# Recent Advances in Water Analysis with Gas Chromatograph Mass Spectrometers

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**We report on progress made in developing a water sampling system for detection and analysis of volatile organic compounds in water with a gas chromatograph mass spectrometer (GCMS). Two approaches are described herein. The first approach uses a custom water pre-concentrator for performing trap and purge of VOCs from water. The second approach uses a custom micro-volume, split-splitless injector that is compatible with air and water. These water sampling systems will enable a single GC-based instrument to analyze air and water samples for VOC content. As reduced mass, volume, and power is crucial for long-duration, manned space-exploration, these water sampling systems will demonstrate the ability of a GCMS to monitor both air and water quality of the astronaut environment, thereby reducing the amount of required instrumentation for long duration habitation. Laboratory prototypes of these water sampling systems have been constructed and tested with a quadrupole ion trap mass spectrometer as well as a thermal conductivity detector. Presented herein are details of these water sampling system with preliminary test results.**

## Nomenclature

| | | |
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| *CEM* | = | channel electron multiplier |
| *FID* | = | flame ionization detector |
| *GC* | = | gas chromatograph |
| *GCMS* | = | gas chromatograph mass spectrometer |
| *MEMS* | = | micro electro-mechanical system |
| *MS* | = | mass spectrometer |
| *PC* | = | pre-concentrator |
| *PDD* | = | pulsed discharge detector |
| *ppm* | = | part-per-million |
| *ppb* | = | part-per-billion |
| *rf* | = | radio-frequency |
| TCD | = | thermal conductivity detector |
| *VOC* | = | volatile organic compound |
| *VCAM* | = | Vehicle Cabin Atmosphere Monitor |

## I. Introduction

THE future of manned space exploration demands a suite of instrumentation that adheres to strict requirements on size, durability, resources and performance. The work presented here is part of a long-standing effort to develop a variety of mass spectrometer technologies for space exploration that address size and reliability requirements, while maintaining or improving analytical performance. Gas chromatography (GC) is one such technology currently under development . Gas chromatograph mass spectrometry (GCMS) is a powerful analytical tool that can be used for a host of tasks relevant to space exploration, and constructing a single GCMS with multiple functions is one way to significantly reduce a mission's instrument payload.

The ability of a GCMS to perform in situ analysis of air quality aboard the International Space Station was successfully demonstrated with the Vehicle Cabin Atmosphere Monitor (VCAM)[1,2]. The VCAM instrument

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performed two functions during its two year demonstration period. The first VCAM function was trace gas analysis, where the GCMS was used to detect and measure concentrations for select volatile organic compounds (VOCs) in air, in the concentration range of 10 part-per-billion (ppb) to 10 part-per-million (ppm). The second VCAM function was major constituent analysis in which the GCMS was used to measure the air concentrations for $H_2O$, $N_2$, $O_2$, Ar, and $CO_2$.

The next evolutionary step in developing and expanding this GCMS technology is to incorporate water analysis. Two approaches for sampling water into a GCMS have been explored to date. The first is analogous to the pre-concentrator method used in VCAM for its trace gas air measurements, where a large volume of sample is passed through a sorbent trap, purged and then thermally desorbed into the gas chromatograph. The second approach uses a custom split-splitless injector to volatilize a small ( $\leq 10$ µL) sample of liquid water just prior to injection into the gas chromatograph column.

## II. Experimental Setup

### A. Pre-concentrator water sampler

The pre-concentrator (PC) used in this work is comprised of a thin-walled metal tube with a bed of carbon molecular sieve inside and packed between two porous screens. A thermocouple is affixed to the outer wall of the tube for measuring temperature. The PC also has a NiCr heater wire wrapped over its entire length to provide uniform heating up to 400 °C. The carbon molecular sieve has a very high affinity for light VOCs. As water flows through the carbon molecular sieve, any VOCs contained within will become trapped in the carbon molecular sieve.

