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Sensor systems for the Altair Lunar Lander:

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**Sensor systems for the Altair Lunar Lander:
No net is perfect – make the holes as small as you can afford**
Ray Mariella Jr.
Sep 2010

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The Altair Lunar Lander will enable astronauts to learn to live and work on the moon for extended periods of time, providing the experience needed to expand human exploration farther into the solar system.

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I. Unsolicited Comments

First, unsolicited comment, regarding terrestrial “Field Trials”: I have contacted numerous possible commercial sources of sensors that, at first view, seem applicable to the measurements that NASA needs, *if only they were performed on earth*. I have found that manufacturers can show little interest in braving the gauntlet of bureaucratic challenges that one must traverse in order to get their instruments into space, even if the physical robustness of their instruments might already be flight-worthy. It is far outside of the mission of the Altair Lunar Lander project, but, to make the bureaucratic gauntlet less daunting, I strongly encourage NASA to hold workshops for prospective manufacturers of sensors and instruments that could protect crew health, both in order to outline the specifics of how to demonstrate a high TRL and, ultimately, fly on a mission as well as to provide specific [administrative] assistance to those prospective companies that might be willing to proceed. Whether or not such instrumentation could be demonstrated as flight-worthy, I suggest that NASA should have a terrestrial test laboratory in which the state of the art in commercial sensor systems would be compared with instruments that NASA intends to fly. I expect that both the crew and the taxpayers would be well served if the flyable instruments had performance that was shown to be comparable to the state of the art in scenarios that were relevant to NASA’s needs.

Second unsolicited comment: although this report is not primarily directed at biomedical measurements of crew health, there are several occasions in this report in which I refer to sensors that can monitor both cabin air as well as exhaled breath or bioaerosols or vapors from foodstuffs, thus serving dual purposes.

II. Recommendations

My overriding recommendation: Use independent and complementary [sometimes referred to as “orthogonal”] **techniques to disambiguate confounding/interfering signals.**

E.g.: a mass spectrometer [“MS”], which currently serves as a Majority Constituent Analyzer [“MCA”] can be very valuable in detecting the presence of a gaseous specie, so long as it falls on a mass-to-charge ratio [“m/z”] that is not already occupied by a majority constituent of cabin air. Consider the toxic gas, CO. Both N₂ and CO have parent peaks of m/z = 28, and CO₂ has a fragment peak at m/z = 28 [and at 16 and 12], so the N₂ and CO₂ m/z=28 signals could mask low, but potentially-dangerous levels of CO. However there are numerous surface-sensitive CO detectors, as well as tunable-diode-laser-based CO sensors that could provide independent monitoring of CO. Also, by appending a gas chromatograph [“GC”] as the front-end sample processor, prior to the inlet of the MS, one can rely upon the GC to separate CO from N₂ and CO₂, providing the crew with another CO monitor. [See Section 3, below, on Hyphenated techniques]

If the Altair Lunar Lander is able to include a *Raman*-based MCA for N₂, O₂, H₂O, and CO₂ [see Section 5], then each type of MCA would have cross-references, providing more confidence in the ongoing performance of each technique, and decreasing the risk that one instrument might fail to perform properly, without being noticed. See, also Dr. Pete Snyder’s work, which states¹ “An orthogonal technologies sensor system appears to be attractive for a high confidence detection of presence and temporal characterization of bioaerosols.”

Another recommendation: Use data fusion for event detection to decrease uncertainty: tie together the outputs from multiple sensing modalities – eNose, solid-state sensors, GC-IMS, GC-MS – via nonlinear algorithms, such as an “artificial neural net.” MA Ryan² at the JPL and Henry Abarbanel³ at UCSD are possible candidates to implement such an approach.

III. Initial Guidance from Altair Lunar Lander:

Measurement Requirements:

O₂	0 to 5 psia [5 psia \approx 260 mmHg or Torr]
CO₂	0 to 30 mmHg [30 mmHg \approx 4% = 4000 ppm at 1 atm]
CO	5 to 500 ppm
HCN	1 to 50 ppm
HCl	1 to 50 ppm
H₂O/Relative Humidity	

Mission profile: Operate in microgravity, 1/6 g, and 1g
 Operate in dirty/dusty environment
 Survive launch loads, etc
 Long enough calibration life desired (explain mission profile)
 Voltage drifts
 Vacuum compatibility

Others:

Desirable to monitor nitrogen [mass spec and Raman spec]
 Desirable to monitor ammonia [mass spec and IMS]
 Desirable to monitor [Hydrofluorocarbon] HFC-245fa: CHF₂CH₂CF₃ [see⁴ Appendix A1]

SMACs [spacecraft maximum allowable concentrations] [numerous possibilities⁵⁻⁷]

Particulate counting to sizes less than 0.1 μ m

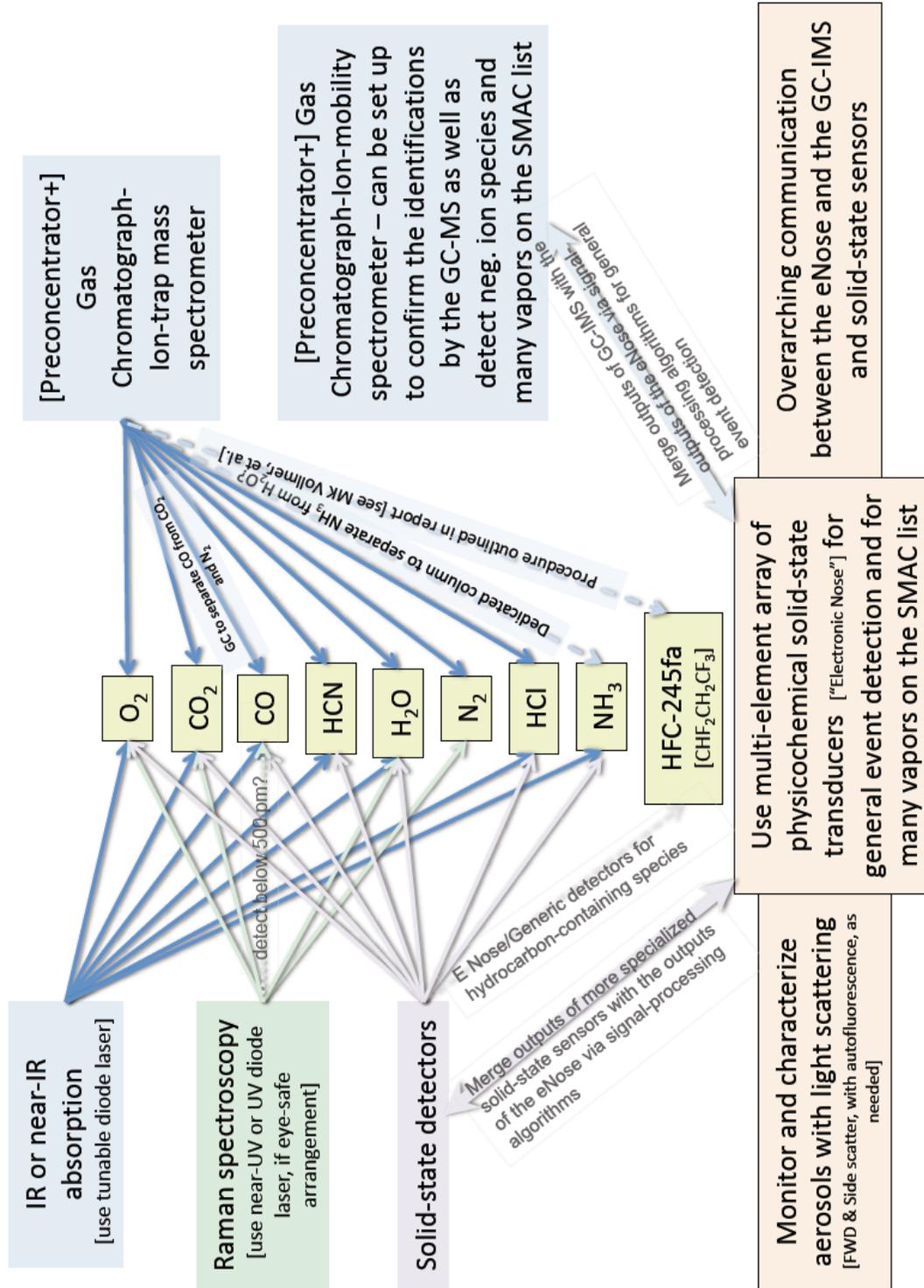
Differentiate between lunar regolith [recommended⁸ mean value for density of 3.1 g/cm³] & fire-product smoke.

This report does not deal extensively with the problem of lunar regolith and resulting dust^{9,10} within the cabin. However, aerosols and their health risks have been studied due to terrestrial health concerns¹¹⁻¹³ and the presence of in-cabin aerosolized lunar regolith only exacerbates these risks. The ease with which nanoparticles and agglomerates can strike the surface of our alveoli and be ingested has already been seen as an *advantage* for inhalation-based drug delivery.¹⁴⁻¹⁶ The physiological implications for adverse effects, based on such easy access to the walls of astronaut alveoli, not to mention other threats to health and operations, deserves considerable attention. In any case, in order to detect and characterize aerosols, there are certainly charging/electrostatic techniques¹² as well as optical scattering techniques¹⁷⁻²⁰, including analysis of polarization¹⁰, that seem appropriate and can monitor aerosols particles down to 0.1- μ m diameter. Additionally, aerosol particles have been studied via single-particle mass spectroscopy²¹⁻²³.

