC but shorter in length and lacking a stationary coating on the inside. The output of the GC column, through the second guard column leads to the input of the DMS instrument. The GC column separates the VOCs in time while the DMS separates based on compensation voltage and peak intensity; thus, a three dimensional data plot can be created. After DMS analysis, the received sample is discharged into the surrounding air.

Component Layout:

The interior layout of the system (Figure 2) was designed with several qualities in mind, including: portability, ease of reconfiguration, thermal properties, effective heat dissipation, electrical properties and wiring, optimization of chemical detection performance, and ease of maintenance and repair.

To provide maximum passive heat dissipation, the device is housed in a light-weight locking aluminum case with a handle and a hinged lid. The aluminum frame prevents the system from having localized hotspots from embedded heated components. Additionally, the metal frame dissipates heat faster and allows faster cool down times. While working with the high voltage DMS instrument and sensitive electronics, it is critical to prevent the accumulation of static charge. The metal frame impedes any static charge built up and provides protection to our additional embedded electronics and printed circuit boards inside. Finally, the rigid metal frame gives physical protection to the components housed inside from damage during transport and/or operation.

Inside the metal housing, the components are arranged in three layers stacked on top of each other (Figure 2). On the bottom-most **Layer III** sits the DMS instrument and the power supplies for the entire device. It is anticipated that these components would be serviced with the lowest frequency, thus were placed on the least accessible layer. The middle **Layer II** contains: the GC and guard columns, pre-concentrator trap, 2-way valve and the control circuitry for the device. These components are the most fragile components and thus were placed in the middle layer so as to be shielded by and additional layer from the bottom and from the top. The top **Layer I** contains the sample pump, 3-way valve, 2 mass flow controllers, filter and a fan. These components are likely to be replaced and/or serviced most frequently, and they were placed on the most accessible layer of the device.

The components are packed closely inside the metal frame to reduce the overall size of the device for portability. The unused spaces inside the components are used to channel air for cooling components. The channels are located such that temperature-sensitive components such as wires and electronics are not affected.

Component Consideration and Selection:

We selected COTS components whenever possible for overall system performance and simplicity. The core element of the system is a stand-alone DMS (Sionex Value Added Component, SVAC model; Bedford, MA), and the overall system design was organized around this critical element. This working off-the-shelf detection module we employed was originally developed for either standalone evaluation of DMS performance or as a

component that could be integrated into custom solutions. This particular DMS can later be replaced by another instrument in the future, such as a custom-made differential mobility spectrometer or another commercial module from a different vendor.

The first subsystem designed for the MR-GC-DMS was the gas delivery and sample flow path needed for the overall architecture. We employed two mass flow controllers (MFC) to allow precise control over the flow rate of the gasses under different atmospheric conditions and temperatures. The two MFCs manage the circulation gas flow rate through the DMS and the sample gas flow rate through the trap. One MFC (Cole-Parmer, EW-32907–63) was chosen to regulate the overall nitrogen or air carrier gas flowing through the system. The second MFC (Cole-Parmer, EW-32907–61) was chosen for helium regulation as the carrier gas moving through only the GC column. To avoid hand winding a column and dealing with temperature control issues, we opted to purchase a stand-alone plug-and-play GC column module from a commercial vendor (Part 100–2000LTM, Agilent Technologies, Wilmington, DE), which had the following parameters: DB-XLB phase type, 10 m × 0.25 m × 1.0 μm. Guard columns were included to protect the GC column and DMS from impurities. This generic column provided us with the most robust evaluation platform for our system.

A carbon filter (Parker Balston, 9922-11-000) was added before the MFC inlet to ensure ambient exogenous chemicals would not contaminate the MFC with the impurities in the circulation gas. The filter on the gas line was chosen such that for any given flow rate selected on the MFC, the pressure drop across the filter was negligible. Tubing was sized based on the flow rate required by the components. The DMS flow rate range is 100–500 sccm while the flow rate range through the trap and GC column is 0.5–2.0 sccm. With those numbers in mind, DMS flow tubing was sized at 1/8 inch PTFE (McMaster-Carr, 5239K24) and trap/column tubing was 1/16 inch PTFE (McMaster-Carr, 5239K23) As with the filter, the miniature sample pump (KNF, NMP-015-B) was sized for the flow rate it was able to provide through the pre-concentrator trap. The pump without load is able to provide air at 400 sccm; however, the pump has to work against a tightly packed sorbent material in the pre-concentrator, and during sampling, the flow rate through the pre-concentrator is reduced to ~50 sccm.

The trap itself is one of the few custom manufactured components of the system. Briefly, a hollow stainless steel tube was hand-packed with a series of sorbents, including Carbopack B, C, X and Carboxen 1000 (Sigma Aldrich, St. Louis, MO). Due to the inherent adsorption properties of the four sorbents, we increased the range of VOCs that could be pre-concentrated and thus detected. The sorbents were sandwiched between two stainless steel frits to hold the material in place. The tube was first wrapped with a resistance temperature detector (RTD), followed by a jacket of braided glass wool, then wound with heating element at even intervals and finally layered with a heat-resistant epoxy. This ensures that the trap would evenly rise to a programmed temperature.

We next tackled the thermal properties of the system. A fan (MassCool, FD09025B1M3/4) was added to the top of the aluminum housing for more effective cooling of the pre-concentrator trap. The fan was not originally in our design, but had to be included to avoid temperature coupling between the guard column and the pre-concentrator (warning for

others). A total of five heaters are located in the system. Four of the heaters came pre-installed with the various components, and one was purchased separately. The transfer lines, GC column and pre-concentrator come with heaters pre-installed. The guard column heater (KaMo, ST-429) was sized based on the guard column enclosure dimensions which were: 4 in × 5.5 in × 2 in. To ensure heated components hold a constant temperature, a common proportional-integral-derivative controller (PID) algorithm was implemented on 5 different components: the GC column heater; the pre-concentrator trap heater; the two heated transfer lines; and the heated guard columns.

Power supplies were selected based on the maximum wattage of all the heaters and peripherals combined. The wattage of the valves, MFC, fan, and pump are negligible in comparison to the heat wattage so these components were grouped together and given a rough estimate of their total power consumption. From the maximum wattage used by our system, a 24 V 156 W (Mouser, 709-LRS150F-24) and a 12 V 200 W (Mean Well, LRS-200–12) power supplies were selected. This extreme power use is likely not observed on a regular basis, but we over-designed the system to ensure performance would not fail in the field. To put this in context, this particular common COTS mobile power source the Yeti 400 (GoalZero, B06WVDG9BS) would allow approximately 3–6 h of continuous MR-GC-DMS system usage in the field without recharging.