The PC water sampler is intended to operate with a GC without requiring modification. The PC water sampler designed in this work is a liquid water analog of the air PC sampling system used in VCAM for its trace gas air monitoring. A schematic of the PC water sampler and gas chromatograph is shown in Fig. 1. Water is drawn through a PC with the aid of a miniature pump. The pump is shut off after a sufficient volume of water has passed through the PC, and the water sample path is then purged with helium from the carrier supply. The water PC is isolated with two miniature liquid isolation valves following the purge sequence. The PC is then desorbed with a fast temperature ramp while opening the inlet to the gas chromatograph and pressurizing the water PC with helium. The helium will flow from the supply manifold through the water PC and entrain any desorbed VOCs before proceeding into the gas chromatograph where the VOCs are adsorbed onto the air PC. The gas chromatograph can proceed just as it would for an air sample analysis at this point. The gas chromatograph used in the PC water sampler is functionally equivalent to that used in VCAM, with only minor changes by way of parts selection. Despite changing the injector, valves and pressure controllers, the flow rates, pressures, and temperature profiles remain the same as in the VCAM instrument. The GC column used here is also the same as in VCAM. This ensures the GCs tested here perform identically to the GC of the VCAM instrument.

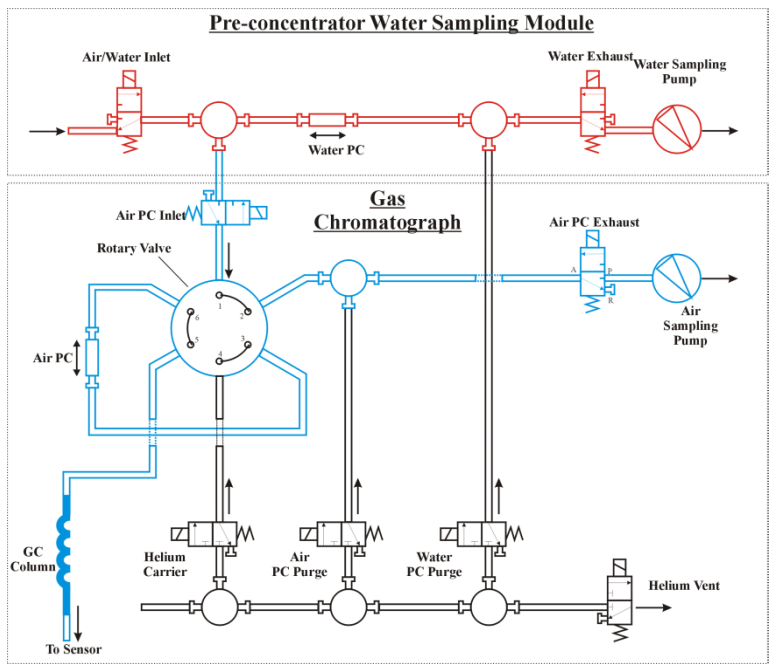


**Figure 1. Schematic of the PC water sampler (*red*), gas chromatograph (*blue*), and helium manifold (*black*). Air or water is drawn in through a common inlet where it can be directed to the appropriate subassembly for processing. Air samples are diverted directly to the air PC mounted on a 6-port, 2-way rotary valve where VOCs become trapped and can then be thermally desorbed into the GC column. Water samples are diverted to the water PC where VOCs are trapped. Water is then purged from the system used pressurized helium and VOCs are thermally desorbed from the water PC and directed into the GC for further processing with the air PC.**

## B. Split-Splitless water sampler

The split-splitless water sampler developed for this work incorporates a custom, miniaturized version of the split-splitless injector commonly found in commercial GCMS systems, and integrates it into a custom GC assembly as shown in Fig. 2. The GC assembly used in this water sampler closely resembles that of the PC water sampler, with the only major difference being the 6-port, 2-way rotary valve is replaced with a 10-port, 2-way rotary valve that accommodates an additional sample path for water. This additional sample path uses a fixed-volume, external sample loop to provide a precise dosing of liquid water to the split-splitless injector assembly placed between the rotary valve and the GC column. A 10 µL sample loop was used for the work reported here.