Also, Kaduchak and colleagues demonstrated that ultrasonic acoustic waves can efficiently manipulate aerosol particles²⁴⁻²⁷ [without forced convection of the air in which they are suspended], which can be a more energy-efficient method of concentrating aerosol particles than forcing the air and the particles through a physical filter or through a hydrodynamic focuser/virtual impactor. This may or may not have applicability to monitoring cabin air, depending upon the audible levels that are associated with an ultrasonic device. Whether a corona-discharge/electrostatic precipitator could be appropriate as an air filter and/or part of an aerosol characterization instrument might depend upon any collateral production of ozone.

Note that every target gas, except for the hydrofluorocarbon HFC-245fa, can be detected and identified by at least two candidate technologies.

IV. Architecture for detection and/or identification of constituents of cabin air



Straw-Man Example:

VCAM; Raman spectrometer; eNose; GC-IMS; solid-state-sensors; IR-absorption to cover major constituents and trace gases in the cabin atmosphere. [A light-scattering instrument, *per se*, that monitored aerosol particles would not consume significant power, but an aerosol collector/concentrator that fed a gas stream into such an aerosol particle monitor could very well draw watts of power and occupy several liters of cabin volume. This Straw-Man Example addresses only gases/vapors]

VCAM: **monitor N_2 , O_2 , CO_2 , CO , CH_4 , HCN , HCl** and SMAC-listed trace gases
 [This instrument would perform both routine MCA and trace-gas/off-normal event detection]
 VCAM Development Unit mass is 25.2 kg (without consumables) and consumes 140 W (peak) and 100W (nominal) power as derived from the EXPRESS 28V rack. Gas consumables sufficient for one year of operational life are packaged into a separate orbital replacement unit (ORU). Its mass is 5.1 kg. The DU is form, fit, and function of the flight VCAM units and is used for engineering and chemical-detection testing. Its dimensions are 18.1" (width) '10.8" (height) '20.5" (depth). Volume \approx 66 liters

ConOps: VCAM is designed to autonomously sample and analyze the ISS cabin-air based upon an internal clock, astronaut front-panel commands, or *via* ground commands transmitted to ISS. VCAM baseline design is to operate once per day, with a nominal one-year life on orbit as limited by the helium carrier gas and calibration supplies.

Should also have the overall Monitor&Control System be able to trigger a demand-based analysis, if any of the other sensors showed an off-normal result.

MCA measurements, independent of Mass Spectrometer:

Raman Spectrometer with an efficient near-UV diode laser in an eye-safe configuration.

ConOps: depending upon the power requirements of its analysis computer, it might be able to run continuously. If its power consumption precluded continuous operation, then I recommend that the Raman-based MCA perform periodic analysis [once per hour?] of the cabin atmosphere and in synchrony with the VCAM. Unit does not exist, yet, but we can take a guess:

Spectrometer power for laser and detector \approx 10W, when operating and near-0 W in idle mode.

Control/analysis computer might need 20 W, when performing analysis, and a few W in idle/standby mode. Shared LCD display with overall system? Size of laser, optics, and spectrometer might be several liters. Mass \approx 10 kg [a wild guess]

Oxygen also has several alternatives:

Laser-based triplet-singlet absorption in the near IR [Vaisala, etc] \approx 1 kg, several 100 cm³, several W, when operating, near-0 W in idle/standby mode

Solid-state sensors based on Oxygen-deficient solids, such as hot ZrO₂. [Makel Engineering etc] Vol \approx few 10's of cm³, housing shared with other solid-state sensors, mass 10's of g, power \approx few W

CO₂ has solid-state electrochemical [galvanic] detectors – 20 g mass, little or no power required, few-cm³ size.

eNose [JPL or other versions] < 10 W – continuous operation with a “learning algorithm” to create the capability to recognize normal crew movements and operations and, thus, better to alarm at off-normal conditions. Vol < 1 liter, Mass < 1 kg

GC-IMS [Sionex?] 10's of W with preconcentrator heat-flashing, 1W idling – if possible, run continuously and, if not, synchronize with MCA's [Sionex or other mfg] Vol \approx 2.5 liters, Mass \approx 2.5 kg

Solid-state sensors – sub-W power consumption, not including communications and power consumed by the monitor computer system. Distribute several around the cabin. Again, the monitor&control algorithm needs to “learn” and recognize signals from normal crew movements and operations, enabling recognition of signals from off-normal events.

IR absorption spectroscopy for O₂, H₂O, HCl, HCN, and other small molecules [various detection schemes – solid-state detectors monitoring transmitted power, photoacoustic techniques to pick up absorbed pulsed laser power that is converted to a pressure pulse{Maugh, 1975 #180}]

Power < 10 W, mass \approx 1 kg, Vol \approx 1 liter

Since the communications network, i/o system, and computer/monitor&control system that I proffer do not exist, I am providing a guess, based on my past experience with using desktop computers with commercial i/o cards to control a multifunctional, complex apparatus that grew crystals over many-hour periods and was always at least on “idle,” when not growing.

One or more monitors at \approx 20W to 50 W each, when not in sleep mode, depending upon size and brightness. Perhaps \approx 1 W in “sleep mode” and 0 W if switched off. I don't have the ConOps for how often the crew would check the monitor, so the duty cycle of higher-power draw is unknown.

Filters for the forced-convection cooling – maintenance interval dependent upon load of aerosol particles, including lunar dust. Hermetically-sealed power switches, if instruments/control computers are powered down, when not in use. [Protect contacts from dust/film formation]

V. Applicable Instrumentation

Some cursory comments on Mass Spectroscopy and Ion-Mobility Spectroscopy:

For #1 - #3: MS, IMS, and differential-mobility spectrometers all provide information that, when one has *a priori* information about the sample, can serve to identify components in the sample. For mixtures of unknown/uncharacterized samples, training, experience, and scenario-dependent intuition are all likely to be necessary to identify unexpected/surprising constituents. Mass spectroscopy, which is a mainstay of analytical chemistry, provides the mass/charge ratio of detected ions. Most commercial mass spectrometers view only positive ions, so that operators must include in their interpretation that some ions decompose rapidly when forming positive ions [e.g., alcohols] and the parent peak may not be dominant, such as can occur under some conditions for NH_3 ^{28,29} nor even be easily visible⁴. Also negative ions that might provide valuable insights are not, typically, available [exceptions: ions detected from bombardment of solids using dual-polarity detection^{28,29} and aerosol flow cytometer/mass spec^{21,23}]. Both positive and negative ions are available with an IMS³⁰⁻³².

One failure mode is that the ionizer on a MS can become degraded or burn out, particularly if the MS sees high gas loads. Also, if insulating deposits grow on surfaces over time, then they can become charged, changing and degrading the performance of the MS or IMS. [This is especially true of a miniaturized or microfabricated system that is exposed to high loads of unfiltered air, because a smaller instrument tends to have a larger surface-to-volume ratio – it is easier for vital surfaces to become covered in an undesirable film, although progress is certainly being made³³.]

In general, even “low-power” mass spectrometers require 10’s of watts of power to operate and require extensive supporting electronics to observe all the masses on a scan and to assign an observed [potentially-complex!] fragmentation pattern back to one or more parent compounds with varying concentrations. By contrast, there are numerous, battery-powered, handheld IMS instruments that can detect a variety of vapors but that offer far less identification powers than are available with a MS.

It is easy to envision scenarios in which unknown and/or unexpected vapors could be produced, in flight, not just due to equipment malfunction/overheating, but also due to metabolic and by-product gases from microbes and even from the crew, and a MS [particularly if available with a preconcentrator/gas chromatograph as its front end sample processor] offers the most powerful tool for the identification of such unknown/unexpected vapors. Hence, I recommend including a MS, preferably a GC-MS instrument, as part of the flyable suite for the Altair Lunar Lander. [The non-scanning, fixed-magnetic sector mass spectrometer that serves as a Major Constituent Analyzer would not be adequate for such identifications, for numerous reasons]

1. Mass spectrometers [“MS”]

Mass spectrometers, *which generally need to operate under vacuum [often under high vacuum]*, produce and disperse/separate beams of atomic and molecular ions according to their differing mass-to-charge ratios, and are general-purpose analytical devices that are particularly useful for the identification of one or a few gaseous species. With

training, the operator can increase the identification power of a MS by analyzing the fragmentation pattern⁷, resulting from the ionization of the parent molecule that is observed from a sample. R. Cooks and co-workers have published numerous articles on small, portable MS's³⁴⁻³⁷, including some designs that operate at ambient pressure³⁸⁻⁴⁰ and have biomedical applications.³⁹

Within mass spectroscopy, there are various ways to disperse ions according to their m/z ratio, including fixed magnetic sectors, which tend to be relatively large and massive, but which suffer very little drift in position of ions on the detector surface⁴¹, time-of-flight³³, quadrupole⁴², and ion-trap designs⁴³. Please see the excellent review by Palmer and Limer⁴⁴. The advantage of mass spectrometers that are based on ion traps is their relatively small size and weight, which makes them particularly appropriate for NASA applications.

