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Characterization of ion processes in a GC/DMS air quality monitor by integration of the instrument to a mass spectrometer

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The air quality monitor (AQM), which included a portable gas chromatograph (GC) and detector was interfaced to a mass spectrometer (MS) through introducing flow from the GC detector to the atmospheric pressure ion source of the MS. This small GC system, with a gas recirculation loop for carrier and detector make-up gases, comprised an inlet to preconcentrate volatile organic compounds (VOCs) in air, a thermal desorber before the GC column, differential mobility spectrometer (DMS), and another DMS as an atmospheric pressure ionization source for the MS. Return flow to the internally recirculated air system of the AQM's DMS was replenished using purified air. Although ions and unreacted neutral vapors flowed from the detector through Viton® tubing into the source of the MS, ions were not detected in the MS without the auxillary ion source, ^{63}Ni as in the mobility detector. The GC-DMS-MS instrument provided a 3-D measurement platform (GC, DMS, and MS analysis) to explore the gas composition inside the GC-DMS recirculation loop and provide DMS-MS measurement of the components of a complex VOC mixture with performance significantly enhanced by mass-analysis, either with mass spectral scans or with extracted ion chromatogram. This combination of mobility spectrometer and mass spectrometer was possible as vapors and ions are carried together through the DMS analyzer, thereby preserving chromatographic separation efficiency. The critical benefit of this instrument concept is that all flows in and through the thoroughly integrated GC DMS analyzer are kept intact allowing a full measure of the ion and vapor composition in the complete system. Performance has been evaluated using a synthetic air sample and a sample of airborne vapors in a laboratory. Capabilities and performance values are described using results from AQM MS analysis of purified air, ambient air from a research laboratory in a chemistry building, and a sample of synthetic air of known composition. Quantitative measures of a stand-alone AQM are disclosed for VOCs in the ppb to ppm levels with average precision of 5.8% RSD and accuracy from 4% to 28% error against a standard method.

Introduction

Habitation on the International Space Station (ISS) commonly involves periods of 6 months or more with crews in an environment that is largely closed, forming a direct association between air quality and human health.[1] Air quality is assessed through regularly scheduled chemical analyses of the recirculated air for volatile organic compounds (VOCs) that may accumulate to levels of high part-per-billion (ppb) from ordinary activities. Until recently, VOCs were determined mainly using grab samples taken on board and returned to Earth for analyses using gas chromatography-mass spectrometry. Contingency events, such as thermo-degradations, system leaks, or chemical spills, present another level of challenge to safety, and immediate, on-board measurements of air quality are necessary. Such near real-time or on-demand analysis had been provided from 2001 by the volatile organic analyzer (VOA), a gas chromatograph with an ion mobility spectrometer detector and a preconcentration sorbent inlet. The VOA was a rack mounted instrument and provided analytical capabilities to quantitatively determine ~23 VOCs on schedule or on demand until July 2009 when the instrument was decommissioned.[2-4] A successor instrument, the air quality monitor or AQM, is a gas chromatograph with a differential ion mobility spectrometer as the detector and also a preconcentration inlet. Two portable AQMs are currently in service aboard the ISS[5-6] and allow flexibility for air monitoring as the 2 AQMs are equipped with different liquid-phase chromatographic columns. The inlet and detector are identical in the 2 AQMs and can either be operated independently in separate locations in ISS or in a single location to use differences in chromatographic behavior.

In differential mobility spectrometry (DMS), a variant of ion mobility spectrometry (IMS), ions are characterized for mobility coefficients at two extremes of an asymmetric waveform where electric fields may reach 30 kV/cm at 1.2 MHz.[7] The difference in mobility in the low and high fields of the waveform is the basis for separation of ions and assignment of identity. During the past decade, micro- and sub-micro geometries for drift tubes in DMS have emerged with several practical advantages including simple drift tube design without ion shutters or aperture grids as found in conventional drift tubes for IMS.[8-11] Additionally ions of positive and negative polarity, which are transported through the

drift tube by gas flow, can be measured simultaneously. The instrument's small size and ambient pressure operation (no vacuum) has resulted in a highly portability instrument with limits of detection approaching 10 pg. As with other embodiments of IMS, calibrations remain stable for years as previously demonstrated with VOA. Disadvantages of DMS are shared with other mobility spectrometers or even mass spectrometers with ambient pressure ionization (API) sources. In an API source, where ionization of sample occurs through chemical reactions, linear ranges for response are often narrow with ready saturation of response (greater number of analyte molecules than available charge transfer ions) and competitive charge exchange. This restricted pool of charge for ionization affects analytical reliability for simultaneous analysis of all ion species that are formed from complex mixtures. This latter limitation can be improved significantly though the addition of a gas chromatograph to prefractionate a sample mixture, thereby simplifying the ionization chemistry. Ion mobility spectra become qualitatively and quantitatively reliable when substances are introduced singularly into the ion source and the advantages are realized through simple patterns in spectra where commonly only a single ion peak is derived from a substance.[12,13] An additional benefit for a two-dimensional measurement is a lessened demand for high resolving power in the mobility analyzer.[14] Some have attributed the greater part of analytical performance in a GC-DMS instrument to the gas chromatograph; however, these studies were made with known chemical standards. The benefits of two dimensions of analyses with unexpected and unknown substances have not been described for a GC/DMS instrument. While DMS has shown response for a wide range of VOCs, a GC/DMS is suitable for analysis of even complex mixtures such as pyrolyzate of bacteria.[15,16]