Open-Source Custom and Programmable Electronics:

The electronics used in the device are a combination of COTS components and custom circuitry required to control the overall system performance. These custom-designed printed circuit boards (PCBs) are a critical part in making the system function in the desired manner, and we are making their design available through an open source repository (https://github.com/BioMEMS). Briefly, our circuit boards were designed in EAGLE (version 7.0), and were manufactured by Oshpark. In addition, control programming code and the software/firmware required for this system are also in this repository.

Two custom PCB boards were designed for this system: a serial peripheral interface (SPI) board for communication (Supplemental Information 1); and the metal-oxide-semiconductor field-effect transistor (MOSFET) board for supplying a variable amount of power to the powered components (Supplemental Information 2). These boards reduced the amount of wiring required for the system. Two additional COTS components are the Trinket Pro (Adafruit, ID: 2010) and the Arduino Due (Arduino, A000062). These were chosen for their fast clock speed (84MHz for the Due and 12MHz for the Trinket) and the large number of IO ports (54 ports for the Due and 18 ports for the Trinket).

Control Software and Graphical User Interface (GUI):

Software modules were written in both high level (Python version 3.6) and low level (C/C++ using Arduino IDE version 1.0.6) programing languages to control the overall system performance and operation. Low level programming language was used for: reading data from thermocouples (McMaster-Carr, 6441T672) placed at the pre-concentrator, transfer lines and guard column locations; the RTD (built into the COTS GC column); and, for

having pulse-width modulation (PWM) control over the previously identified heaters and pumps.

Inside the device, the Arduino Due acts as the master and the Trinket as a slave device. The Trinket constantly scans the thermocouples and RTDs at a predefined 4Hz frequency for temperature readings. The Due then polls the Trinket for the updated temperature values collected from the sensor. After obtaining temperature values, the Due checks to make sure all components are in the correct temperature range and moves on to executing the next command. The pre-concentrator can have a temperature of up to 300 °C, the GC column and transfer line temperature can be up to 210 °C and the guard column temperature goes up to 160 °C. The user uploads commands onto the Due at the beginning of the experiment, and the commands are executed at a user specified time; therefore, the Due waits until it is time to execute a particular instruction, while continuously sampling the Trinket. For example, when the command to increase temperature of the pre-concentrator is scheduled for 30,000 ms after initialization and the current time is 20,000 ms, the Due continues to maintain a previously commanded temperature while interacting with the Trinket until 30,000 ms. After the correct time is reached, the Due increases the temperature of the pre-concentrator. The Due is connected via a USB cable to a miniature laptop running a custom graphical user interface described below (Figure 3).

The GUI was coded in Python. The interface is user friendly and was designed so that users with no programming experience can easily use it. While the device is running, the interface provides the user with real time feedback on the temperature values of heated components as well as the current status of command execution. As a safety measure, the device can operate if the USB link between it and the GUI interface is severed. If the connection is lost, the system halts all heaters and pumps while providing helium and nitrogen to purge the gas lines for a safe shut-down. This will prevent the GC column and the DMS from being damaged.

The main purpose of the GUI software is to allow the user to enter a series of chronological events to control the pumps, valves and heating elements of the MR-GC-DMS unit. One complete cycle of these events is known as an analysis, in which the device will collect a chemical sample for a user-defined period of time, heat the pre-concentrator to release the VOCs through a user-defined heating profile and direct the VOCs to the GC column (which has its own user-programmed heating profile) and the DMS for detection. Users also define initial temperature states. Together, these parameters can be saved as a “Profile”, so that users can easily re-load profiles for repeated analysis.

The GUI has 3 modes from which to operate on the MR-GC-DMS device: Idle, Active and Run modes. In the Idle mode, the device has shut off all power to the heated components and allows the user to input run parameters for the analysis. In this mode, the GUI polls the Arduino Due installed inside the MR-GC-DMS device for temperature data and updates the live temperature plot at 1 Hz. From Idle mode, the user can only enter Active mode to heat components to initial temperature values. The initial temperature values must be entered in Idle mode. These temperature values will be the ones the device returns to after each analysis and the system cannot start a new analysis if the temperatures of components do not

match the initial values. In Active mode, the user waits until all the initial conditions are met and can modify the run profile. From active mode, the user can return to Idle mode or move into Run mode, which initiates the analysis. In Run mode, the user watches the progress of the analysis and has the authority to halt it. The GUI has built-in error handling that scans for errors made during run parameter entry. For example, the user defines how long the analysis lasts (noted as “End” under section 6 of Figure 3). If the user meant to define an analysis to last “10,000” ms but has instead put in “10,)00” ms, the GUI would warn the user of this input error. The software was written for safety of the user and safety of the MR-GC-DMS device as a top priority.

Hardware Operations:

Functionality of the device is illustrated in Figure 4. The hardware has intended three modes of operation: sampling, analyzing and cleaning. The first diagram shows the **sample collection mode** in which the 2-way and 3-way valves open and the sampling pump turns on, allowing the sample to pass through the inlet, across the pre-concentrator trap and out of the sample pump (Figure 4A). The pre-concentrator traps the VOCs for a user-defined time, after which the sampling mode is complete and the sampling pump turns off.

Sample analysis mode begins with the 2-way valve closing and the 3-way valve redirecting a flow of helium between 0.5–2.0 sccm into the pre-concentrator (Figure 4B). The pre-concentrator trap is then heated to a desired user-defined value, causing the VOCs to release and flow through the first guard column, through the GC column (where the VOCs separate), pass the second guard column and finally reach the DMS for data genesis. The temperature of the GC column is ramped by a user-defined protocol until a maximum value is reached. Together, the sampling mode and analysis mode complete one “profile”, or one discreet chemical analysis of a sample.

The **cleaning mode** is intended to be a separate profile from a chemical analysis (Figure 4C). Depending on the sorbent material packed inside the pre-concentrators, memory effects can sometimes interfere with chemical analysis. This is because of incomplete desorption of VOCs from the sorbent. Some sampling matrices require aggressive sorbent types to trap small molecular-weight volatiles, but a side effect is that these sorbents are also too aggressive to completely release these compounds with only one heating cycle. Thus, it is common to have a secondary purge of the pre-concentrator trap to ensure it is refreshed for another analysis. Furthermore, if the MR-GC-DMS has not been used recently, it is customary to purge the entire system to evacuate volatiles that have collected while it was unused. To clean the system and refresh the sorbent trap, a flow of helium scrubs all tubing and heated components are set to a high temperature to ensure all residual VOCs are removed.