NASA has at least two promising Ion-Trap-based systems, the Ion-Trap spectrometer used on VCAM, from the Jet Propulsion Laboratory, and the 1st Detect, from SpaceHab. See Appendix A1, A3. Assuming that the VCAM can achieve the necessary TRL, it would offer more features than the 1st-Detect ion-trap mass spectrometer, alone.

Torion, Inc., has produced a portable [13 kg] ion-trap-based MS system that draws ≈ 35 W peak power consumption during analysis⁴⁵. Public information about this unit indicated that it could only scan an m/z range from 50 to 400, which would not be adequate for NASA's needs.

The Space Station Major Constituent Analyzer (MCA) from Hamilton Sundstrand⁴¹ uses a fixed magnetic sector and four, continuous Faraday-collector monitoring of the m/z peaks corresponding to H_2O^+ , N_2^+ , O_2^+ , and CO_2^+ ions. [See Appendix A1]

2. Ion Mobility spectrometers [“IMS”]

An IMS, which can be miniaturized/handheld, ionizes gaseous molecules and analyzes their various drift speeds in an applied electric field. The analysis and characterization via IMS are based on differing ionic mobilities through a background or carrier gas rather than simply their differing m/z . *An IMS typically operates at or near atmospheric pressure.* [IMS units can analyze air, vapor, soil, and water samples; for analysis of volatile components of liquid or solid materials, the volatile components must be introduced to the instrument in the gas phase, requiring sample preparation.]

R&D teams working³¹ with or independent of NASA have created portable IMS and/or GC-IMS systems: amongst others – Gary Eiceman and Erkinjon Nazarov^{31,46-53}. [Dr. Nazarov invented a new kind of differential ion-mobility spectrometer^{46-50,52-58} with reduced volume and weight, now incorporated in the Sionex microAnalyzer™. See, e.g., Thomas Limer, et al.^{5,59-61}] Such systems can be very small and lightweight and the Sionex instrument, which is already under test by NASA personnel, appears well-suited for space applications. Numerous hand-held IMS instruments incorporate drift tubes manufactured by Graesby⁶². See Appendix **A2**. Including the Chemical Agent Monitor [CAM] that is used by the military and police.

Also, see work by Dr. Pete Snyder¹, including detection and characterization of bioaerosols⁶³⁻⁶⁵.

3. Hyphenated techniques have greatly increased the power of MS&IMS^{66,67}

Separation of major constituents of air, CO, and light-chain hydrocarbons via GC was demonstrated, nearly 30 years ago⁶⁸, which separation could easily be followed by a mass spectrometer or an IMS. The presence of a heated GC column increases the power requirements, of course, above that of a MS or IMS, alone.

The VCAM team has reported detection of major constituents of air as well as numerous vapors from the SMAC list⁷.



mass is 25.2 kg (without consumables) and consumes 140 W (peak power)

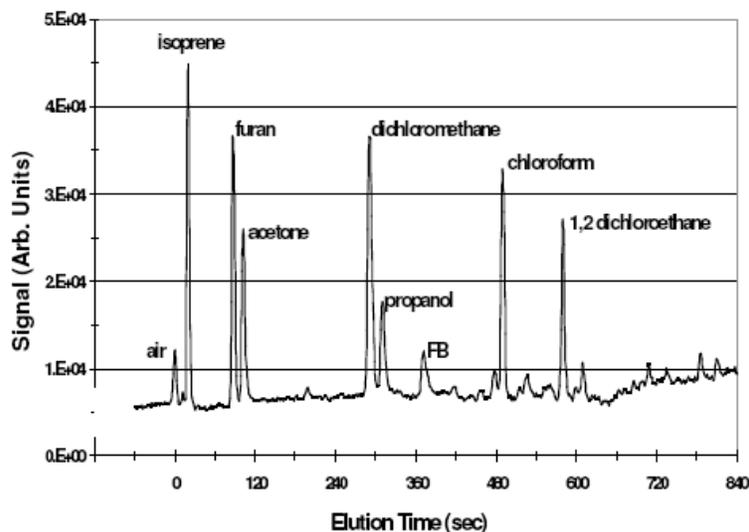


Figure 4. Total Ion Chromatogram for a Mixture of SMAC Species. The concentrations of isoprene, furan, dichloromethane, propanol, chloroform, and 1,2- dichloroethane are 24 ppb, 38 ppb, 30 ppb, and 31 ppb, respectively. PCGC conditions are: carrier gas at 15 psig, PC adsorb time of 6 min, GC temp isothermal at 25°C for 320 sec then ramped to 85°C at 5C/min. Acetone and FB are the calibration species. Propanol and the remaining unlabeled small elution peaks (< 10 ppb) are off-gassing products from the sample bag material.

The VCAM design includes calibration gases that will be used to validate and verify the following key operating parameters of VCAM while on-orbit: (1) the enhancement factor of the preconcentrator, (2) proper operation of the GC column by measuring the elution time and system sensitivity of the calibrant mixture, and (3) the mass range, mass resolution, mass cross talk, and system sensitivity of the Paul trap. Use will be made of a modified TO15 EPA Protocol for testing the instrument stability and response [6]. The TO15 protocol employs daily tests

using fluorobenzene (FB, C_6H_5F , mass 96 amu) and bromofluorobenzene (BFB, C_6H_4FBr , mass 174 amu for the ^{79}Br isotope and 176 amu for the abundant ^{81}Br isotope acetone ($^{12}C_3H_6O$, 58 amu). For VCAM only FB and acetone ($^{12}C_3H_6O$) will be used to test the PCGC at the high- and low-mass ranges of the MS, respectively. VCAM groundbased testing suggests that once/week runs of the calibration gas mixture will be sufficient while onorbit. Use of these calibrant gases in the closed ISS environment does not pose an astronaut health risk, even in the event of a total release.

Torion, Inc., has produced an integrated, portable [13 kg] ion-trap-based MS system with solid-phase microextraction [“SPME”] and GC front end that draws $\approx 80\text{W}$ peak power consumption during analysis⁶⁹. Although it has worked well with its SPME/GC front end, it is unclear whether the MS portion can scan to low-enough m/z 's to satisfy the needs of NASA.

J Am Soc Mass Spectrom 2008, 19, 1425–1434

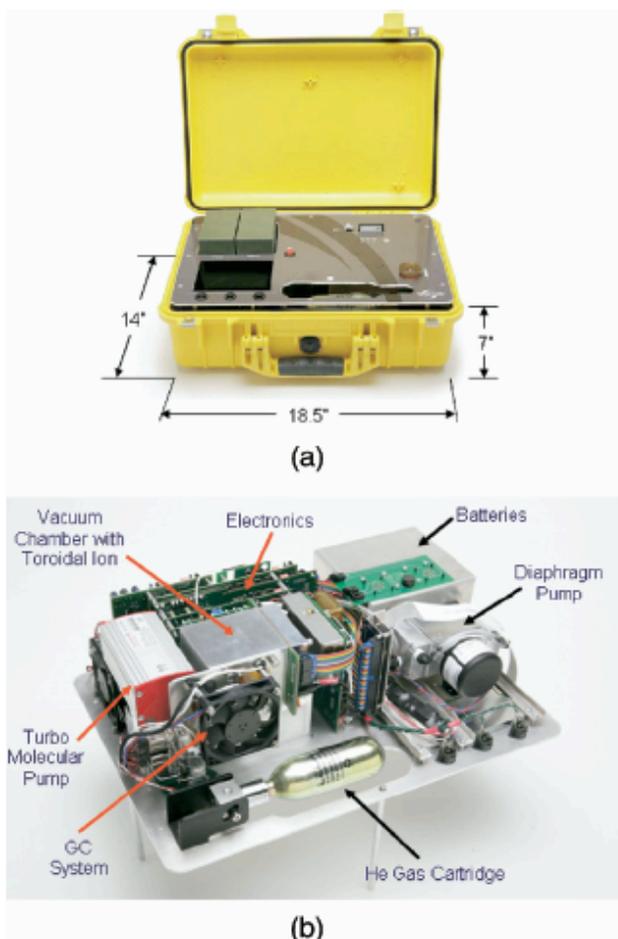
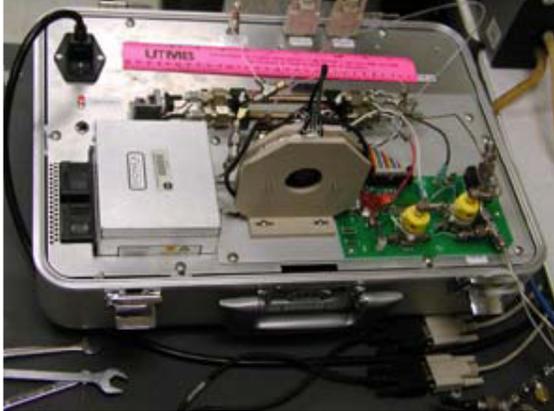


Figure 1. Photographs of the Guardian-7 GC-TMS showing (a) dimensions and (b) internal components.

The applicability of GC-IMS to: HF, HCl, Cl₂, N-methyl 2-pyrrolidone [NMP], NH₃, NO₂, SO₂, HCN, CH₂O, organic compounds, H₂S, mercaptans has been reported⁷⁰. Limero, Reese, and Cheng, have reported a compact, low-mass IMS that can serve as a volatile organic analyzer⁵.