The first version of the AQM was developed by Sionex Corp. to specifications from, and in significant cooperation with, the Toxicology Group at NASA's Johnson Space Center and includes a self-contained GC, which operates with recirculated purified air as a carrier gas, thus negating the need for gas cylinders (eg, helium) that are typically required by commercial gas chromatographs. The inlet is based on preconcentration of VOCs on an adsorbent trap with flash thermal desorption to the GC column. The DMS detector is also operated in purified air, near ambient pressure, and provides detection limits near 1 to 10 ppb for substances with reasonably strong proton affinities or strongly electronegative atoms such as halogens. A second version of AQM, built at Draper Laboratory, is termed the microAnalyzer™ v2.0, integrates the sorbent trap, low thermal mass GC, microDMx sensor, and a Windows XP computer in a 3 kg, 25.4 cm × 15.2 cm × 13.2 cm size package with peak power demand nominally of 72W. Considering the importance of the AQM in monitoring VOCs, routine assessments of performance and refurbishment or repair may be essential components of long-term ground-based support for uninterrupted air quality monitoring on ISS. An aspect of performance includes chromatographic efficiency and retention behavior with standards and in some instances with unknown substances. Another facet is the efficiency of the air purification in a recirculation loop in the AQM and, in long-term operation, the appearance of impurities from off-gassing of materials, which is a consideration with ultra-trace instruments. The capabilities to explore and understand these concerns would be enhanced through mass analysis of the composition of the recirculated gas atmosphere of the instrument or mass analysis of substances eluting through the GC into the DMS. A requirement for such a diagnostic capability is to preserve the integrated features of the AQM with changes sufficiently minor that the instrument could be returned to qualified use on the ISS. A new configuration or concept of combining DMS and MS was developed here where effluent from the DMS drift tube was passed into the ion source of an atmospheric pressure ionization-mass spectrometer. This effluent was re-ionized for mass analysis and provided:

a. A diagnostic platform for AQMs that allows routine and experimental testing or validation of performance.
b. An analytical instrument, GC-DMS-MS with an ambient air preconcentration inlet. This combination of components has not previously existed and may have independent value for chemical measurements. The enhanced analytical capability for such an instrument and relatively facile assembly may have significant beyond NASA interests, which includes the fields of metabolomics, biomarkers, and other analyses performed on samples with complex matrices.

The combination of the AQM with a tandem API mass spectrometer and aspects of performance are described. In addition, the quantitative performance of an AQM is given in a first disclosure.

Experimental

Instrumentation

The mass spectrometer was a model API-*III* tandem mass spectrometer (MS/MS) from PE-SCIEX (Toronto, Ontario, Canada). The MS/MS was equipped with an Apple PowerMac 7100/66 computer and API Standard Software, v2.5.1 (PE SCIEX). A detailed description of this spectrometer has been given and operating conditions were: vacuum interface plate, 0.6 kV, L6, -40 V; orifice (OR) potential, -60 V; R1 or Q1, -40, V; L2, -53 V; R2 or Q2, 0 V; L3, -45 V; R3 or Q3, -40 V; L4, -40 V; operating vacuum, 2×10^{-5} torr; and L5, 250 V. Lens voltages were unchanged for positive and negative ions. Mass scans were m/z 10 to 400 in 1 s unless noted. The corona discharge source supplied with the API-III was replaced with a 10 mCi foil of ^{63}Ni held in a metal body and thermostated to 80ºC, the temperature of the ion source in the differential mobility spectrometer (see below).

A GC-DMS was the AQM (Sionex Corp, now Draper Laboratory, Boston, MA). A block diagram of the AQM is shown in Figure 1A. A sampling pump acquires an air sample for 5 s or 10 s at ~140 mL/min. The sample flows through a one-way check valve and the preconcentrator adsorbent bed composed of 60/80 mesh Carbopack B (3.7 mg) and Carboxen 1000 (4.0 mg). An option is available to flush the preconcentrator with clean, dry air to remove trapped moisture by pulling the ambient air through a purge cartridge prior to it flowing through the preconcentrator. The trapped VOCs are transferred from the preconcentrator to the GC column by the

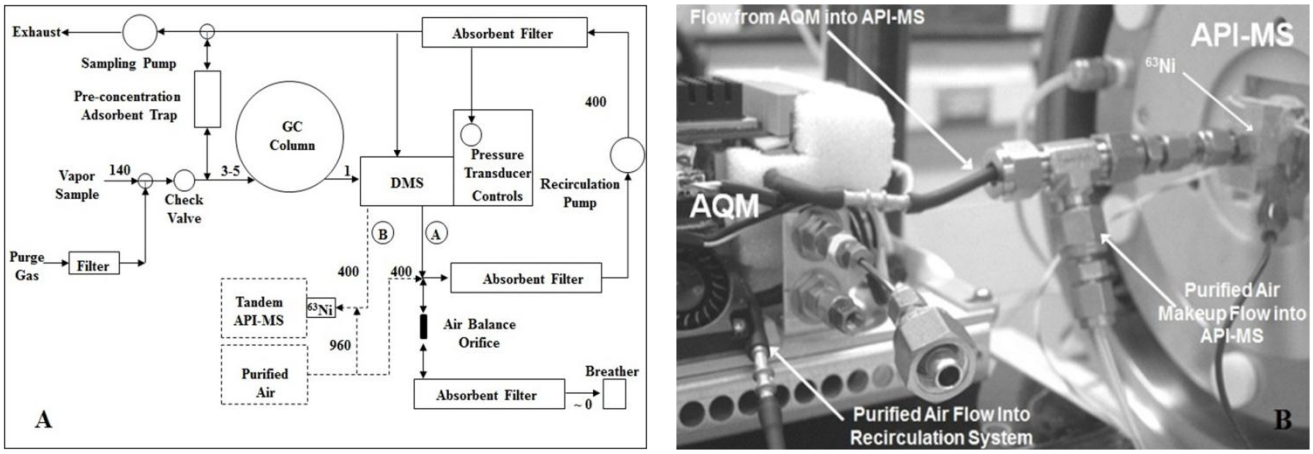


Figure 1 (A) Detailed schematic showing flow pattern and flow rates (mL/min) for AQM DMS MS includes the original flow (solid lines) and modifications for interfacing the tandem mass spectrometer (in grey box and dotted lines) to sample flow from the AQM recirculated gas system. **(B)** Photograph of the AQM region showing the tube that carries exhaust from the DMS drift tube into a "filter" and into the recirculated flow system. A cut at the location shown, with stainless steel tube unions and additional Viton® tubing will allow the vapors from the DMS to be passed directly to a DMS MS operated in series with the AQM. Viton® tubing is 4 mm OD.