This split-splitless injector is comprised of concentric tubes as shown in Fig. 3. The inner tube is the inlet and connects to the outlet port of the rotary valve. The outer tube is connected to the inlet of the GC column with two exhaust ports located at the opposite so that any analyte must flow past the GC column inlet before being exhausted. One of the exhaust ports is connected to a valve with an electronic, mass-flow controller and functions as the split flow path. The second exhaust port is connected to a valve without regulation and functions as the purge. The outer tube of the injector has a thermocouple attached and NiCr heater wrapped over its exposed length to provide uniform heating up to 400 °C. The mass flow into the GC column can now be precisely controlled using the mass flow controller governing total flow into the GC and split-splitless injector assembly, and the mass flow controller on the split port. In this work, the flow rate in the column can be continuously varied from ~10 µL/min to 5 mL/min.

This split-splitless injector provides extra functionality for air analysis by allowing high-concentration samples to be split prior to injection thereby increasing effective dynamic range for the attached sensor. Air analysis is otherwise unaffected by the presence of the split-splitless injector. Water introduced into the split-splitless injector proceeds through the inner tube into the heated region of the injector where it is rapidly vaporized. The expansion of water and any VOCs rapidly fills and pressurizes the internal (100 µL) volume of the injector assembly, which requires splitting and possibly purging during the injection into the GC column. The injector assembly can be quickly purged of any remnant water and VOC following the injection to improve chromatographic peak shapes and separations.

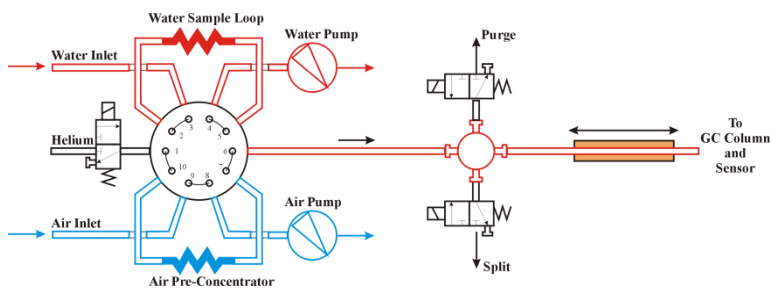


**Figure 2. Schematic of the split-splitless water sampler showing the water sample path (red) and air sample path(blue). Air and water samples are transferred from the rotary valve to the GC column via the split-splitless injector assembly.**

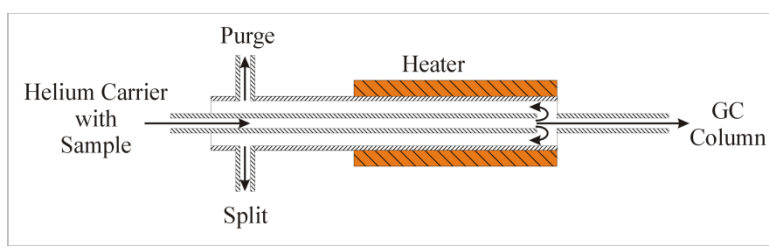


**Figure 3. A schematic of the split-splitless injector assembly showing the various flow paths. Operation of the injector with both purge and split ports closed results in a splitless injection where all analyte flows into the GC column. The split port can be opened and flow into the GC column can be precisely controlled by varying mass flow out of the injector assembly. The injector can also be quickly vented by opening the purge valve.**

The split-splitless injector system developed for this work is based on the same concept as found in commercial GCMS split-splitless injectors. However, this injector has several modifications that distinguish it from its commercial counterparts. This injector has no glass liner and offers an all-metal construction. The internal volume of this injector at 100 µL is approximately 100 times smaller than commercial injectors. This affords an improved sensitivity and detection limit for water sampling, but requires careful attention to all injection parameters to ensure that no liquid sample enters the GC column, and that water vapor, once inside the column, does not condense. This injector also has a small thermal mass allowing for very fast temperature ramps.