Early Sionex integrated GC-Differential-Mobility Spectrometer development unit

Second version of integrated preconcentrator&GC-DMS from Sionex



[Note: There is at least one company that uses an IMS as the front end for a MS: Excellims, Inc.]

Both bacterial and non-bacterial aerosols have been analyzed via pyrolysis-GC-IMS in field tests^{63,65}.

[see Appendix A3]

4. Solid-State Sensors

Solid-state sensors can be very compact, low-mass, and low-power, but they are susceptible to deposition of films from continuous exposure to the atmosphere as well as gradual oxidation or other chemical reactions or physical changes of the transduction components that could degrade its performance. The influence of interfering gases such as O₂, H₂O, CO, NO, NO₂, CH₄ and SO₂ on a CO₂ sensor has been reported in literature, such as O₂ for a CO₂ sensor⁷¹. Degradation due to exposure to ionizing radiation may also be an issue.

Here is a study of interferences for a carbonate-based CO₂ sensor⁷², showing that SO₂ causes irreversible changes in performance:

Influence of interfering gases on the sensor signal in the presence of CO₂

Interfering gas	Partial pressure/ conc.	Changes of EMF		
		Type A open ref.	Type B and C solid ref.	Problem
O ₂ influence	>0.1 bar	No	No	–
	<0.1 bar	No	Nernst (38 mV/dec.)	RE (solid)
H ₂ O	0.012 bar (50% r.h.)	+10 mV reversible	No	RE (open)
CO	30 ppm	No	No	–
CH ₄	200 ppm	No	No	–
NO ₂	100 ppm	Reversible	No	RE (open)
SO ₂	≥500 ppb	Irrevers.	Irrevers.	WE
	50–500 ppb	Irrevers.	No	RE (open)
	≤50 ppb	No	No	

and adding chemical filters can reduce interference by NO and SO₂ on CO₂ sensor⁷³

Water vapor shows interferences for solid-state CO or NH₃ sensors⁷⁴, and here is an excerpt⁷⁵, that mentions interference from methane and water vapor for two xylene detectors, including Figaro units:

Both the Adsistor and Figaro sensors have properties that are useful for UST leak detection. The two sensors respond well to xylene and are relatively insensitive to methane, which is the primary interfering compound to sensor systems in subsurface detection of leaking underground storage tanks. The Figaro sensor is more sensitive to lower levels of solvents than the Adsistor. The Adsistor sensors as a group had better reproducibility and had a much smaller humidity interference in comparison to the Figaro sensors. These facts make the Adsistor easier to deal with from an instrumentation and calibration point of view. However, the Adsistor sensors were observed to have longer xylene recovery times than the Figaro sensor, which is a factor one must take into consideration when choosing a sensor technology.

Because of possible drift and confounding chemicals, I recommend combining the signals from a – c [see below] and even real-time light-scattering data, using artificial neural-net or other nonlinear algorithms, both to enhance the probability of detecting events and to decrease uncertainty in “normal” measurements. If possible, performing “data fusion” with additional, independent in-flight sensing modalities can further reduce uncertainties in the interpretation of signals.]

a. Electrochemical Sensors

Solid or membrane electrolytes or fuel-cell arrangements - used in some hand-held CO sensors for breathable air⁷⁶, exhaled alcohol and exhaled NO sensors^{77,78}. Cross reactivity/confounding gases may be a source of degraded accuracy/reliability. These can be very compact and draw little power – see Appendix A4.

b. Surface-sensitive Sensors

Dr. Meyyappan and co-workers, using principal component analysis, have created nanotube-based sensors^{79,80} and some are currently incorporated into the JPL electronic nose and serving on the ISS.

Possibly the most ubiquitous sensors for terrestrial applications are the numerous semiconductor-based sensors for gases/vapors – see Appendix A4 [and A5].

c. Multi-element arrays: Electronic Nose or “eNose”

Many-element sensors, with principal-component analysis or advanced signal processing algorithms; a wide variety of individual sensing elements that respond to relatively specific vapors. Porous Si with CO has been studied⁸¹

Dr. M. A. Ryan and colleagues have designed, built, and flown versions of electronic noses for NASA missions^{2,82} and Ryan⁶ & Goddard⁸³ & Meyyappan elements⁸⁰ are on the ISS, now.

A mass-spectrometer-based eNose has been compared with solid-phase microextraction/GC/MS to characterize volatiles above infant formula⁸⁴, with the statement

The term “electronic nose” has been used to describe these instruments because the sensors detect volatiles in a sample and attempt to discriminate among samples based on their “aroma” profile. Nevertheless, no combination of sensors today available has the selective sensitivity or discriminating power of the human nose.

For #5, launch ruggedness and longevity of optical components, both active and passive, must be addressed, including susceptibility of lasers, detectors, and ancillary electronics to degradation from exposure to ionizing radiation, if any. Power consumption is typically a few watts per unit.

5. Optical and Infrared Spectroscopy, including Raman Spectroscopy

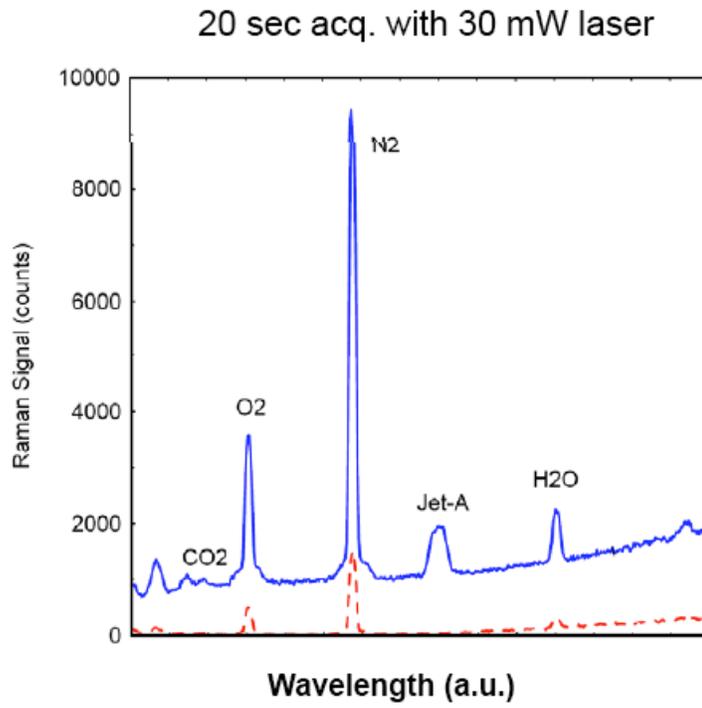
All molecules, including N₂, O₂, CO, H₂O, and CO₂, possess identifying excited electronic states at higher energies than their lowest [“ground”] electronic states, and these excited states can be accessed by the absorption of electromagnetic radiation [“light”], usually falling in the ultraviolet wavelengths. Strongly-allowed transitions occur between ground and electronic states that maintain the overall electron spin, such as singlet to singlet [no unpaired electrons] and triplet to triplet [two unpaired electrons]. Accessing the strongly-allowed electronic transitions for all five of the gases just listed requires the use of ultraviolet light that is not eye safe and this report recommends against using such an approach to monitor them.

Weakly-allowed transitions between a ground-state and states with different overall electron spins can occur. The most famous of these is the triplet-to-singlet transition of ground state O₂, which is a triplet, and its lowest excited state, which is a singlet. Although absorption of the corresponding 765-nm light for this transition is relatively weak, it can be observed, nonetheless, for the O₂ in breathable air and is the basis for numerous oxygen monitors.

For many molecules of interest that happen to possess polar bonds [HCN, HCl, NH₃, CO, CO₂, H₂O, chlorofluorocarbons, gases on the SMAC list], characteristic “fingerprint” vibrational spectra are observed via absorption of light at infrared [IR] wavelengths.

N₂ and O₂ do not possess polar bonds and do not exhibit vibrational spectra in the infrared light region. However, as present within typical, breathable air, N₂ and O₂ can be monitored using *Raman spectroscopy*, in which light [usually visible light] almost always from a laser, is inelastically scattered off of the molecule with the characteristic energy change corresponding to the vibrational frequencies of the molecule. Although the cross sections for such Raman scattering of blue light are very small [$\approx 10^{-31}$ cm²/molecule/steradian], Raman scattering by N₂, O₂, H₂O, and CO₂ is routinely observed in breathable air, nonetheless.

Assuming that such spectroscopy-based gas monitors use solid-state sources and detectors, power consumption of 1 W or less per target gas can be anticipated.



Raman spectra showing N₂, O₂, CO₂, and H₂O taken using a single-pass, fiber-optic system by Q-V Nguyen, of NASA GRC⁸⁵

VI. Appendices

A1. Mass Spectrometers

Interpreting mass spectra can be difficult, both due to the complexity the spectrum for even a pure compound as well as due to missing parent peaks. [see following Fig. – perfluorodecalin from blood⁸⁶ the parent peak at 462 is basically missing and the peak at 443 is very weak, compared with the peak at 393 For B, the parent peak at 596 is absent and the spectrum appears to start at 181. Imagine the difficulty of superimposing the spectra from numerous such compounds in varying concentrations!].