Chemical Experiments

We measured overall HR-GC-DMS repeatability by sampling the headspace of a vial containing 60 VOCs (Part 30603, Restek, Bellefonte, PA) for 10 sec. The GC temperature was ramped from 50 °C to 180 °C at a rate of 0.5 °C/sec. We focused on 3 chemical peaks to evaluate the repeatability of the instrument. Because the samples were identical, the

corresponding peaks across different samples should match in intensity, RT, and CV. Variation in any of those values may reflect instrument error of the MR-GC-DMS system. Using our previously described AnalyzeIMS software [40], a smoothing filter and baseline removal was applied to all the samples. Two sets of data with n=5 samples per set were collected. In the first set, the hardware system components simply returned to their initial values between samples, upon which the next analysis immediately occurred. The second data set was collected in the same manner as above, with the exception of having a cool-to-ambient cycle in between samples. During the cooling cycle, the DMS device was turned off. During the start up before each sample run, the system conducted a cleaning cycle.

To further demonstrate device performance, we tested if the MR-GC-DMS could confirm VOC work previously accomplished with a commercial gas chromatography-mass spectrometer (GC-MS). It was previously shown that the *Phytophthora ramorum* pathogen changes the off-gassed VOC profile of *Rhododendron*, a common ornamental plant. In this previous work, volatiles were collected and returned to the laboratory for analysis. Our MR-GC-DMS should be able to measure volatile profiles altered by the plant-pathogen interaction but perform the analysis on site. To isolate off-gassed plant VOCs, *Rhododendron* were maintained in branch enclosures [41], collecting n=12 control plant samples and n=12 *P. ramorum*-infected plant samples.

RESULTS:

Control System Performance:

To insure the different heated components hold a constant temperature, a common proportional-integral-derivative controller (PID) algorithm was implemented on 5 different components: the GC column heater; the pre-concentrator trap heater; the two heated transfer lines; and the heated guard columns. Figure 5 shows the step responses of only 3 of the 5 different components because the transfer lines from and into the GC column act as the same component in all operating modes, therefore their time response graphs match perfectly with the GC column. The components were tuned individually until a desired heat profile response was achieved for each. The pre-concentrator trap was tuned with the goal of having the fastest possible ramp rate. During an analysis, the trap holds a low temperature while sampling and rapidly increases to its programmed peak temperature (e.g. 300 °C) and holds for VOC desorption from the sorbent. The trap has a heating rate of 15–18 °C/s, a 5 % overshoot and a steady state error no greater than ±0.5 °C. The maximum temperature of the pre-concentrator trap is 330 °C.

The GC was tuned with the goal of having the least amount of overshoot and steady state error. The two transfer lines connecting the GC to the guard column have temperature profiles that match the GC temperature; therefore, their separate step responses are not included. During operation, the GC is initially at a low, steady state value (e.g. 50 °C) during sample desorption from the trap. It is then ramped to a desired temperature and holds again. The GC heater achieves rates of up to 2 °C/s with no overshoot and a steady state error no greater than ±0.5 °C. The same holds true for the transfer lines.

The guard columns are coiled inside small metal packets with its own designated heater. This system was designed to have the least amount of steady state error. The response time was deemed less important because typically guard columns do not deviate from an initial value. The guard column heater is capable of heating at 6 °C/min with no overshoot and steady state error of no greater than ±0.5 °C. The maximum temperature the guard column can reach is 170 °C.

When many heated components are packaged together yet set to different temperatures, temperature coupling can occur. For example, the contiguous guard column and pre-concentrator trap can differ by 150 °C. Experiments showed that the guard column increased the initial trap temperature by 20 °C higher than desired (data not shown). To avoid temperature coupling, these two components required active cooling systems. A fan was placed directly above the pre-concentrator to shed the heat absorbed from the guard column heater.

Reproducibility Performance Assessment:

To make sure the MR-GC-DMS system is fully functional, a series of tests were conducted. The testing was split between software and hardware tests. The GUI and Arduino software were subjected to an endurance test as well as user error tests. During the endurance test, the system was left running uninterrupted for 6 days to make sure the software was stable and had no memory leaks. After 6 days of uninterrupted operations, the amount of computer RAM memory used by the system remained unchanged showing that no memory leaks are present in the code (data not shown). Afterwards, a series of faulty user commands were entered to make sure the error handling systems were functioning properly. The user should only input numbers into the GUI, and the GUI must be able to distinguish between numbers and accidentally typed letters. If a non-numerical character/s is entered, the GUI successfully presents an error message without compromising the stability of the system. Additionally, the GUI ensures the temperature parameters are within the proper range for each heating element. For example, if the user inputs “350” as the commanded pre-concentrator temperature, the GUI will present an error message and set the temperature to the maximum possible (300 °C) for the pre-concentrator.

For the hardware, individual components were first tested and then the system as a whole. The individual components were subjected to at least 10 heating/cooling cycles to test their response stability in rapid succession. The heating responses showed consistency over time with no significant fluctuations. Afterwards an overheating test was conducted in which all of the heated components were heated up to their maximum temperature values to see if any non-heated components would have adverse side effects. The MR-GC-DMS device maintained maximum heat for 3 hours with no adverse effects to device performance recorded (data not shown).

Analyzing a chemical sample is the ultimate device performance metric. The repeatability of the DMS data over time from the same sample and sampling conditions was tested. DMS data is in the form of a 2D surface with the x and y components of the surface corresponding to compensation voltage (CV) of the DMS instrument and retention time (RT) in the GC column, respectively. The height of the surface corresponds to the intensity of the recorded

ions at a particular RT and CV. A peak on the surface represents a compound being detected by the DMS. We measured repeatability by sampling the headspace of a vial containing 60 VOCs (Part 30603, Restek, Bellefonte, PA; Figure 6). We focused on 3 chemical peaks to evaluate the repeatability of the instrument. Because the samples were identical, the corresponding peaks across different samples should match in intensity, RT, and CV. Variation in any of those values may reflect instrument error of the MR-GC-DMS system. Using our previously described AnalyzeIMS software, a smoothing filter and baseline removal was applied to all the samples For our 3 selected chemical peaks (Figure 6), we calculated the peak volume as well as the averaged RT and CV value (Table 1). Two sets of data with n=5 samples per set were collected. In the first set, the hardware system components simply returned to their initial values between samples, upon which the next analysis immediately occurred. The GC temperature was ramped from 50–180 °C at a rate of 0.5 °C/sec.