## C. Sensors

There were two quadrupole ion trap mass spectrometers used for testing the PC and split-splitless water samplers. The mass spectrometers were of identical construction, and outlined in previous work[3,4]. To summarize,

each mass spectrometer consisted of a quadrupole ion trap with three hyperboloidal electrodes – a central electrode, commonly referred to as the ring electrode, and two exterior electrodes, commonly referred to as the end cap electrodes. Both end cap electrodes have a 1 mm diameter hole on their center axis. The ion trap has a gas inlet line that connects to the GC. The gas leaving the GC enters the ion trap and is ionized with a pulsed electron beam traversing along the central axis. The electron beam is produced by a tantalum disc-emitter and is focused into the ion trap with an Einzel lens assembly.

Ions are trapped between the three hyperboloidal electrodes when a high-voltage radio-frequency (*rf*) waveform is applied to the ring electrode, and the end caps are grounded or have a low-voltage, AC waveform impressed upon them. Trapped ions can be destabilized from the trap and ejected through one of two endcaps when the ring's *rf* amplitude exceeds the ion stability condition determined by the Mathieu equation. In the event of grounded end caps the stability condition reduces to:

$$q_z = 0.908 = \frac{4eV}{mr_0^2\Omega_0^2}, \tag{1}$$

where $e$ is the elementary charge, $V$ and $\Omega_0$ are the ring electrode's *rf* amplitude and frequency respectively, $m$ is the ion mass, and $r_0$ is the characteristic radius of the ion trap. Both mass spectrometers have a characteristic radius of 1 cm. Ions can also be destabilized and ejected from the ion trap when a pair of low-voltage *rf* waveforms out of phase from one another are applied to the end caps. This created an auxiliary dipole field that can be used for resonant or non-resonant excitation of ions[3].

The ion detector consists of two retarding grids and a channel electron multiplier (CEM). The two grids are used to shield the CEM from electrons and untrapped ions during the ionization phase. This ionization phase occurs when the electron beam is pulsed on to ionize the gas inside the ion trap. The ionization phase is then followed by an analysis phase, in which the electron beam is switched off, the ions are allowed to settle, and the *rf* amplitude is ramped linearly to eject ions of increasing mass. A time-resolved digitization of charge pulses from the CEM during this linear ramp in amplitude provides a mass spectrum. The ion traps used here, with their associated drive electronics[4,5], are capable of repeating this process at a rate of up to 100 Hz.

In this work, the ion trap mass spectrometers were operated with trapping frequencies of 620, 820 and 1250 kHz. Resonant and non-resonant dipole excitations were also used to help remove water ions from the ion traps as well as to improve mass resolution ($m/\Delta m = 2000$ at mass 28) and increase mass range (> 600 amu).

The quadrupole ion trap mass spectrometer is the sensor of choice for this work owing to its trapping capabilities, high sensitivity, fast scan speed, and small form-factor, but virtually any mass spectrometer could be used as the sensor. The water samplers developed here will also work with a wide variety of sensors that include thermal conductivity detectors (TCD), flame ionization detectors (FID), and pulsed-discharge detectors (PDD). As part of this work, the water samplers developed here were coupled to a TCD in order to assess performance. A TCD was chosen for this work as it is completely non-destructive and so can be installed inline between the GC and a mass spectrometer.

A path for miniaturization to a MEMS platform was also considered during the design and construction of both the PC and split-splitless water samplers. Recent efforts[6] have explored the miniaturization of several GC and MS components. Their GC column and air PC are interchangeable with those used here. Both MEMS components target the same range of VOCs and operate with the same range of flow rates.

## III. Measurements and Results

Performance for both water samplers was assessed by performing repeated measurements of prepared water samples with varying parameters such as injection duration, injection temperature, desorption temperature, and desorption pressure. Sample preparation was a key component to successfully performing these measurements. All samples in this work used precise microliter volumes of specific VOCs added to 500 mL of deionized water. The VOCs used were primarily methanol, ethanol, acetone, ethyl acetate, and acetonitrile. These specific compounds were chosen because of their high solubilities in water and because they have a large historical database of performance with the VCAM instrument in its air analysis.