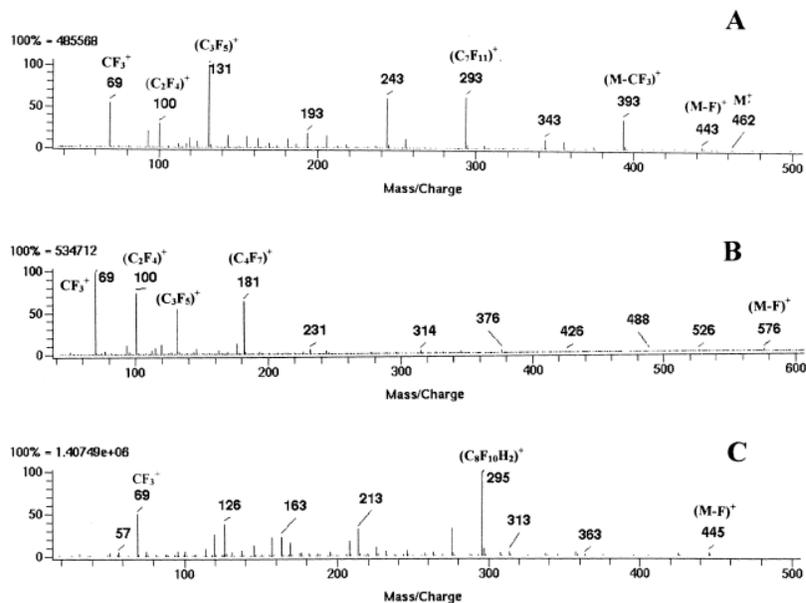


Fig. 2. Mass spectra (SCAN mode) of perfluorodecalin (A), perfluoro-N-methylcyclohexylpiperidine (B) and bis(F-butyl)ethene used as an internal standard (C).

Also – Parent peak missing with HFC-245fa⁴ [$CHF_2CH_2CF_3$, see Altair Guidance]

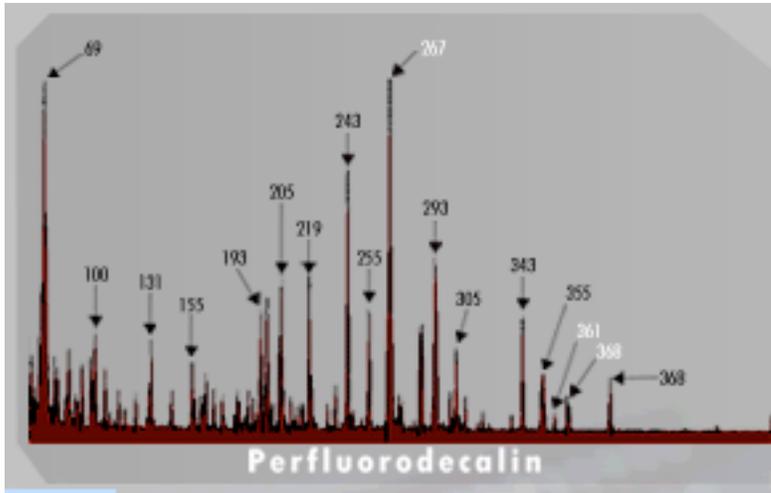
Procedure to detect HFC-245fa⁴:

Collected on a microtrap at $-50^\circ C$ and thermally desorbed at $\approx 240^\circ C$.

They are then chromatographically separated on a 120 m X 0.32 mm I.D. CP-SIL 5CB capillary column (Chrompack) with 5- μm film thickness, and detected using single-ion mode quadrupole mass spectrometry. The HFC-245fa elution time was determined using a high-concentration reference gas and is quantified using the $C_3H_3F_4^+$ m/z 115 mass fragment. The $C_3H_2F_5^+$ m/z 133 mass fragment was also detectable, but less abundant, in our high-concentration reference gas. **It is not detectable on our instruments in current air samples.**

Spacehab.com

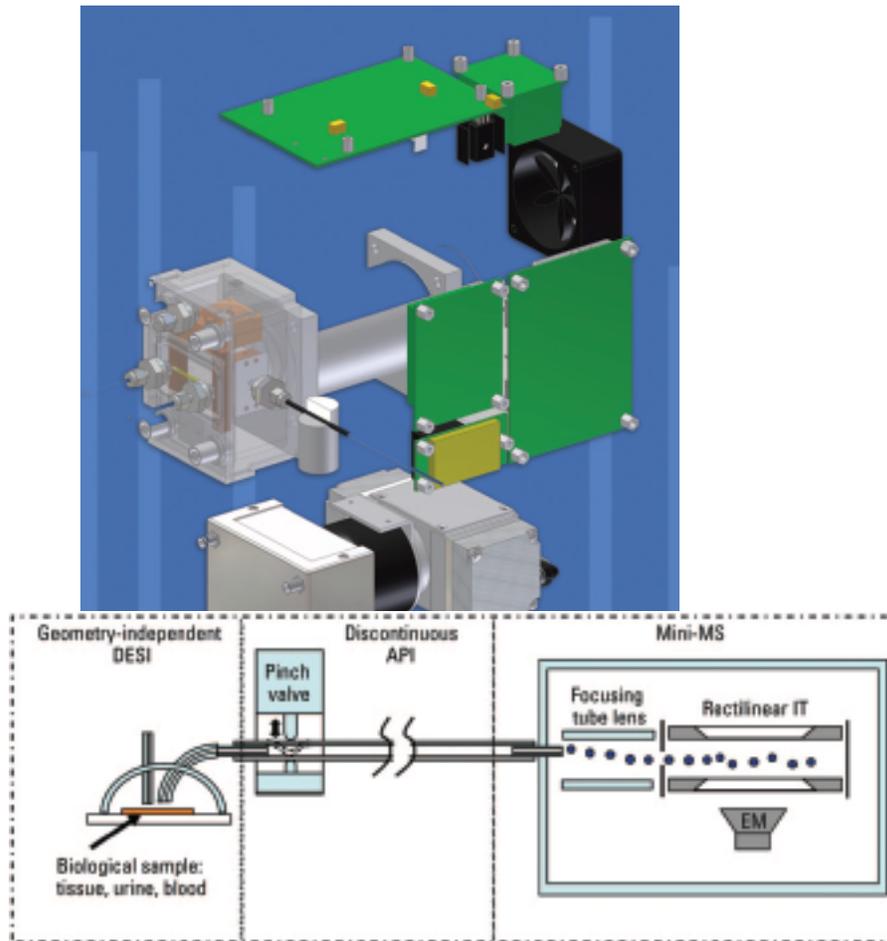
The 1st Detect ion-trap MS is able to detect the major fragments, but not the parent peak, from perfluorodecalin, for example:



- * Weight: <15 lbs (~6.8 kg)
- * Mass Range: 10 - 450 amu
- * Chemicals Detected (examples):
 - CWAs: GA, GB, VX, mustards, cyanides
- TICs per NIJ Guide 100-0
 - * Resolution: <1 amu
 - * Detection Limit: 1 ppb VOC, 1ppm SVOC
 - * Power Supply: 120/240VAC, 24VDC or supplied batteries
 - * Low False Alarm Rate: True Mass Spectrometer (not IMS) and MSn Capability
- * Custom Sample Collection - 1st detect can be coupled to a wide variety of sample collection or pre-concentration/ separation systems to suit the needs of a particular application. **These include GC/LC**, API sources, thermal desorbers, SPME, and many other custom sample inlets.
- * Battery operation - For field portable systems, 1st Detect can offer an integrated rechargeable power source using standard UBI-2590 batteries.
- * OEM component - For applications where customer packaging is desirable, 1st Detect can provide the core functionality without packaging for integration into customer specific packaging. *Applications include customer specified hyphenated systems*

Graham Cooks and colleagues have published, extensively, on miniature ion-trap-based mass spectrometers^{34-40,87-92} and specifically discussed⁸⁷ the challenges of achieving high performance in such a handheld instrument, including bio-medical applications.

For toxic gases, such as phosgene, ethylene oxide, sulfur dioxide, acrylonitrile, cyanogen chloride, hydrogen cyanide, acrolein, formaldehyde, and ethyl parathion, a 1-minute preconcentration time is required. Detection limits range from 800 ppt to 3 ppm, depending on the analyte. For these particular compounds, a linear dynamic range of 1-2 orders of magnitude was obtained over the concentration range (sub-parts per billion to parts per million) for all analytes.¹⁸



Hamilton Sundstrand: Major Constituent Analyzer uses a fixed-magnetic sector with specific detectors for charge/masses of interest = 100% duty cycle. Based on 7+ years' experience on ISS.