The second data set was collected in the same manner as above, with the exception of having a cool-to-ambient cycle in between samples. During the cooling cycle, the DMS device was turned off. During the start up before each sample run, the system conducted a cleaning cycle. The results of the second variability test are shown in Table 1. As expected, the peak magnitude variations are greatest in the consecutive samples. This can be attributed to the lack of a cleaning cycle between samples, as discussed previously.

Field Application and Demonstration of System Performance:

To further demonstrate device performance, we tested if the MR-GC-DMS could confirm VOC work previously accomplished with a commercial gas chromatography-mass spectrometer (GC-MS). It was previously shown that the *Phytophthora ramorum* pathogen changes the off-gassed VOC profile of *Rhododendron*, a common ornamental plant.

Our MR-GC-DMS device analyzed volatile profiles of *Rhododendron* maintained in branch enclosures. Using the AnalyzeIMS software [40], a multiway partial least squares (nPLS) model was built based on DMS spectra of the healthy and *P. ramorum*-infected plants (Figure 7). The model was able to distinguish between healthy and infected plant profiles, just as was previously confirmed with GC-MS. While the biological relevance of this phenomenon is discussed elsewhere [41], this experiment herein confirms that the MR-GC-DMS can be used to measure VOCs from environments and be used to distinguish between categories of samples, such as healthy and infected. In the case of *P. ramorum*, screening nurseries for the pathogen has become an important task to abate disease propagation; thus, having a device perform diagnostics in the field, such as the MR-GC-DMS, could alieve certain issues with VOC-based detection strategies when it is difficult to bring samples into a laboratory. This small study simply serves to represent the possibilities of types of analyses a MR-GC-DMS could perform.

DISCUSSION:

With the advancement of general purpose microcontrollers such as the Arduino, custom devices such as the MR-GC-DMS are now possible. The MR-GC-DMS system demonstrates that platforms for analytical chemistry can be designed that are easily modified

and can be tailored on-demand by small groups. The device is designed to be easily reconfigurable in order to meet the needs of the user. An Arduino- and Python-powered hardware and GUI platform enables the user to easily change the system without the need of having to be a software/hardware professional. Open source software allows the user to tailor the device to their specific needs, if desired. The components selected for the device are COTS components which makes them easily replaceable in case of failure or in case a vendor is no longer manufacturing or supporting specific equipment. The device is highly modular and allows different components to be swapped in and out without affecting the functionality of the device.

CONCLUSION:

In this present paper, we create and describe the hybrid and custom-made MR-GC-DMS to detect volatile organic compounds (VOCs). We have shown how a custom device can be built out of commercially available “off the shelf” parts as well as how those parts work together to make a functioning GC-DMS system. All system parts are modular and can be replaced at will. System control is achieved through our custom graphical user interface running onboard the data collection computer as well as our programmed microprocessor inside of the system. The MR-GC-DMS was subjected to a variety of tests to show its practicability in gas phase chemical analysis and also for a specific agriculture application. This showed stability in the response of the device to variable conditions during sampling, and we showed the ability to distinguish between healthy and *Phytophthora*-infected *Rhododendron* plants by sampling the VOCs produces by the leaves.

SOFTWARE AND DEVICE DESIGN INFORMATION:

The software code and PCB design specifications for our MR-GC-DMS are available on GitHub. Please refer to Professor Cristina Davis’ webpage for more information. This material is available as open source for research and personal use under a modified BSD license. Commercial licensing may be available, and a license fee may be required. The Regents of the University of California own the copyrights to the software and PCB designs. Future published scientific manuscripts or reports using this software and/or hardware designs must cite this original publication (DOI: 10.1007/s12127-018-0240-4).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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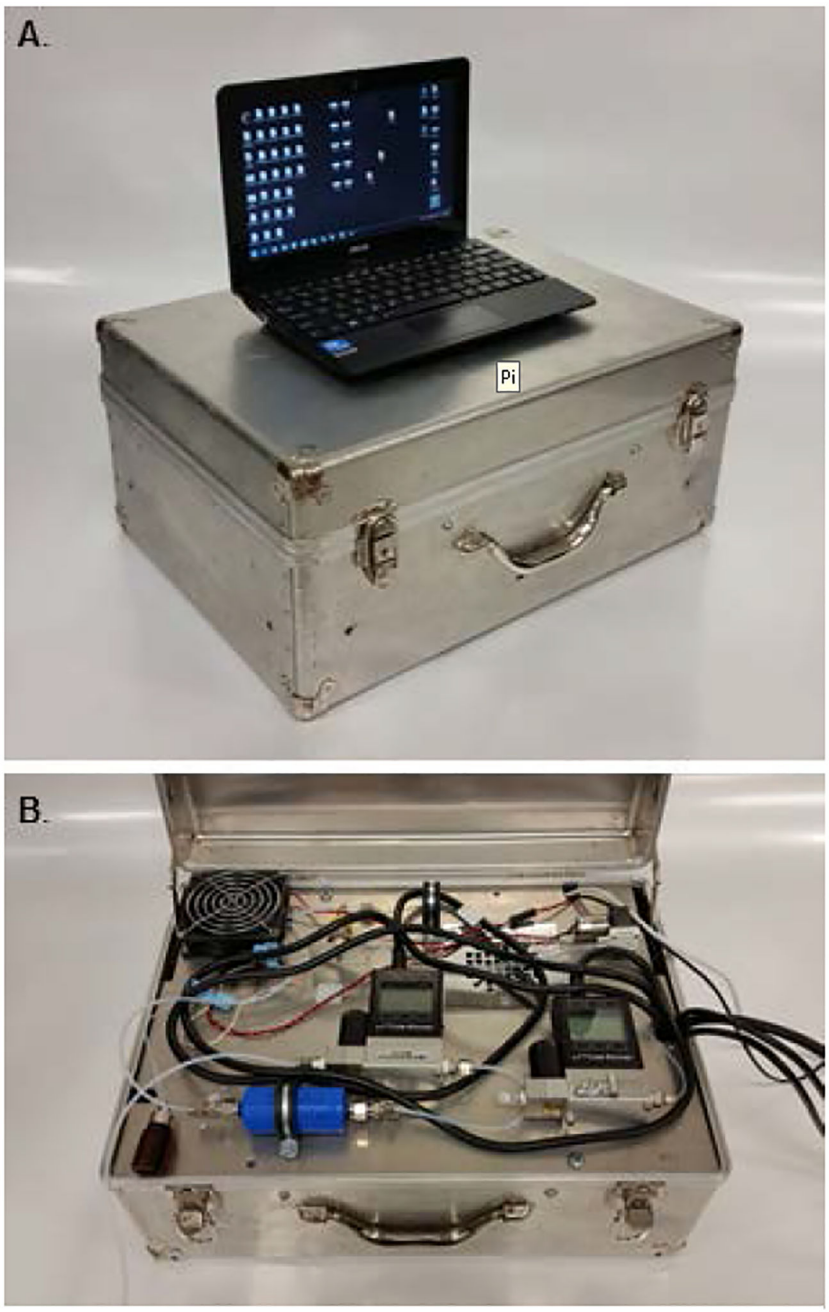