### A. Pre-concentrator water sampler

The PC water sampler shown in Fig. 1 is capable of performing air analyses using the same procedure as found in VCAM without the need for any additional steps or resources. Air can be drawn in through the air PC using the

air sample pump. The air PC can be flushed with helium by toggling the state of the rotary valve, and then the PC can be thermally desorbed directly into the GC column. The operation becomes considerably more complex when performing a water analysis.

In a water analysis, the water PC must be loaded with VOCs from the water and then purged and dried before transferring as much of the VOC load from the water PC to the air PC and then from the air PC into the GC column. Several purge steps are required during each transfer of VOCs to ensure that liquid does not get injected onto the GC column. This requires a lengthy and detailed state machine for controlling all of the valves, pumps, heaters, and flow and pressure controllers, while also increasing resource consumption for the GC.

Having multiple PCs in close proximity to one another also creates issues with cross-contamination. This is a problem during the various cleaning cycles where a portion of material desorbed from one PC can be adsorbed by the other, the end result being the total time for a cleaning cycle is dramatically increased. In this work, cleaning cycles on the water PC were typically an hour in duration.

While using multiple PCs gives rise to longer cleaning cycles, they do provide a benefit via enhanced sensitivity. In Fig. 4, an ion chromatogram is shown for an elution of deionized water sample prepared with 10 ppb of ethanol, acetone, ethyl acetate, and acetonitrile. Also shown in Fig. 4 is a baseline measurement that was made using the same sequence just prior to the water sample, but without any water present. This baseline gives an accurate measure of the remnant VOC load on the air and water PCs. Both chromatograms were analyzed using the NIST AMDIS software[7]. The difference between the two chromatograms shows the VOCs present in that particular water sample with some small residue of predominantly dimethylamine and acetone carried over between measurements.

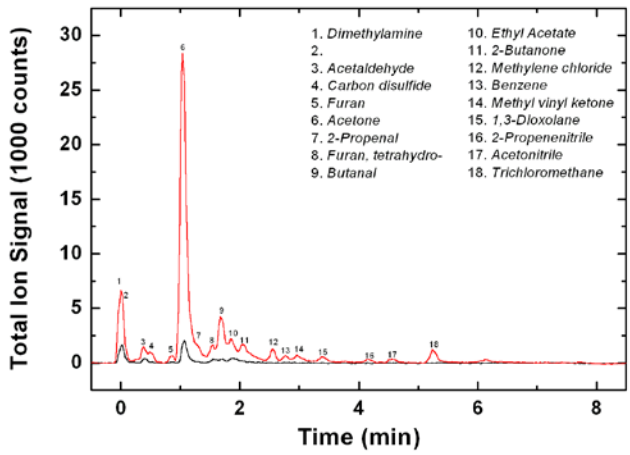


**Figure 4. Ion chromatograms for a 10 µL water sample (red) and a baseline (black). The water sample was prepared with 10 ppb each of ethanol, acetone, ethyl acetate, and acetonitrile. Enumerated identifications from the NIST AMDIS program are also shown, indicating 15 additonal compounds sourced from the deionized water that was used to create the sample.**