International Conference on Environmental Systems, Burchfield & Steiner⁴¹, Hamilton Sundstrand

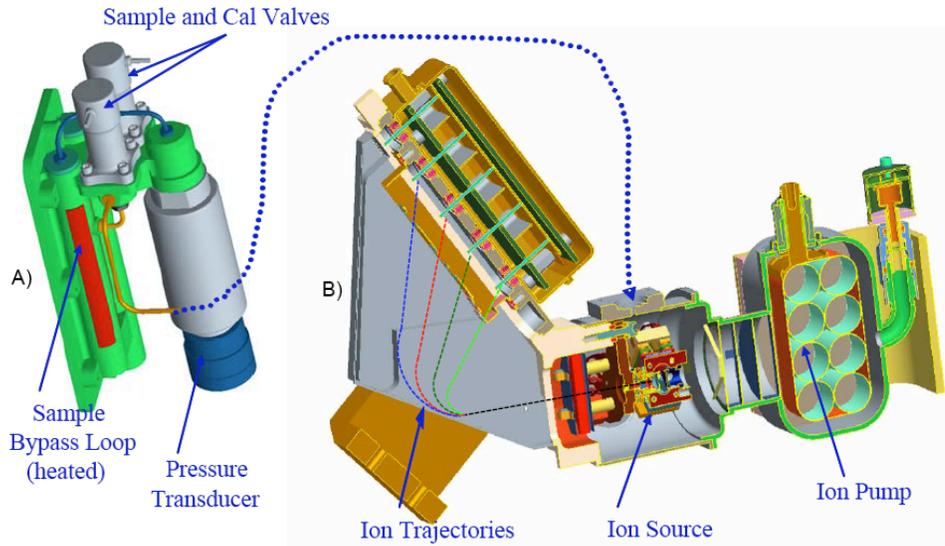


Figure 1, Cutaway representation of the Orion Air Monitor, showing the sample inlet (A) and analyzer (B) assemblies.

Table 1. Orion Air Monitor Sensitivity Requirements

Analyte	Pressure Range /psia	Accuracy at Nominal Concentration /psia	Response Time /sec
Oxygen	0 – 24	0.1	10
Nitrogen	0 – 13	0.1	10
Carbon Dioxide	0 – 1.5	0.005	10
Water Vapor	0 – 1	0.005	15

Table 2. Key Air Monitor Performance Requirements

Parameter	Specification	Performance Target
Mass	7 kg	6.4 kg
Power	24V, 25 W	17 W nominal
Communications	RS422	300kbps

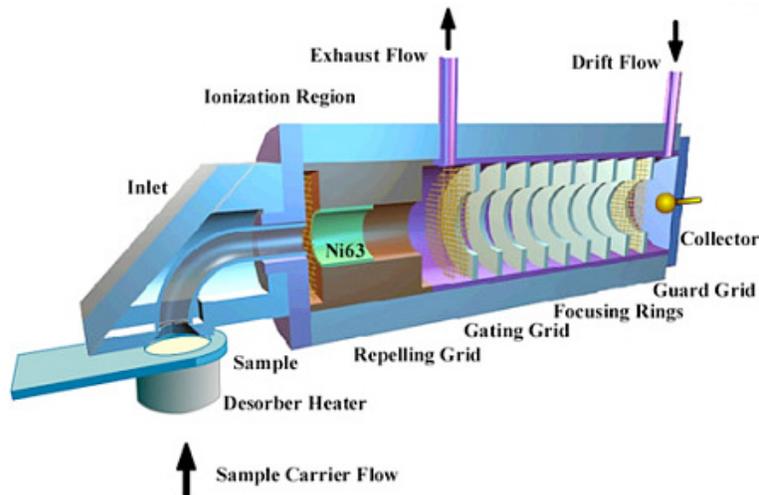
This gives the shell a 7.5-inch height and a 9.5-inch depth. The width of the assembly is driven to 8.8 inches

Wt is less than 15 lbs and draws approximately 17 W in operation. It may be powered-down indefinitely and will recover to an operating state autonomously with the application of power.

Of the four [MCA] instruments evaluated on-orbit, each shows a small drift in gain with time, on the order of -0.01 to -0.07 percent per day for oxygen, corresponding to an error of 0.0003 – 0.002 psia per day of O₂ between calibrations, and a measurement uncertainty of only 0.001 to 0.005 psia O₂ (1 standard deviation). The drift was not unexpected and a verification gas assembly is included in both the MCA and OAM designs to deal both with gain and offset drift. On ISS, calibrations are performed every 6 weeks, regularly nulling the effect of the gain drift before it approaches 0.1psia. A calibration cycle can be commanded just prior to the Shuttle undocking, allowing just the measurement uncertainty to limit how much Shuttle oxygen is dumped into the ISS.

A2. Ion-Mobility Spectrometers

Graseby Ionics, Ltd. (Graseby) has a self-contained IMS that weighs about 2 kilograms (kg).



Smiths Detection

Ion Mobility Spectrometry (IMS)

Smiths-Detection/Graesby: IONSCAN Sentinel II®

use soft ionization. Selectable positive and negative ionization enhances identification or sensitivity. Used in portal monitors, such as airport security.



The ions in question are generated by atmospheric-pressure chemical ionization. Sample material is heated to yield a vapor that is swept into a small drift chamber where a beta radiation source ionizes the molecules. The resulting ions – separated according to size, mass and geometry – accelerate towards a detector.

Mobility (K) is determined from the drift velocity (vd) attained by ions in a weak electric field (E) in the drift tube, according to the equation, $vd = K \times E$. The distribution of these signals forms an ion spectrum, with an ion mobility band corresponding to each of the unique ionic species. The spectrum is a fingerprint of the parent compound. Libraries of these ion spectra remain resident in the IONSCAN software and are in the screening process.

During analysis, the IONSCAN will look for ions that take the same amount of time and peak within an expected range of the target substances. If it finds ions that fit those parameters, it will detect the substance and “alarm”. If the IONSCAN does not find ions that fit those parameters, it will not alarm.

Improved Chemical Agent Monitor (ICAM)



[Photo of ICAM]The Improved Chemical Agent Monitor is an improvement over the currently fielded CAM. The modular design is less expensive to repair, requires less maintenance, and eliminates depot level repair now required for the CAM. The ICAM also starts up faster after prolonged storage and is more reliable.

<http://www.afcintl.com/gasdet/rae/chemrae.htm>

The ChemRae weighs less than 2 pounds and can be powered by a rechargeable lithium ion battery pack or AA batteries.



ChemRae is the latest in state of the art handheld Chemical Warfare Agent detection and identification systems. It is Rae Systems' next generation sensor technology based on tested and proven Open Loop Ion Mobility Spectrometry (IMS) technology. The ChemRae uses an improved Ion Mobility Cell, which provides enhanced selectivity and sensitivity. It is designed to detect chemical warfare agents (CWAs) and toxic industrial chemical (TICs).

ChemRae can be used as a stand alone portable monitor or integrated into an AreaRae network by using a RaeLink2 modem. Integration into an AreaRae network allows users to add CWA detection to their existing complement of AreaRae and Rae Systems portable gas monitors.

	Low Alarm Limit ppm	Low Alarm Limit mg/m ³
GA (Tabun), GB (Sarin)	0.2	0.02
GD (Soman), GF (Cyclo-Sarin)/VX	0.1	0.01
HD (Sulfur Mustard)	0.312	2.00
L (Lewisite)	0.242	2.00
Blood Agents	-	30.0
Ethylene Oxide	100	180
Acrylonitrile	100	217
Hydrogen Sulfide	10	14
Arsine	5	16
Ammonia	400	278
Phosphor Trichloride	25	140
Carbon Disulfide	500	1557
Allyl Alcohol	40	95
Line Power	120/240 VAC	
Rechargeable Battery	Li-Ion	
Recharge Time	About 5 hours	
Charger	Battery charges in the monitor or in an optional stand alone charger	
Alkaline Battery	6 AA batteries using optional alkaline battery adapter	
Operating Temperature	-22 to 131°F	
Storage Temperature	-40 to 158°F	
EMI	MIL-STD-461C	
EMP	MIL-STD-462	
Vibration	MIL-STD-810D	
Shock	MIL-STD-810D	
Size	9" x 4" x 2"	
Weight	1.8 pounds	

Bruker Daltonics Inc. RAID-M, commercial IMS

Testing was limited to detecting chemicals in the vapor phase because that mode of application is most relevant to use by first responders. Testing was conducted in two phases: detection of TICs (conducted in a non-surety laboratory at Battelle) and detection of CW agents (conducted in a certified surety laboratory at Battelle's Hazardous Materials Research Center). The TICs used in testing were cyanogen chloride (CICN; North Atlantic Treaty Organization [NATO] military designation CK), hydrogen cyanide (**HCN; designated AC**), phosgene (COCl₂; designated CG), chlorine (Cl₂; no military designation), and arsine (AsH₃; designated SA). The CW agents were sarin (GB) and sulfur mustard (HD). The RAID-Ms were not programmed to respond to SA, so testing with that TIC was minimal.

Of particular interest in the ETV report are the consequences of interferents⁹³

Table 2. Summary Results for Key Performance Parameters

Performance Parameter	TICs				CW Agents	
	AC	CK	CG	Cl ₂	GB	HD
Response time (seconds)	3 to 5	3 to 5	3 to 5	9	10	5 to 8
Recovery time (seconds)	15 to >600	10 to 40	<10	10 to 40	15 to 70	10 to 100
Identification accuracy (%)	nearly 100	nearly 100	nearly 100	nearly 100	97.5	99.4
Response threshold (ppm)	<0.06	<0.6	0.08 to 0.33 ^(a)	0.25 to 0.5 ^(a)	0.0035 to 0.007 ^(a)	0.01 to 0.02 ^(a)
Interferent effects: False negatives ^(b)				Latex paint fumes, floor cleaner vapors	Latex paint fumes, floor cleaner vapors, air freshener vapors	Latex paint fumes, air freshener vapors, DEAE, ^(c) gasoline exhaust hydrocarbons

^(a) Range shown is based on results from two different RAID-M units.