Figure 1.
(A) The MR-GC-DMS device in storage state along with the operator mini-command computer. (B) The system in the open state, ready for sampling and data analysis.

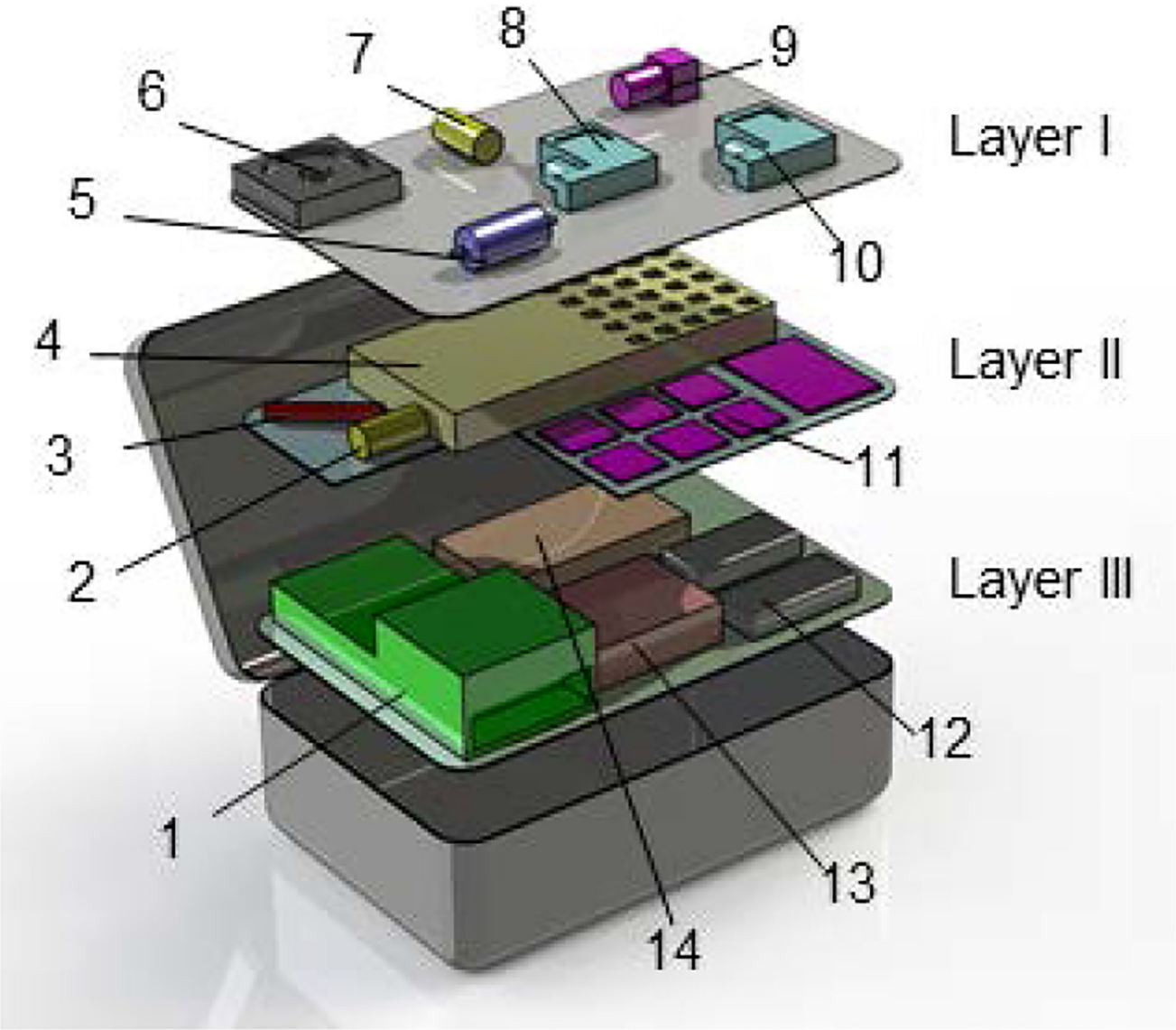

Figure 2.

The MR-GC-DMS device is divided into 3 stacked layers in a metal case. The parts are numbered as follows: 1 DMS; 2 two-way-valve; 3 pre-concentrator trap; 4 GC and guard columns; 5 filter; 6 fan; 7 three-way-valve; 8 nitrogen MFC; 9 sample pump; 10 helium MFC; 11 electronic PCB control boards; 12 DMS power supplies; 13 power supply (12V); 14 power supply (24V).