carrier gas flow. The GC column is 15 m × 0.25 mm, bonded DB5 (1 µm 5% phenyl polydimethylsiloxane (Agilent, Santa Clara, CA). During cleaning cycles, the preconcentrator is heated to 325ºC for 40 s. The GC column gas flow was calculated at approximately 1 mL/min and the makeup gas flow was ~400 mL/min into the DMS analyzer. The recirculation system uses only air for the GC carrier gas and detector makeup gas. The required GC column pressure is obtained when, at initial start-up, the recirculation pump pulls air from the environment until the specified pressure is obtained. The air is cleaned when passing through a scrubber after exiting the DMS cell. The scrubbers (including the purge cartridge) contain 20/45-mesh molecular sieves (HCRMS) and a small amount of Carboxen 569, to remove moisture and VOCs, respectively. The computer for the AQM is PicoITX with wireless feature with Windows XP operating system. The Sionex software controls the instrument parameters (such as temperatures and pressures) and performs the data reduction. The method files are uploaded to the computer either from another computer or via wireless connection. Results are processed on the unit and are displayed on the graphical user interface (GUI) and downloaded via USB drive or wireless to ground-based computers.

Interface of AQM to API Mass Spectrometer. Schematic and principles for interfacing a single planar micro DMS interface to atmospheric pressure mass spectrometry were developed and described in early publications.[17,18] The specific technical challenge in this work was the requirement to integrate the API mass spectrometer in to the recirculation loop of the AQM without disturbing the operation regime of the AQM system. The solution is presented by schematic shown in Figure 1A. The gas line, labelled A, was removed and tubing, labelled B, was placed into the instrument as shown. In practice, this means a cut in the Viton® tube coming from the DMS and re-routing the flow with additional Viton® tubing into the ion source of the API-MS (Figure 1B). Gas flow leaving the DMS drift tube at 400 ml/min passes through a 4 mm OD, 2 mm ID Viton® tube and is combined with 960 mL/min of purified makeup gas to equal the pumping speed of the vacuum chamber of the mass spectrometer. Ions measured in the DMS are neutralized on the Faraday plate detectors and flow, along with any un-reacted neutrals passing through the DMS drift tube, to the API mass spectrometer. Gas flow normally returning for gas purification through the gas recirculation system of the GC-DMS is replenished with purified air from an external gas cylinder that is directed into the adsorbent filter leading to the recirculation pump. Excess flow if any is vented through the breather.

Mass spectra of positive and negative ions were collected in separate mass spectrometry runs of the same sample, however both ion types were created and analysed by DMS in each run.

Reagents and Standards

Synthetic mixture included 7 substances, mg/m3 (ppb): acetaldehyde, 1.19 (660); ethanol, 3.95 (2097); dichloromethane, 184 (529); Trimethylsilanol, 2.64 (716); methylethylketone, 2.08(686); n-butanol, 1.96 (648); and ethyl acetate, 2.02 (561). These were prepared in a solid canister of stainless steel according to NASA procedures. The concentrations were determined by GC/MS following a modified Environmental Protection Agency's TO-15 protocol.[19]

Procedures

General Procedures. The AQM is programmed to operate in the following sequence. At starting time (0 s), the sample pump starts gas flowing through the sampling line, check valve, and

preconcentrator to vent. Timing is under computer control and after 10 s for pump stabilization, 5 s are commonly used to enrich an air sample. The adsorbent trap is 40ºC during sampling. After the sampling pump is stopped (15 s), 2 are switched, the preconcentrator is disconnected from the sampling line, and instead is connected to the recirculation loop
of the AQM with clean air flowing at 3 to 5 mL/min through the preconcentrator into the GC column. Then the trap is flash heated to 300□C and VOCs on the trap are desorbed directly into the GC column. The AQM has an instrument method file, which defines the timing for sample acquisition, preconcentrator heating/desorption, and GC temperature heating profile. The GC temperature profile (rate of heating and/or length of the GC run) is the only variation in the instrument methods between units. Additionally, a set of unique controls of the AQM including sample acquisition are loaded on to each instrument. The GC methods provide the parameters for locating the peak for each compound in the target list. Each AQM unit has a unique set of GC methods though most parameters are very similar. Typical parameters were (unless noted): sample time, 5 s: 120 s isothermal period at 35ºC; GC column temperature ramp to 140ºC in 120 s; post-analysis cleaning of GC column at 150ºC for 190 s.

Quantitative Performance of AQM as Standalone Instrument. Calibration standards were created in 6 L pressurized canisters and a 5-s sample was acquired for each data point, followed by a 10-s purge (laboratory air). Standards at 5 different concentrations were used to generate the data required to build calibration curves for each compound. Once calibrated, a challenge mixture was sampled to determine accuracy. The average of 3 or 4 samples (external sample line passivation led to discarding 1 sample for some compounds)

Analysis of Purified Air (internal gas control). Purified air was regarded as air already inside the flow path of the AQM inlet and the preconcentrator. Thus the purified air measurement includes only the air inside the flow path between check valves. No sample was acquired, but all other events (preconcentrator and GC temperature ramps, etc.) in the method described above were completed. In this, the purified air sample also closely resembles an instrument control, though sample flow into the DMS cannot be excluded for a true instrument control.

Analysis of Laboratory Air. Unfiltered ambient air from the laboratory was sampled and analyzed by the AQM and AQM-MS combination with 10-s sample time. Other parameters were standard as used for analysis of purified air.

Analysis of Synthetic Air. Flow of sample from the pressured gas cylinder was begun 10 s in advance of the measurement to passivate surfaces and provided a consistent composition of sample to the AQM. Measurements were standard except the sample time was 10 s.

Results and Discussion

Quantitative Performance of AQM as Independent Analyzer

The AQM's quantitative performance that includes variance for sample enrichment and thermal desorption of the trap is shown in Table 1 from replicated determinations of VOCs in a

synthetic mixture with a range of concentrations. The number of replicates was 4 for most samples and 7 for the lowest concentration, which reach into the tens of ppb (s). The chemicals include those of toxicologic significance for the ISS, with some being strongly polar substances. The percentage relative standard deviation (%RSD) over the entire set of measurements ranged from a low of 0.7 for ethyl acetate at 235 ppb to a high 20.4 for acetaldehyde at 117 ppb. The only significant trend in Table 1 is the values for acetaldehyde below 500 ppb where %RSD are 2 × or 3 × the overall value. The overall %RSD for all chemicals at all concentrations from ~22 to 4504 ppb was 5.8 and even alcohols, which are polar molecules and exhibit adsorptive behavior in inlets and columns of gas chromatographs, showed repeatability largely at or below the overall %RSD. This level of repeatability, which includes collection of the sample and thermal desorption from the preconcentrating inlet at trace levels, was obtained from direct measurements without corrections using an internal standard calibration.