^(b) The indicated interferents reduced or eliminated response to the indicated TIC or CW agent. See text below.

^(c) N,N-diethylaminoethanol.

A3. Instruments using Hyphenated Techniques

VCAM Development Unit



Its mass is 25.2 kg (without consumables) and consumes 140 W (peak) and 100W (nominal) power as derived from the EXPRESS 28V rack. Gas consumables sufficient for one year of operational life are packaged into a separate orbital replacement unit (ORU). Its mass is 5.1 kg. In addition to trace species detection capabilities VCAM units will quantify the three major atmospheric constituents N_2 , O_2 , and CO_2 in the cabin atmosphere. This provides dissimilar redundancy to the Major Constituents Analyzer already aboard ISS. The major constituent measurements will not use the PCGC system. Instead a sample of cabin atmosphere is directly introduced into the MS through a separate pulsed valve and conduction-limited tubing.

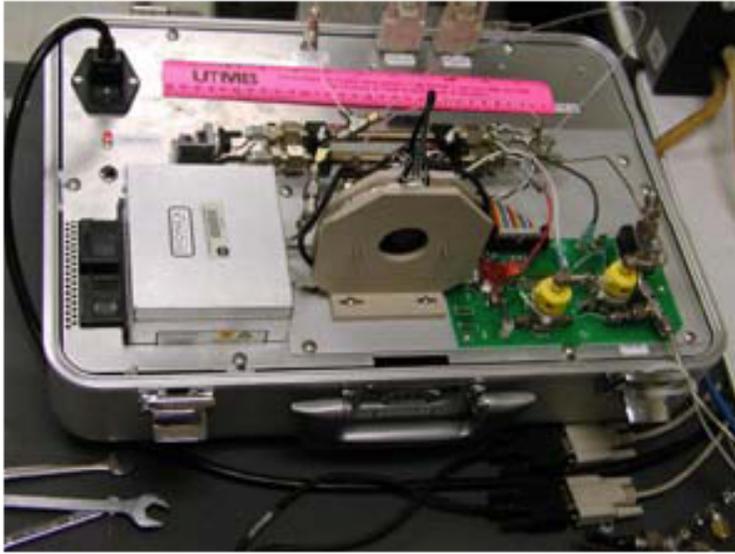
The JPL team has continuously improved and miniaturized a mass spectrometer, recently adding GC and preconcentrator capabilities to the front end⁹⁴ with good performance for most of the listed compounds:

Table 1. Summary of the lowest limits of detection (LLDs) for volatile organic compounds as measured with the miniature GC/QIT system, together with NASA-required minimum detection levels (MDLs)¹²

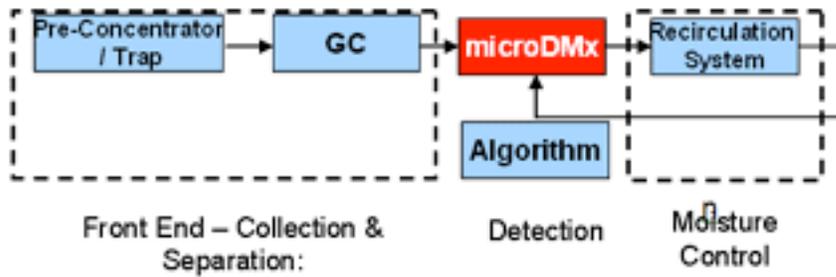
Compound	MDL/LLD (ppb)	Compound	MDL/LLD (ppb)
Acetaldehyde	100/136	Furan	10/1
Acetone	10 ³ /1	Hexamethyl- cyclotrisiloxane	100/5 × 10 ³
Benzene	10/0.2	Isoprene	50/0.8
1-Butanol	500/0.7	Methanol	200/2 × 10 ^{3a}
2-Butanone	500/0.6	Octamethyl- cyclotrisiloxane	50/4
1,2- Dichloroethane	10/1	2-Propanol	3 × 10 ³ /17
Dichloromethane	30/0.7	Propylene glycol	500/8.5
Ethanol	10 ⁴ /4	Toluene	10 ³ /1.8
Ethyl acetate	10 ³ /0.6	Xylenes	2 × 10 ³ /5
Freon 113	2 × 10 ³ /9		

^a Can be lowered by removing interference with impurity O₂ and N₂ in the helium carrier gas.

Sionex GC/IMS



Early version of Sionex GC-IMS.



Limero and colleagues⁵ have shown good performance for this system in varying relative humidities:

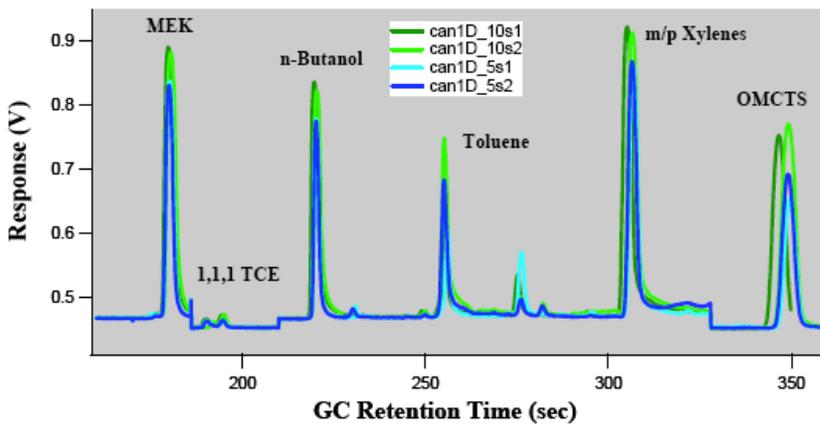


Figure 13: Overlay of late-eluting compounds for four runs of a complex mixture containing 50% RH. OMCTS is

/lcyctotetrasiloxane.

FemtoScan: EVM II instrument uses Graesby drift tubes,



from Detection Of Pesticide Vapors Via Hand Portable Gas Chromatography/Ion Mobility Spectrometry, Application Note #9701

GC/IMS responses for eight of these analytes are presented here as "false color" contour displays. Detection limits at 1 ppbv were obtained for both DMMP and Dichlorvos. Also included in the false color displays is a GC/IMS separation of 5 analytes which includes a number of impurities. This illustrates the effectiveness of this approach when separating complex analyte mixtures.

Chemical	Sample Time	Concentration	Retention Time	Drift Time	Chemical	Sample Time	Concentration	Retention Time	Drift Time
Aldrin (1)					Hexachlorobenzene(4)	10 s	HS(5)	82 s	5.2 ms
Cygon (2)					Lindane (1)				
DEMP (3)	1 s	7 ppbv	8.8 s	5.0 ms	Malathion (1)				
Diazinon (1)					Meta Systox	10 s	HS (5)	33 s	5.4 ms
Dichlorvos	2 s	1 ppbv	6.3 s	5.2 ms	Methyl Parathion (1)				
DIMP(3)	1 s	4 ppbv	10.3 s	5.4 ms	Monitor (2)				
Disulfoton	10 s	HS(5)	86 s	5.8 ms	Naled				
DMMP(3)	1 s	1 ppbv	5.5 s	4.6 ms	Phorate	4 s	<1.3 ppmv	39.6 s	5.9 ms
Endrin(1)					Phosdrin	2 s	<390 ppbv	52.5 s	5.5 ms
Ethion(1)					Zolone (2)	4 s	<150 ppbv	14.3 s	5.0 ms
Heptochlor(1)									

(1) Unable to detect; (2) Results inconclusive; (3) AVS, GC and IMS temperatures are all 70 C; (4) Detected in negative ion mode; (5) includes only headspace data due to unknown vapor pressure

CONCLUSIONS

* Effective detection of low volatile pesticides can be obtained with a low power, hand portable, hyphenated GC/IMS instrument.

* The combination of short column GC and a sensitive, chemically specific IMS detector allows even mixtures of analytes and/or analytes in complex background matrices to be detected.

* A broad range of volatilities may be addressed using this technology. Future advances in low power temperature programming may further extend the volatility range of analytes suitable for determination during a single analysis.

* While this technique has shown the strength of hyphenated systems, it is not suitable for stand-alone detection of unknown analytes. Even for the case of known analytes shown here, trace amounts of volatile impurities may give the impression of a positive target analyte response.

* Modulation of the AVS sampling pulse duration provides an effective means to modify the GC separation characteristics to optimize the sensitivity and specificity of the method for a particular analyte.

* For suitable analytes, GC/IMS represents an extremely sensitive means to detect and quantitate target analytes over an appropriate dynamic range, even in a field portable setting.