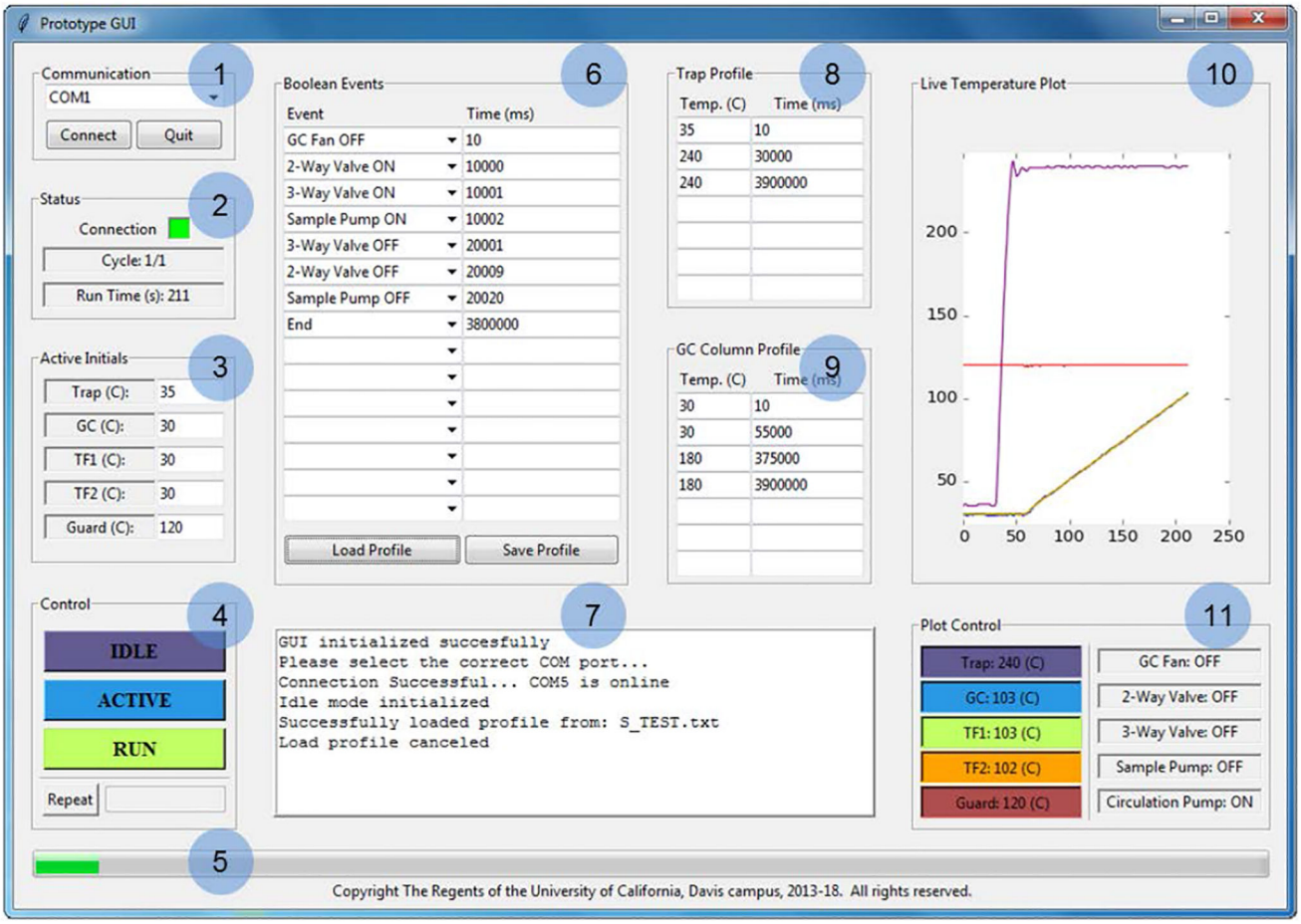

Figure 3.

Graphical User Interface (GUI) screenshot as it would appear to the user. The screen is segmented into blocks which are as follows: 1 communication, 2 status, 3 initial conditions setup, 4 control, 5 progress bar, 6 event logic, 7 event relay to user, 8 pre-concentrator temperature profile, 9 GC temperature profile, 10 live temperature graph, 11 temperature graph control.

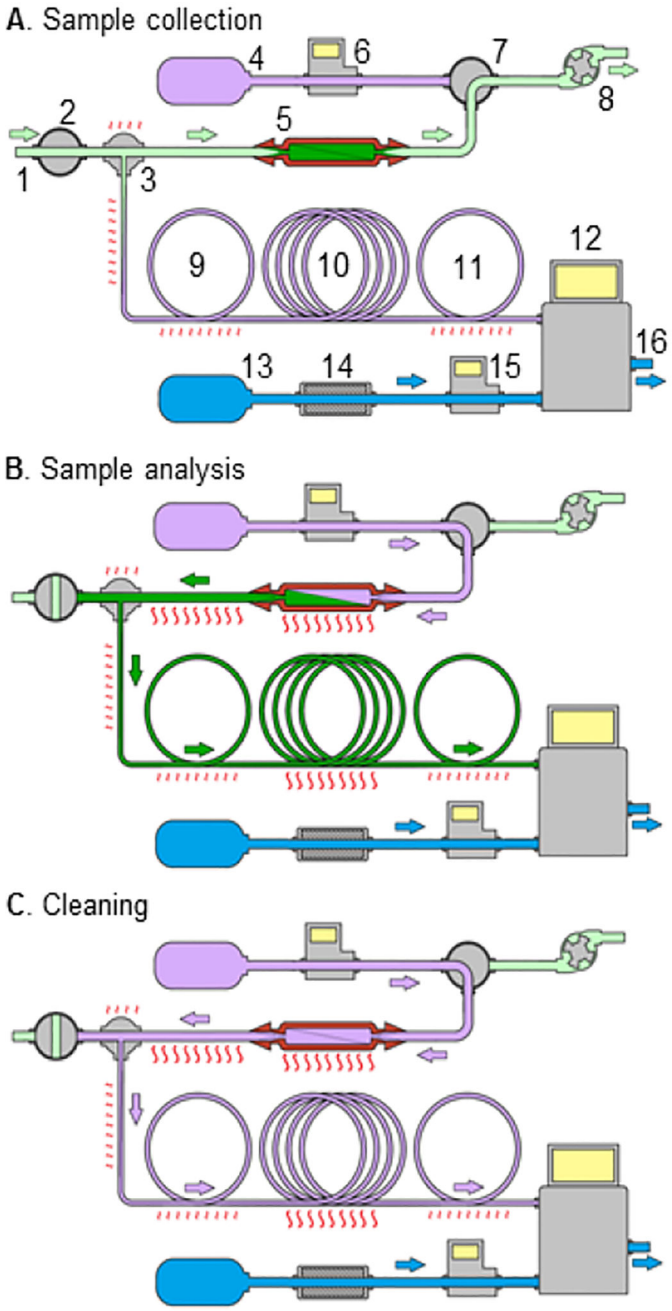

Figure 4.