Table 1. Results from Quantitative Determinations of VOCs
was used to determine accuracy. At the lowest concentration, seven replicates were used to assess detection limit.

	Acetaldehyde	Ethanol	Dichloromethane	Trimethylsilanol	2-butanone	Ethyl Acetate	n_Butanol
Concentration (ppb)	**59**	**121**	**28**	**50**	**28**	**22**	**33**
Average*	0.0277	0.2981	0.2094	0.2169	0.0711	0.0926	0.0889
STDEV	0.0037	0.015	0.0055	0.0258	0.0039	0.0056	0.0074
%RSD	13.5	5	2.6	11.9	5.5	6.1	8.3
Concentration (ppb)	**117**	**254**	**58**	**101**	**52**	**44**	**68**
Average*	0.0403	0.514	0.3285	0.5133	0.1223	0.1623	0.1935
STDEV	0.0082	0.0241	0.0119	0.027	0.0055	0.0052	0.0064
%RSD	20.4	4.7	3.6	5.3	4.5	3.2	3.3
Concentration (ppb)	**482**	**990**	**245**	**425**	**262**	**235**	**265**
Average*	0.11	1.206	0.8988	1.1798	0.3148	0.378	0.3538
STDEV	0.0147	0.0123	0.0182	0.0267	0.0204	0.0028	0.0126
%RSD	13.3	1	2	2.3	6.5	0.7	3.6
Concentration (ppb)	**660**	**2097**	**529**	**716**	**686**	**561**	**648**
Average*	0.1625	1.6385	1.0295	1.7175	0.585	0.6343	0.401
STDEV	0.0122	0.09	0.0269	0.1736	0.0578	0.0438	0.0184
%RSD	7.5	5.5	2.6	10.1	9.9	6.9	4.6
Concentration (ppb)	**1530**	**4504**	**1446**	**2022**	**1654**	**1308**	**1190**
Average*	0.1768	2.1063	1.3285	2.1958	0.946	0.9225	0.4628
STDEV	0.0144	0.0239	0.025	0.0507	0.0171	0.0259	0.0211
%RSD	8.1	1.1	1.9	2.3	1.8	2.8	4.6

Quantitative accuracy for VOCs in airborne vapors was determined using synthetic mixtures after the AQM had been calibrated to provide concentrations for each chemical and through comparison to those obtained by the standard method, a gas chromatograph with mass spectrometer. Data analysis was wholly automated without any interpretation by the user. The results from these measurements are shown in Table 2, and the accuracies ranged from 3.4 to 27 for chemicals in the DB5 mixture, apart from acetaldehyde at 92. The extreme error was attributed to the co-elution of water with the acetaldehyde, even with the purge. This co-elution distorted the peak finding and processing algorithm, but the measurement could be recovered by manual intervention. This was not done here; however, subsequent improvements include manually analyzing

Table 2. Results of Determination of VOC Concentrations (ppm) in Synthetic Mixture for AQM and GC-MS Reference Method. Also Shown is theAbsolute error Against the Reference Method.

Compound	AQM average	GC MS average	% Difference
Acetaldehyde	0.023	0.28	-92
xEthanol	0.40	0.43	-3.4
Dichloromethane	0.12	0.098	27
Trimethylsilanol	0.20	0.20	-0.6*
2-Butanone	0.096	0.11	-7.4
Ethyl Acetate	0.088	0.11	-17
n-Butanol	0.13	0.12	17

acetaldehyde on a different GC column (V-624MS). Significantly, there was no systematic error in results from the AQM. A complete description of quantitative performance with a complex integrated instrument is complicated and should be addressed in future efforts. The precision and accuracy of AQM, for purposes here, were seen as suitable for continued development with GC DMS MS. While the values for precision and accuracy of an AQM have not been previously disclosed, results compare favorably to the same measurements with a predecessor AQM, a station detailed test objectives (SDTO) model that shared nearly identical technology without the on-board computer or purge.

Results of Sampling and Analysis of Purified Air

Data obtained by sampling purified air, used as an internal gas quality control, is shown in Figure 2A as contour plots of intensity, retention time, and compensation voltage for both positive (left) and negative (right) polarity. A prominent feature in spectra of each polarity for the DMS detector is the reactant ion peak (RIP) at -9.7 V in positive polarity and -11.8V (Figure 2B) which is formed in the ^{63}Ni ion source through beta-emission into air at ambient pressure. Mass spectra of the RIPs obtained during periods of "clean" regions of the chromatogram (eg, 0 to 50 s), where substances were not eluting from the column and are shown in Figure 2C. The mass spectra contained major ions that are expected from such an ion source with purified air and included, in positive polarity, m/z 37, 55, and 73 for hydrated protons $(H_2O)_nH^+$ where n=2 to 4, respectively. In the negative polarity, ions for $O_2^-(H_2O)_n$ (n=0 and 1) should be seen and were at m/z 32 and 50. This should be the dominant ions in negative polarity and the presence of other ions at m/z 76 for CO_4^- (O_2*CO_2^-) and m/z 94 for O_2*CO_2^-*H_2O disclose that the internal atmosphere of this AQM contained an excessive level of CO_2. Although ions derived from CO_2 are commonly observed in API instruments, relative abundances here were excessive, and this is discussed elsewhere.