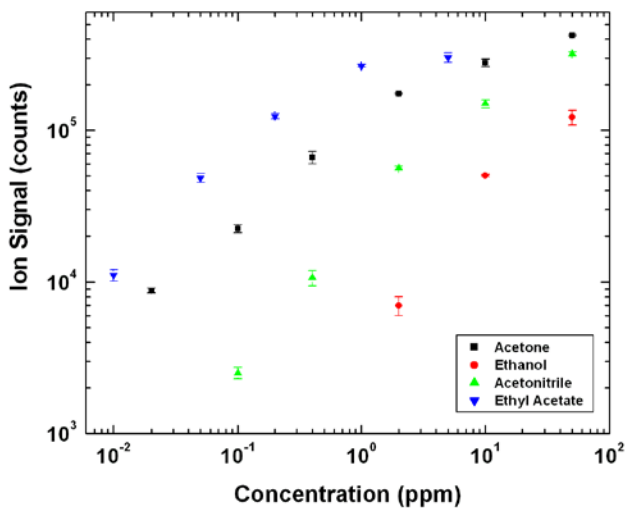


**Figure 5. Calibration curves for acetone, ethanol, acetonitrile, and ethyl acetate obtained with the first generation of pre-concentrator water sampler using a quadrupole ion trap mass spectrometer as the sensor.**

While only three of the four test compounds were observed in the water chromatogram, fifteen additional compounds were detected. All peaks were successfully identified by the NIST AMDIS software with the exception of peak 2, which is a small-signal, co-elution with peak 1. Despite AMDIS recognizing a co-elution occurred, there was insufficient signal to provide positive compound identification for this peak. The absence of ethanol in this measurement is expected as the sample concentration is below the minimum detection level of the GCMS for ethanol. The appearance of the additional VOCs is attributed to the total organic content of the deionized water used to prepare the samples. Deionized water has total organic content typically < 500 ppb and distributed amongst a variety of VOCs. As such, it serves as an additional means of estimating detection levels and is also independent of the method used for sample preparation. The signal level for acetone in this run would yield a minimum detection level of ~0.2 ppb. Having dual PCs would allow this system to perform multiple water samples, with multiple desorptions from the water PC used to load the air PC for a single desorption and improve the sensitivity and minimum detection level further.

Several performance issues were identified while developing the PC water sampler. The first issue realized was that calibration curves were non-linear and compound-specific. A set of calibration curves for the first generation of PC

water sampler we developed is shown in Fig. 5 for ethanol, acetone, ethyl acetate and acetonitrile as measured with a quadrupole ion trap MS sensor. Fig. 5 reveals that there are variations of over two orders of magnitude for the same concentration of different analytes. The minimum detection limits can be estimated from Fig. 5 by identifying the concentration that would yield 100 counts. Estimates for the minimum detection limits for acetone, and ethyl acetate are well below 10 ppb, while acetonitrile has a minimum detection limit of ~10 ppb and ethanol has a minimum detection limit of close to ~100 ppb. The absence of ethanol at 10 ppb from the sample measurement in Fig. 4 is in agreement with this estimate for minimum detection limit. The wide spread in detection limits is due in large part to the nature of the sorbent material used in the PC. An analyte's affinity for the sorbent will depend on not only temperature, but the molecular size, chemical structure, and polarity of the analyte. When using a quadrupole ion trap MS as the sensor, as was the case for Figures 4 – 6, the MS also introduces a decrease in sensitivity for any light VOCs that have major interferences with water (15 – 20 amu) and air (26 – 34 amu). Most VOCs are not significantly impacted by these interferences, however methanol and to a lesser extent, ethanol are severely impacted. A decrease in signal with increasing concentration was also observed for some of these species at elevated concentrations that hints at saturation effects for the PC.

The second issue is that it is crucial to know precisely how much water was sampled during each measurement. Water samples in this work were nominally 100 – 200 mL. However, large variations in sampled water volumes were observed due to the severe flow restriction presented by the water PC. This excluded the possibility of using the sample pump's pre-determined flow rate as an estimate of sample volume. Ultimately, sampled water volumes had to be measured using graduated cylinders or mass balances. While this is not necessarily an issue for laboratory work, the desire is to have an autonomous system for space exploration.

Finally, it was observed that the flow rate through the water PC degraded over time until at some point, the flow would become completely blocked. Examination of the carbon molecular sieve afterwards revealed fracturing that could have arisen from hydraulic pressure variations transmitted from the sample pump, repeated thermal cycling with liquid water present, or some combination of the two.