Illustrated view of hardware operation. Arrows indicate the direction of gas flow. The red lines indicate the application of heat. Green signals the presence of a VOC mixture. Blue shading is nitrogen only. Violet shading is helium only. Parts correspond to: 1 sample inlet; 2 two-way-valve; 3 ZDVT; 4 helium source; 5 pre-concentrator trap; 6 helium MFC; 7 three-way-valve; 8 sample pump and sample exit; 9 guard column I; 10 GC column; 11 guard column II; 12 DMS; 13 Nitrogen source; 14 filter; 15 nitrogen MFC; 16 exhaust from the instrument.

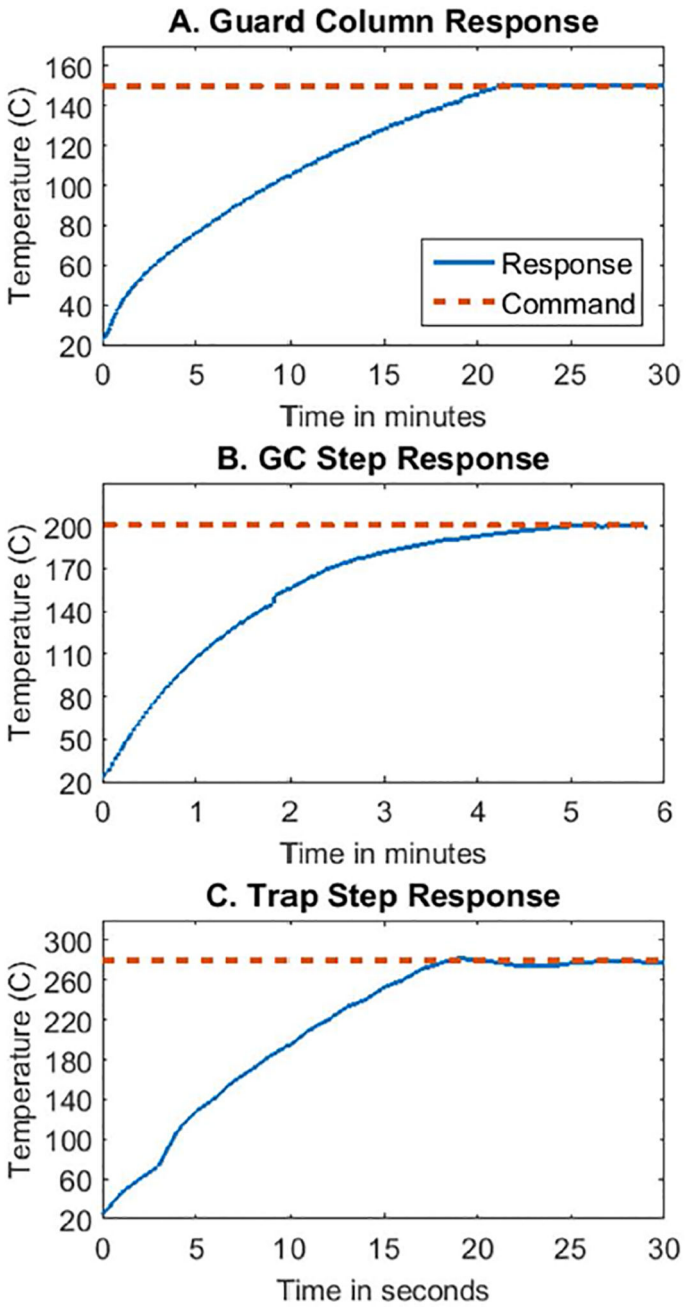

Figure 5.

Step response of three heated components of the MR-GC-DMS device. (A) guard column; (B) gas chromatography column; (C) pre-concentrator