Additional substances are seen in the contour plots at particular compensation voltages and retention times, which can be associated with elution temperatures from the temperature ramp applied to the GC column. In each instance where a substance elutes in Figure 2, the intensity of the RIP decreases as a substance elutes consistent with slow kinetics for the formation of reactant ions and fast kinetics for product ion formation according to Equation 1.

$$\underset{\text{analyte}}{M} + \underset{\text{reactant ion}}{H^+(H_2O)_n} \text{--------} > \underset{\text{product ion}}{MH^+(H_2O)_{n-1}} + H2O \quad (1)$$

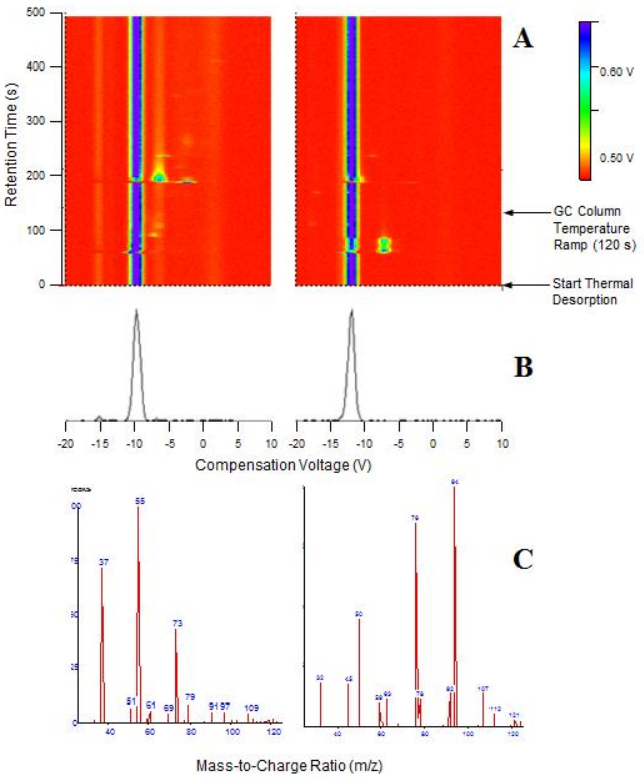


Figure 2 (A) Two-dimensional plot (positive polarity on left and negative polarity on right) of ion intensity, retention time, and compensation voltage from analysis of a purified air sample (blank control). **(B)** Differential mobility spectra for reactant ion peaks. **(C)** Mass spectra of positive and negative reactant ion peaks

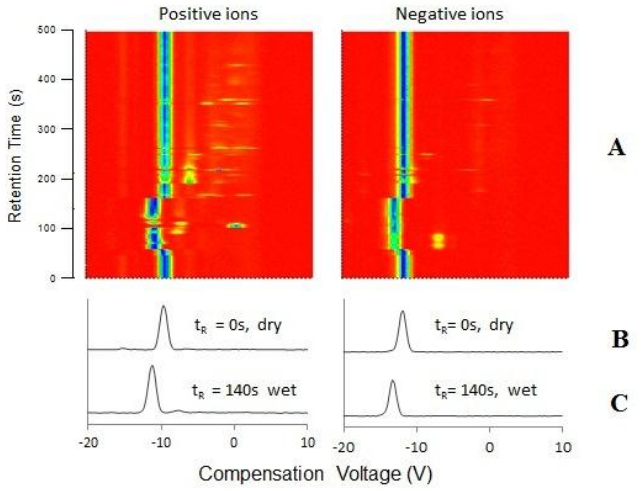
Product ions derived from a substance exhibit characteristic compensation voltages (CV) and retention times (t_r). Pronounced response is seen for a substance appearing in positive polarity at t_r of 200s with a CV of -5.5V and in negative polarity at t_r of 70s with CV of -7 V. The adjacent second peak in positive polarity is seen as the protonated monomer from a dependence of ion identity based on vapor concentrations where the monomer appears first early in the peak elution, is replaced with dimer as concentration in the GC peak increases, and then returns to monomer as concentration decreases on the end of the GC elution peak. Thus, a single constituent is responsible for this pattern of 2 peaks in the contour plot. Efforts to mass analyze constituents by AQM-API-MS were unsuccessful since the concentration of this substance was too low to be detected by the mass spectrometer. Although the peaks appear pronounced in the graphic, concentrations are in the low ppb range. These are thought to be vapors arising from off-gassing of materials inside the AQM and do recede in intensity with time of operation of the instrument, though they are never fully eliminated. Roughly 5 peaks are seen elsewhere in the contour plot and concentrations are at the limits of detection of the instrument, ~1 ppb.

An ion also appears in this purified air sample, which could be considered an instrument blank as the air was internal to the instrument as residual volume, in negative polarity. The peak appears near the void volume in the manifold between the column exit and DMS entrance, at 64 s, and exhibits significant tailing to 82 s. During this elution time the mass spectra showed that the ion m/z 96 increases and is attributed to a cluster ion (O_2^-

SO_2) and is consistent with SO_2, a known contaminant from Carboxen, the material used in the inlet preconcentrator. This will be explored in a subsequent article.

Analysis of Laboratory Air

Measurements of VOCs in air sampled from the NMSU laboratory atmosphere are shown in Figure 3 as topographic plots or two- dimensional graphs. The plot in Figure 3A shows ~20 well resolved constituents in positive mode and additionally ~4 peaks of minor abundance in negative mode.



-Figure 3. Response of AQM to laboratory air sampling, with positive ion analysis on the left and negative ion analysis on the right. **(A)** Two-dimensional plot of ion intensity (color), retention time (vertical axis), and compensation voltage (horizontal axis). **(B)** Differential mobility linear spectra on the beginning analysis (t_R=0s), when recirculation loop is dry and DMS spectrum contains only reactant ion peak (RIP). **(C)** DMS spectrum for t_R =140s, when spectrum contains only RIP peak co-eluting with water vapor from the GC column.

The AQM was operated under the same conditions as in Figure 2 with the sample input opened for direct loading of unfiltered laboratory air for 5 s. Some of the substances arise from fugitive emissions of solvents and other substances from routine experimental work elsewhere in the laboratory or adjacent laboratories. However, air is also drawn from ambient air outside the Chemistry Building and has been associated strongly with vehicular traffic on University Ave, 20 m from the intake louvers of the air conditioning system, similar to that described in our earlier work.[20] A main importance of this measurement is to disclose the detection and separation by AQM of VOCs in a moderately complex mixture in ambient air concentration above the levels seen in the purified air control measurement (Figure 2). The plot in Figure 3 is also important from a method development perspective as all the peaks seen in Figure 2 should also be seen, and were, in Figure 3. The findings have another importance that concerns obtaining samples with elevated moisture, roughly 30% RH.