### B. Split-Splitless Water Sampler

As with the PC water sampler, the split-splitless water sampler performs air analyses in the same fashion as VCAM. Its air analysis performance is comparable to VCAM's despite modification of the GC to install the split-splitless injector assembly between the air PC and the GC column. The reduced component count in the split-splitless water sampler over the PC water sampler provides simpler operations. A water analysis is identical to an air analysis but with the state of the rotary valve toggled to open the water sample loop to the inlet.

The design of the split-splitless water assembly affords many options for performing liquid analysis. Conventional split or splitless injections can be performed just as with air analysis. Each of the split and splitless operations can be performed hot or cold. The water sampler can perform solvent evaporation, similar to the approach outlined in Ref. 8, whereby liquid is discarded prior to injection into the GC column. In this application however, the solvent is water and many of the target VOCs will evaporate before the solvent. This split-splitless injector also allows one to perform programmed temperature vaporization.

All of the measurements presented here used hot split injections with the split-splitless injector heater isothermal at 350 °C. A 10 µL sample of liquid water will evolve into ~ 28 mL of vapor at atmospheric pressure. As this evolved vapor volume is 280 times the internal volume of the injector assembly, the bulk of the evolved gas must be discarded through the split and vent ports to maintain isobaric conditions on the GC column and can be achieved with precisely-timed pulsing of the split and vent valves combined with varying the inlet pressure. However, in this isobaric case the majority (> 99%) of the analyte will be

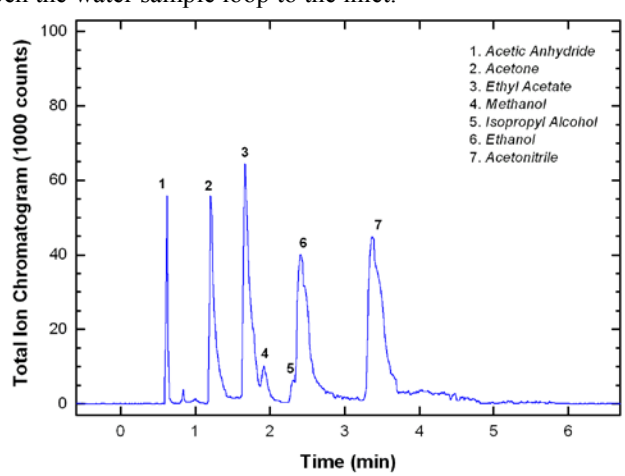


**Figure 6. An ion chromatogram for a 10 µL water sample using the split-splitless water sampler in a hot split mode using a pressure pulsed injection. The water sample in this measurement was prepared with 10 ppm each of acetone, methanol, ethanol, ethyl acetate, and acetonitrile. Enumerated identifications from the NIST AMDIS program are also shown. All of the component VOCs were detected with the addition of isopropyl alcohol, likely sourced from the ethanol used to prepare the sample, and acetic anhydride.**

discarded through the split-vent port. A pressure-pulse technique is employed that involves elevating the inlet pressure up to 150 PSI during the initial liquid injection to force as much of the evolved vapor into the GC column as possible before venting and restoring nominal GC column inlet pressures of 15-25 PSI. Most of the VOCs of interest have boiling points below that of water so that the evolved vapor is enriched for these compounds.

An ion chromatogram for an injection of liquid water with 10 ppm each of acetone, methanol, ethanol, ethyl acetate, and acetonitrile is shown in Fig. 6. This chromatogram shows excellent sensitivities for all of the compounds with minimum detection levels well below 1 ppm for all but methanol. There is some peak-shape degradation for elutions of ethanol and acetonitrile that can be improved by applying a thermal ramp to the GC column, which for this measurement was kept isothermal at 40 °C.

The capability of the split-splitless water sampler to effectively separate water from VOCs, as demonstrated in Fig. 6, is in large part a product of the ability of the GC column to retain water. The columns used here are DB-Wax columns that have a very high polarity phase of polyethylene glycol. Typical retention times for water are 20-40 minutes and provide ample time for light VOCs to elute through the GC column.