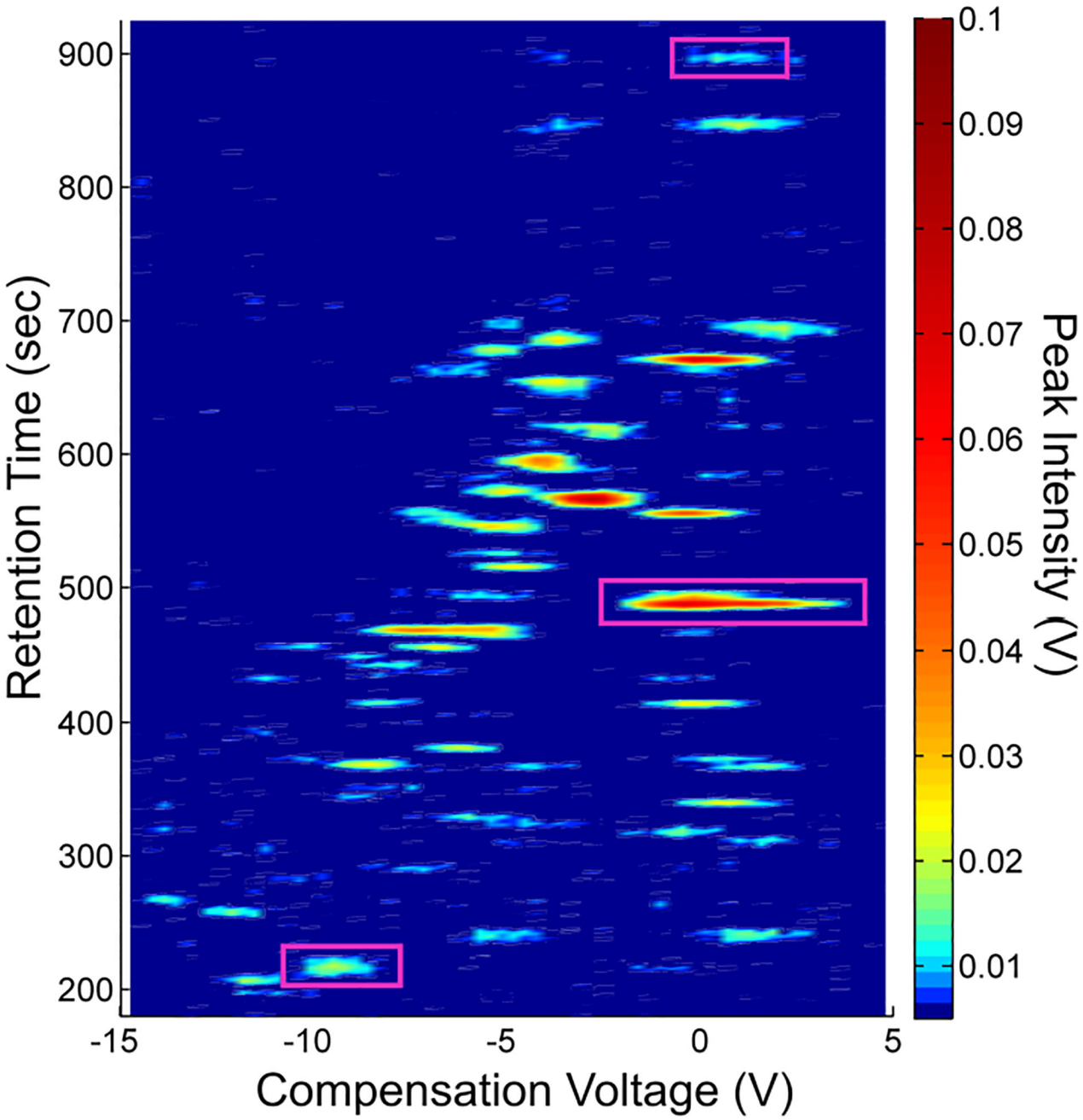

Figure 6.
Locations of the 3 chemical peaks shown as pink rectangles with respect to Retention time and Compensation voltage

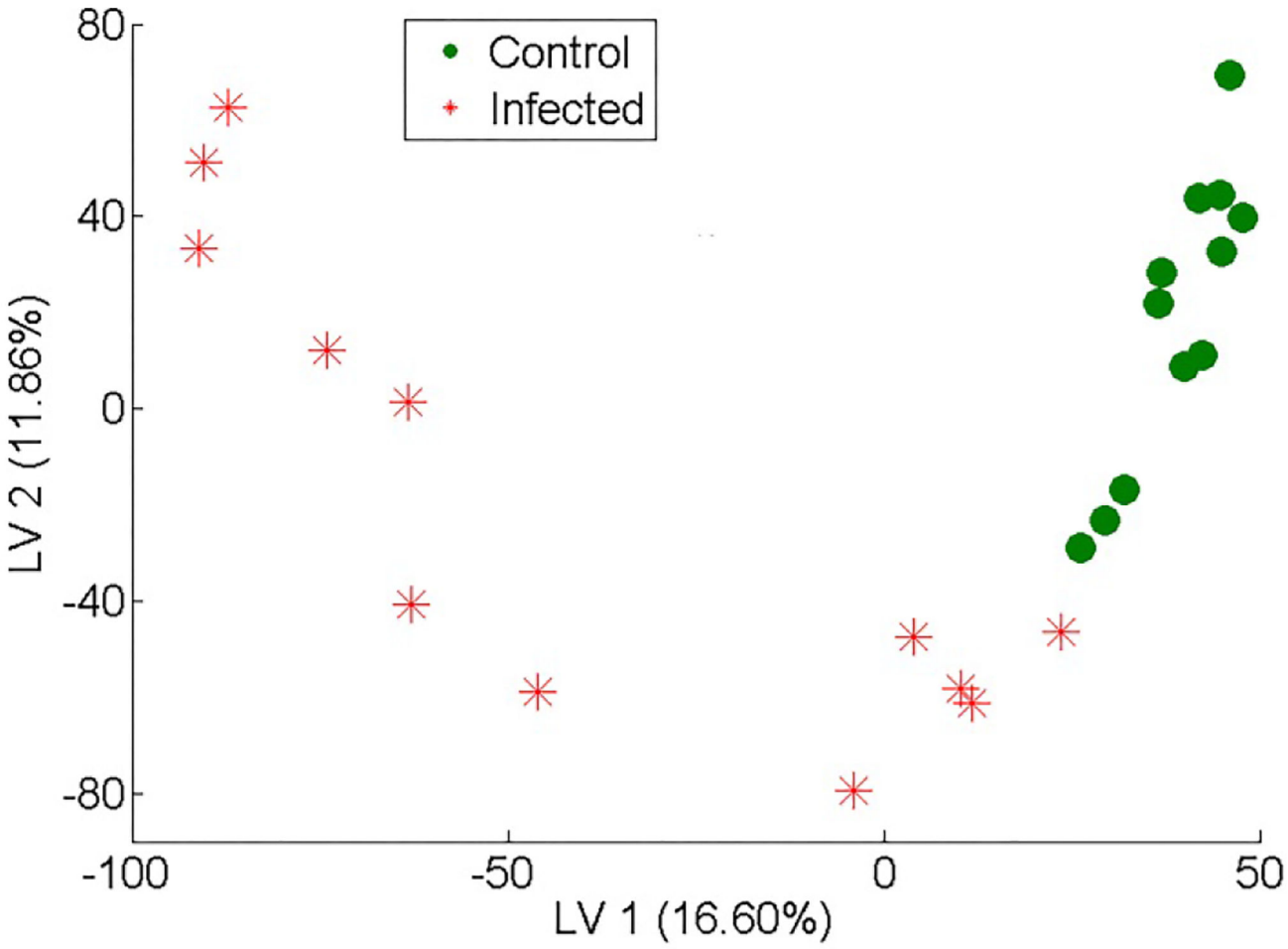

Figure 7.

PLS-DA model of VOC samples of control and *P. ramorum*-infected *Rhododendron* plants collected with the MR-GC-DMS. A VOC profile difference was previously shown between these sample sets; our MR-GC-DMS was also able detect a volatile difference, confirming functionality of the device. A separation of healthy and infected plants can be seen between the two latent variables.

Table 1.

The results of 5 consecutive experiments with no cleaning cycle and no cooling period are shown in the upper table, while the results of the 5 separate experiments with an initial cleaning cycle and a full cooling period in between are shown in the lower table.

Consecutive Sampling			
Measurement	Peak 1	Peak 2	Peak 3
Mean RT (Std Dev)	245.4 (13.44)	501.3 (6.534)	911.6 (2.908)
Mean CV (Std Dev)	−10.14 (0.0989)	0.5365 (0.0447)	1.472 (0.0531)
Intensity (Std Dev)	2.052 (0.4630)	6.046 (0.6086)	5.305 (0.5135)
Extended Sampling			
Measurement	Peak 1	Peak 2	Peak 3
Mean RT (Std Dev)	218.5 (2.942)	490.5 (3.426)	913.9 (1.859)
Mean CV (Std Dev)	−10.10 (0.0779)	0.4472 (0.0170)	1.424 (0.0618)
Intensity (Std Dev)	2.618 (0.2898)	6.431 (0.3456)	4.352 (0.2760)