Sample Relative Humidity. Unlike the plot in Figure 2, where compensation voltage positions of the reactant ion peaks were unchanged throughout the GC elution time, the positions of the reactant ion peaks in both polarities undergo displacements during retention times between 60 to 150 s. In positive polarity, the peak is changed from -9.7 to -11.2 V and in negative polarity from -11.82 to -13.0 V (Figure 3B and Figure 3C). The peaks undergo a rapid change at 60 s seen in the topographic plot and then after 150 s it rapidly returns to normal positions, remaining constant during rest measurement time (500 s). The explanation is that during sampling of ambient air, both VOCs and water are retained in the sorbent trap and when the trap is heated, desorbed water enters the chromatographic column. The AQM sample purge was not used during this study. This change in water vapor was monitored with a Panametric moisture meter and levels of moisture in the effluent of the GC, when diluted into the flow to the DMS, increased from roughly 3.5 ppm to 6.5 ppm. While this change of moisture was sufficient to alter the hydration level of the reactant ions and develop new CV values, the mass spectra contained no new ions, suggesting the change was not associated with elution of VOCs or other gases. Changes observed in relative abundances of m/z 35 for $H^+(H_2O)_2$ decreased and m/z 73 for $H^+(H_2O)_4$ increased as anticipated from an increase in moisture and change in hydration levels. The m/z 55 for $H^+(H_2O)_3$ was relatively constant. All of these ions passed from the API source into vacuum through the mass spectrometer interface, and, thus, the measured quantitative distributions were considered inaccurate. Nonetheless, this was another instance where the mass spectrometer provided direct information on the atmosphere inside the AQM with direct measures (shift in hydrated forms of RIP) and indirect measures (no VOCs detected) for the feature between 60 to 160 s, now known as elution of water when the preconcentrator is heated. The use of a synthetic standard should provide experimental findings with internal consistency to demonstrate the performance of the GC-DMS-MS.

Analysis of Synthetic Air

Results from analysis of a synthetic VOC mixture are shown in Figure 4 for only ions of positive polarity, where the contour plot should contain ion peaks for each of the substances acetaldehyde, ethanol, 2-butanone, n-butanol, trimethylsilanol, and ethyl acetate in air at concentrations near 550 to 660 ppb, except for ethanol at 2.1 ppm. The plot shows as with prior measurements the reactant ion peak at compensation voltage of -8.79V and as with prior results, excursions in peak intensity and position occur as substances elute from the column, beginning with water at 50 s. Substances continue to elute until 420 s and this can be seen in as a line plot of the reactant ion peak vs retention time (from a vector placed at -8.79 V) which has been used in GC-IMS measurements as a type of inverse general response, analogous to other one-dimensional ionization detectors in gas chromatography. Elution times of substances are known and can be associated with ion peaks in the mobility spectra. These are shown in lines that connect peaks in Figure 4A to 4D that is ion intensity taken from a vector at CV of +0.61V. Peaks in the plot of extracted ion intensity can be assigned to each chemical in the synthetic mixture except those with CV positions between -4 to -6. Thus, acetaldehyde (~CV - 9V, poorly resolved from RIP) and ethanol (CV -5V) are not seen in Figure 4D. Ions at 280, 360 and 420 s are impurities in the mixture and are siloxanes.

The reactant ion plot from MS scanning during the AQM measurement is shown in Figure 4C for m/z 55 which is the reactant ion peak $H^+(H_2O)_3$ formed in the ^{63}Ni source of the API MS receiving flow from the DMS. The plot of intensity for the RIP from the MS is equivalent to that from the DMS (Figure 4B) with added selectivity arising from mass analysis. Consequently, the change in CV position from moisture, which causes a large excursion in the DMS response plot is not registered in the MS.

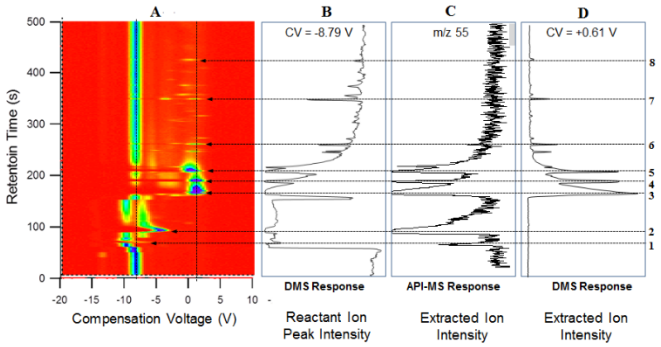


Figure 4. (A) Two-dimensional plot of positive ion intensity, GC (DB5) retention time, and DMS compensation voltage from analysis of a synthetic air sample that includes acetaldehyde (peak 1), ethanol (peak 2), trimethylsilanol (peak 3) ethyl acetate and 2-butanone (peak 4), and n-butanol (peak 5). Peaks 6 to 8 are not part of the synthetic mixture intentionally and are siloxane impurities. Selective plots are shown in **(B)** for the reactant ion peak from the DMS, **(C)** for the reactant ion peak at m/z 55 from the mass spectrometer, and **(D)** from extracted compensation voltage associated with proton bound dimers of the VOCs in the mixture.

The selectivity of response is seen in the peaks for acetaldehyde (peak 1) and ethanol (peak 2) that register minor and significant response against m/z 55. The diminished response to acetaldehyde is attributed to wetting of the reactant ion peak from co-elution of water and acetaldehyde. Other peaks in the MS plot can be assigned by known retention time to trimethylsilanol (peak 3), ethyl acetate and 2-butanone (peak 4), and 1-butanol (Peak 5). Ethyl acetate and 2-butanone elute on the tail of trimethylsilanol. Although these are not well separated in GC retention time or compensation voltage at a separation voltage of 900V for the DMS waveform, these peaks can be separated at 1200V in the compensation voltage axis.