### C. Thermal Conductivity Detector

Some preliminary work has been carried out in characterizing the GCs and water samplers discussed here with a thermal conductivity detector (TCD). A TCD can be used in conjunction with a mass spectrometer as it is non-destructive. A TCD can also be used stand-alone for those situations where samples are well-characterized and no unknowns are anticipated to be present in the samples. In these cases, excluding the mass spectrometer can offer significant reductions in mass, volume, and power as a TCD does not require vacuum chambers and pumps.

The TCD tested here was a Vici-Valco model TCD2 and was initially tested without the use of PC or split-splitless injection in order to demonstrate detection levels and linearity. The TCD was connected to a 6-port, 2-way rotary valve with a 10 µL external sample loop. Air samples were prepared by injecting liquid VOCs into 1L tedlar bags filled with UPC-grade helium. Dilutions were made by extracting 10 mL or 100 mL aliquots from these bags and transferring them to separate bags filled with UPC-grade helium to give precise 100:1 or 10:1 dilutions respectively.

The results for measurements of an air sample made containing 3300 ppm of acetone, 2500 ppm of ethyl acetate, 6000 ppm of methanol, 4200 ppm of ethanol, and 4600 ppm of acetonitrile, along with those for 10:1 and 100:1 dilutions of the same sample are shown in Fig. 7. The effect of diluting the VOCs is evident in the reduction of peak heights for peaks (2) – (6), while the heights of (1) and (7) remain constant. The TCD tested here in this configuration has a minimum detection level of ~10 ppm for those VOCs tested and can be improved upon significantly with better temperature stabilization, heater control, and filtering.

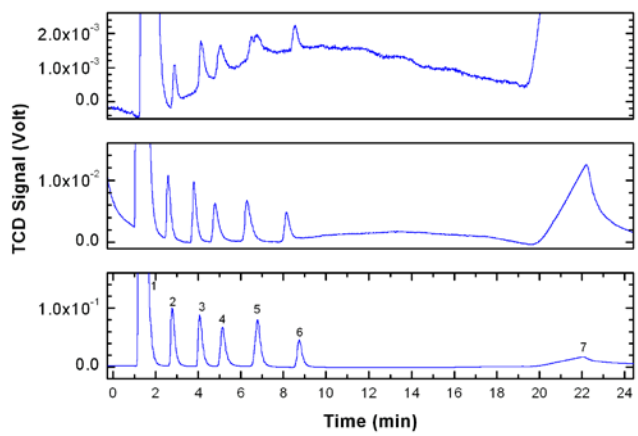


**Figure 7. (*bottom*) Chromatogram for a 10 µL air sample with 3300 ppm of acetone (*2*), 2500 ppm of ethyl acetate (*3*), 6000 ppm of methanol (*4*), 4200 ppm of ethanol (*5*), and 4600 ppm acetonitrile(*6*). Elution peaks (*1*) and (*7*) correspond to air and water, respectively. (*middle*) A chromatogram for a 10:1 dilution of the same air sample used in the bottom measurement. (*top*) A chromatogram for a 100:1 dilution of the same air sample as used in the bottom measurement.**

## IV. Conclusion

Two methods for introducing liquid samples into a GCMS have been studied and two water sampling systems have been developed as part of this investigation. Both systems have successfully detected VOCs in prepared water samples at concentrations at, or below, 1 ppm. A path for miniaturization to a MEMS platform for both water samplers has been identified and will be addressed in future efforts. The PC water sampler described here provides extremely-high sensitivities. These unrivaled sensitivities come at the expense of increased system complexity and shortened operational lifetimes. The PC water sampler developed here relies on sorbent materials, as well as vaporizing water which limits its ability to perform analysis of inorganic material in water. The split-splitless water sampler offers high sensitivities with a robust platform and linear response. It is compatible with a wide range of

applications that includes on-column injection of liquid water into a GCMS, as well as performing sample introduction with electrospray ionization or plasma ionization to process water directly with a mass spectrometer. These will be the subject of future investigations to expand water analysis to include detection of trace metal ions in water.

## Acknowledgments

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