The assignment of identity to peaks in Figure 4A from retention time alone is strengthened when combined with mass spectra as shown in Figure 5 for acetaldehyde, ethanol, and trimethylsilanol for 3 example substances. In the spectrum for acetaldehyde (MM 62), a protonated monomer (MH^+) at m/z 63 is present with significant abundances of the reactant ion peaks at m/z 37, 55, and 73. This is consistent with the diminished response exhibited by acetaldehyde in Figure 4C (peak 1). The spectrum for ethanol (MM 46) shows low intensity (<20% normalized to base peak) of a protonated monomer (m/z 47) and a near equal amount of MH^+H_2O. Instead, the concentration of ethanol is sufficient to push ion abundances to the proton bound dimer (m/z 93), and hydrate MH^+H_2O (m/z 111). There is in this spectrum also a proton bound trimer (M_3H^+) at mz 139. Trimers are not often seen in IMS instruments as ions usually pass through a purified gas atmosphere where ion lifetimes for trimers are below the drift times. In DMS, ions pass through the drift tube in a sample neutral rich environment, and formation of trimers is plausible though not well-studied. An alternative explanation is that the proton bound trimer is formed in supersonic expansion of the interface between the API source and the vacuum of the mass spectrometer chamber. The last example is seen with trimethylsilanol (MM 74) that forms a proton bound dimer (m/z 149), hydrate (m/z 167), and proton bound trimer (m/z 223).

Although mass spectra are valuable in chemical identifications, extracted ion plots combine detailed information on chromatographic performance and specificity of mass analysis of ions. Extracted ion chromatograms in Figure 6 are plotted for the product ion with best relative abundance and includes m/z 63, MH^+H_2O for acetaldehyde; m/z 111, MH^+H_2O for ethanol; m/z 91, MH^+ for silanol; m/z 145, MH^+ for 2 butanone; m/z 177, M_2H^+ for ethylacetate; and m/z 149, M_2H^+ for 1-butanol.

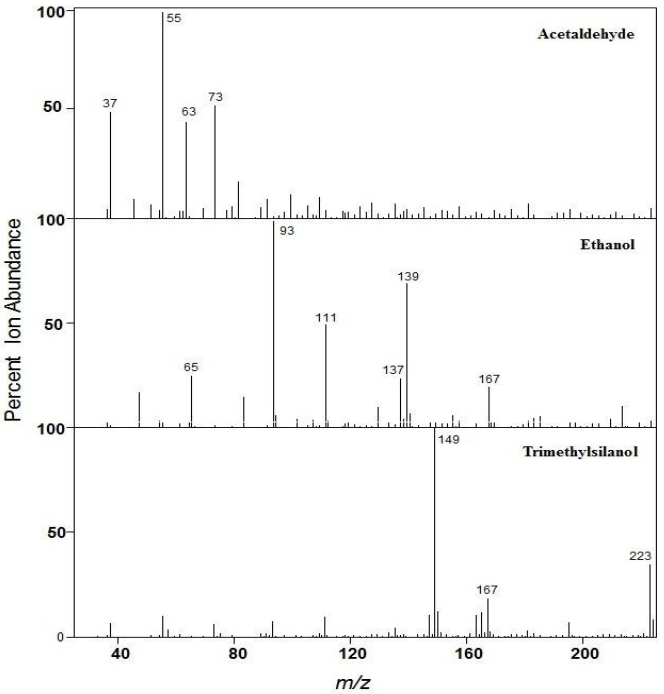


Figure 5. Mass spectra for substances that produced a protonated monomer (acetaldehyde), a proton bound dimer with hydrates (ethanol), and proton bound dimer in simple pattern (trimethysilanol).

Analysis of and parallels in peak shape can be made using Figures 4 and 6. For example, the peak shape for acetaldehyde is sharp, the first eluting peak, and precedes the relatively broad peak for ethanol with some chromatographic tailing. This is seen in the inverted extract ion plot for m/z 55 and the extracted ion plot for the proton bound dimer of ethanol. After ethanol, the elution of trimethylsilanol (peak 3 in Figure 4) is shown with high peak symmetry with narrow peak width (Figure 6). In contrast the peak in Figure 4 shows a significant asymmetry on the tailing edge and this can now be understood from extract ion plots in Figure 6. The elution of 2-butanone and ethyl acetate are close to each other and to trimethylsilanol, and this accounts for the distorted chromatographic peak shape for peak 3 (Figure 4). These findings suggest that little significant extra column band broadening occurs between the DMS analyzer, in the API source, and through the interface with the mass spectrometer.

The repeatability of peak areas in extracted ion chromatograms from GC DMS API MS measurements ranged from 5 to 30% RSD which significantly exceeds that of the AQM alone. These findings however include an asynchronous nature of the scanning process with the mass spectrometer for narrow elution profiles from the GC DMS and no effort was made to improve on quantitative performance using selected ion monitoring where the speed of the mass spectrometer would improve sampling of the eluting peak and definition of peak shape: essential for quantitative analysis without peak fitting methods.

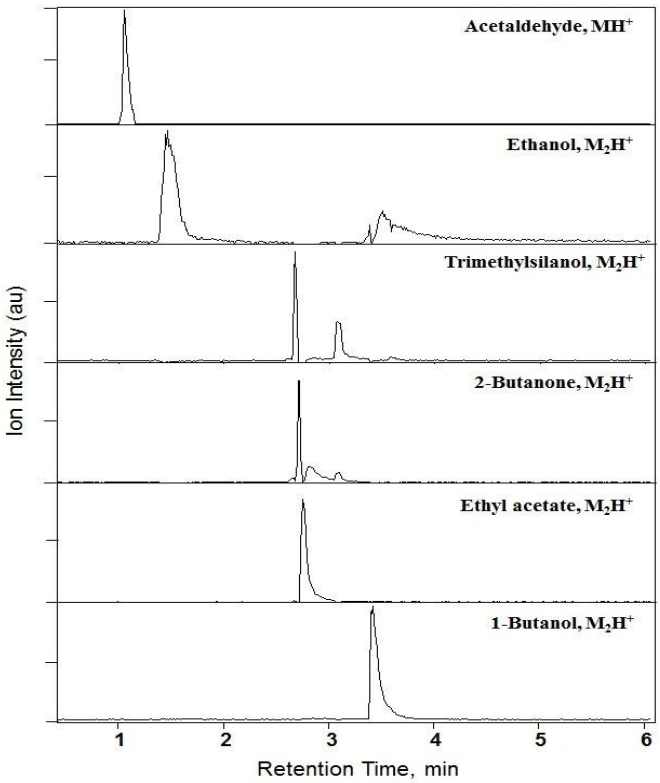


Figure 6. Selected ion plots for substances in the synthetic standard drawn from GC DMS MS analyses. This plot clearly shows that ethyl acetate and 2-butanone co-elute on the trailing edge of the trimethylsilanol peak. This distorts the trimethylsilanol peak in Figure 4D.

Another aspect of precision of the instrument as a combination is seen in Table 3 for repeatability of retention times. Even with manual control on start and stop of the computer for the mass spectrometer acquisition, %RSD values ranged from 0.3 to 1.7.

Table 3. Repeatability of Retention Times from GC-DMS-MS Measurements of DB5 (n=3)

	GC Retention Time (Min)			Average	SD	% RSD
Acetaldehylde	1.09	1.06	1.09	1.08	0.02	1.6
Ethanol	1.48	1,46	1.49	1.49	0.01	0.48
2- Butanone	2.73	2.7	2.73	2.72	0.02	0.64
n- Butanol	3.42	3.41	3.43	3.42	0.01	0.29
Trimethylsilanol	2.63	2.67	2.72	2.67	0.05	1.69
Ethylacetate	2.77	2.74	2.79	2.77	0.03	0.91

Conclusions

The combination of the AQM with an API-MS using the new method based on re-ionization of gas flows from the DMS drift tube exhibited a convenience in evaluating an AQM while allowing the instrument to be restored to original condition. Surprisingly, this was achieved without measurable band broadening in the chromatographic profile. Viton® tubing was shown suitable for these experiments and did not exhibit cold spots or otherwise induce extra column band broadening.

Dilution of substances in the flow from the DMS using additional gas before introduction into the API source presented no obvious limitations apart from erosion of detection limits and the ambient pressure to vacuum interface allowed identification of core ions, though uncertainties on lightly adducted neutrals, as always with an API-MS instrument and 100 micrometer skimmer.

Reported results, from a developed and tested working prototype show how a new analytical instrument can be used for visualization and identification of individual substances at trace concentrations in a complex mixture. Enhanced identification of components occurred due to three-dimensional characterization of each discrete peak (retention time, compensation voltage and m/z parameters provided by the GC- DMS-MS system). This system has strong analytical potential and can be adopted for many practical applications.

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88003, USA

1 J.T. James, T. F. Limero, S. Beck, P. F. Cheng, V. J. de Vera', J. Hand, A. Macatangay, "International Space Station Air Quality Assessed According to Toxicologically-Grouped Compounds", American Institute of Aeronautics and Astronautics. Published date: 2010-01-0. DO1:10.2514/6.2010-6277.
2 T. Limero, E. Reese, Int J Ion Mobil Spectrom 2002 5(3):27-30.
3 T. Limero, E. Reese, J. Trowbridge, R. Hohmann, and J. James, SAE Technical Paper Series 2003-01-2646, 33rd International Conference on Environmental Systems, Vancouver, British Columbia, Canada, July 2003.
4 T. Limero, 37th International Conference on Environmental Systems, SAE Technical Paper 2007-01-3220, Chicago, IL, 2007
5 T. Limero, E. Reese, W.T. Wallace, P. Cheng, and John Trowbridge, Int. J. Ion Mobil. Spec., (2012) 15: 189-198
6 T. Limero, W.T. Wallace, and J.Trowbridge, International Conference on Environmental Systems, AIAA technical paper 2013-3484, Vail, CO., July 2013.
7 I.A. Buryakov, E.V. Krylov, E.G. Nazarov, and U.Kh. Rasulev, Int.J.of Mass-spectrometry and Ion Processes,128,143-148(1993).
8 R.A. Miller, G.A. Eiceman, E.G. Nazarov, A.T. King, Sensors & Actuators, B67, 300- 306, (2000).
9 R.A. Miller, E.G. Nazarov, G.A. Eiceman, A.T. King, Sensors and Actuators A 91 (2001) 301-312.
10 G.A. Eiceman, E.V. Krylov, B. Tadjikov, R.G. Ewing, E.G. Nazarov, and R. Miller, The Analyst 2004, 129(4), 297-304.
11 E.G. Nazarov, R.A. Miller, G.A. Eiceman, E.V. Krylov, International Journal for IMS 5(2002)3, 76-81.

12 G.A. Eiceman, E.G. Nazarov, R.A. Miller, E. Krylov, A. Zapata: Analyst,127, 2002, 466-471.
13 G.A. Eiceman, B. Tadjikov, E. Krylov, E.G. Nazarov, R.A. Miller, J. Westbrook, P.Funk, Journal of Chromatography A, 917 (2001) 205-217.
14 Anderson, A.G; Markoski, K.A.; Shi, Q.; Coy, S.L.; Krylov, K.V.; Nazarov, E.G. DMS-IMS2, GC-DMS, DMS-MS: DME Hybrid Devices Combing Orthogonal Principles of Separation for Challenging Applications, Chemical, Biological, Radiological, Nuclear and Explosives (CBRNE) Sensing IX, Ed A.W. Fountain III and P.J. gardern, Proc. SPIE 2008, 6954, 695OH-1 to 12
15 S. Prasad, K.M. Pierce, H. Schmidt, J.V. Rao, R. Güth, R.E. Synovec, G.B. Smith and G.A. Eiceman, Analyst **2008**, 133 (6), 760-767.
16 Prasad, S.; Pierce, K.M.; Schmidt, H.; Rao, J.V.; Güth, R.; Bader, S.; Synovec, R.E.; Smith, G.B.; Eiceman, G.A., Analyst **2007**, 132(10), 1031-1039
17 G.A. Eiceman, E.G. Nazarov, and R.A. Miller, International Journal for IMS 3(2000)1 15-2.
18 E.Krylov, E.G. Nazarov, R.A Miller, B. Tadjikov, G.A. Eiceman, J. Phys. Chem.A.2002,106,5437-5444.
19 http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-15r.pdf
20 G.A. Eiceman, E.G. Nazarov, B. Tadjikov, and R.A. Miller, FACT, 4(6), 297-308, (2000).