HRIMS by Excellims has an IMS as the front end for a mass spectrometer – not flyable, yet, but FYI



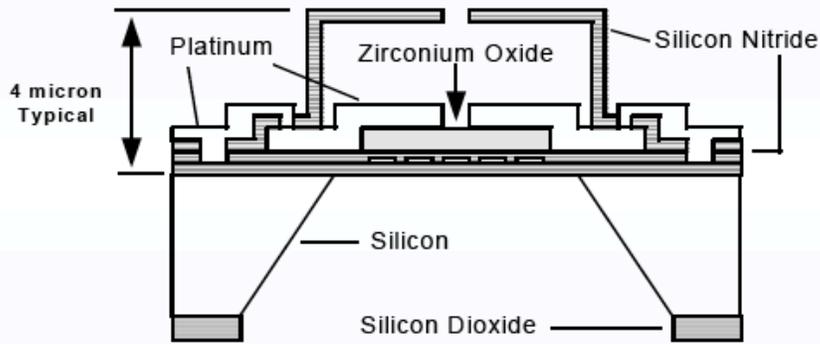
A4. Solid-State Sensors: including semiconductor, electrochemical, and catalytic transduction mechanisms– commonly combined in assembled instruments that detect up to 5 different vapors

Makel Engineering already working with NASA personnel
Makel Engineering – hypergolic fuel detection “Lick and Stick” technology

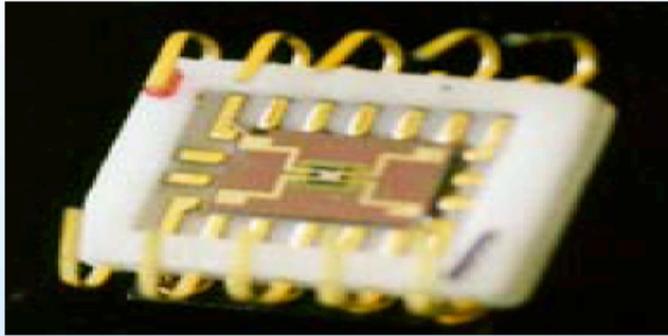


hydrogen, oxygen, and methane.

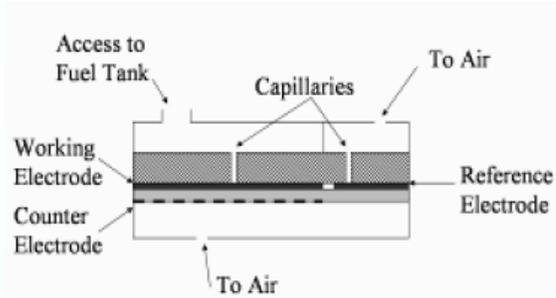




Not to scale:



ZrO₂ Oxygen Sensor



NAFION O₂ Sensor Structure Glenn Research Center

DIMENSIONS: (Approx. 5.63 CM X 3.13 CM X 3.44 CM)

POWER: < 400 mW

MASS: < 300 g PER UNIT

DATA RATE: 50 SAMPLES/SEC

HARDWIRED FOR POWER AND DATA

H₂; RANGE ACCURACY

-50 PPM TO 250 PPM ±25 PPM

250 PPM TO 40,000 PPM ±10% OF READING

RKI Instruments, Inc. [parent Co is in Japan]
 33248 Central Ave.
 Union City, CA 94587

Four Gas Confined Space Monitor: **GX-2009 confined space monitor**
 “smallest and lightest 4-gas monitor in the world,” the GX-2009. Weighing 4.6 ounces, & fits in the palm of your hand (2.75' H x 2.95' L x .98' D). The GX-2009 simultaneously monitors and displays combustibles, oxygen, carbon monoxide, and hydrogen sulfide. Dual audible alarm ports and alarm LED's on 3 sides of the instrument, so that alarm conditions are obvious from multiple perspectives especially in high noise environments. Other features include a **waterproof and dustproof design** with IP 67 rating, an impact-resistant-rubber, over-mold body that is **RFI resistant**, . . .



The GX-2009 simultaneously monitors and displays combustibles (LEL), oxygen (O₂), carbon monoxide (CO), and hydrogen sulfide (H₂S).

- Dual audible alarm ports (95 db @ 30 cm)
- 3 visual alarm LED's
- Vibration alarm
- IP-67 Waterproof/dustproof design

Honeywell: BW Technologies America [note ability to detect numerous Altair Lunar Lander gases and more] GasAlert Micro5®
 H₂S, CO, O₂, SO₂, PH₃, NH₃, NO₂, HCN, Cl₂, ClO₂, O₃, and combustibles as well as CO₂ via IR absorption
 3279 West Pioneer Parkway, Arlington, Texas, USA 76013
 Email: info@gasmonitors.com



Gas	Range (ppm)	Default Resolution (ppm)	High Resolution (ppm)
H2S	0-500	1	0.1
CO	0-999	1	N/A
TwinTox(H2S)	0-500	1	0.1
TwinTox(CO)	0-500	1	N/A
O2	0-30.0%	0.10%	N/A
SO2	0-150	1	0.1
PH3	0-5.0	1	0.1
NH3	0-100	1	0.1
NO2	0-99.9	1	0.1
HCN	0-30.0	1	0.1
Cl2	0-50.0	1	0.1
ClO2	0-1.0	0.1	0.01
O3	0-1.0	0.1	0.01
PID(VOCs)	0-1000	1	N/A
	0-50,000		
IR(CO2)	0-5.0% v/v	150 0.01%	N/A
Combustible gases	0-100% LEL 0-5.0% v/v	1% or 0.1%	N/A

GasAlertMicro 5: water-resistant line of portable gas detectors Continuously monitors and displays concentrations of up to five gases.

- * Integral concussion-proof boot
- * Optional integral motorized pump option for remote sampling

- * Powered by three AA alkaline batteries or a hot-swappable rechargeable battery pack
- * Triple alarms (audible, visual and vibrating)
- * Multi-language support in English, French, German, Spanish and Portuguese
- * Large, user selectable backlit LCD
- * Four alarm levels: Low, High, TWA and STEL
- * Compatible with MicroDock II Automatic Test and Calibration Station
- * Datalogging models store and recall event information
- * Wide range of user selectable field options including password protection, safe and stealth modes.

Self-Tests

- Full function self-test confirms sensor, battery and circuitry integrity and audible/visual alarms on activation



Figaro [Japan]

Model	Target gas	Typical detection range	Ps	Description
TGS2620	Alcohol, Solvent vapors	50 - 5,000ppm	210mW	Compact size, For breath alcohol testers and solvent detectors Ceramic base resistant to severe environments
TGS826	Ammonia	30 - 300ppm	833mW	High selectivity to ammonia
TGS2444	Ammonia	10 - 100ppm	56mW	Precalibrated module
CDM4161	Carbon dioxide Carbon	400-9,000ppm	300mW	
TGS2442	Carbon monoxide	30 - 1,000ppm	14mW	Compact size
TGS2602	General air contaminants	1 - 30ppm	280mW	High sensitivity to VOCs and odorous gases For leak detection from refrigerators and air conditioners Ceramic base resistant to severe environments
TGS832	Halocarbon gas	100 - 3,000ppm	835mW	Precalibrated module, Maintenance free, For gas leak detection in fuel cell systems
FCM6812	Hydrogen Methane LP gas	0 - 35%LEL	1.0 W	Ceramic base resistant to severe environments
TGS825	Hydrogen sulfide	5 - 100ppm	660mW	Catalytic type, Wide detection range, Linear output, For residential gas alarms
TGS6810	LP gas, Methane	0 - 100%LEL	525mW	High selectivity to methane gas
TGS2611-E00	Methane	500 - 10,000ppm	280mW	Stable relative sensitivity between CH ₄ & LP gas, Good durability, For residential gas alarms
TGS2612	Methane, LP gas	500 - 10,000ppm 500 - 12,500ppm	280mW	
TGS3870	Methane & CO	50 - 1,000ppm	38mW	Dual gas detection with one sensor
SK-25	Oxygen	0 - 30%	No power required	Galvanic cell, Good linearity
TGS2180	Water vapor	1 - 150g/m ³	830mW	High selectivity to water vapor



CO₂:



Figaro's CDM4161-L00 solid electrolyte CO₂ sensor [5VDC, 0.3W. -10°C to 60°C, 5 to 95% RH [avoid condensation]

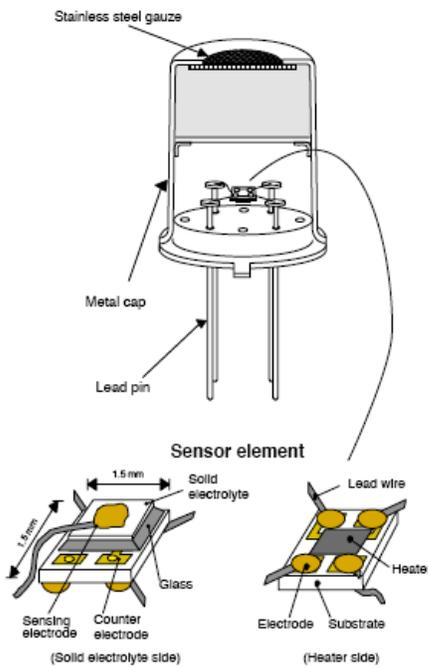
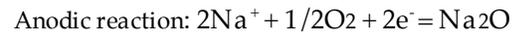
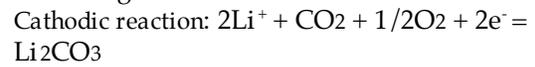
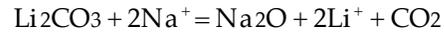


Fig. 1 - Sensor structure

When the sensor is exposed to CO₂ gas, the following electrochemical reaction occurs:



Overall chemical reaction:



As a result of the electrochemical reaction, electro-motive force (EMF) would be generated according to Nernst's equation:

$$\text{EMF} = E_c - (R \times T) / (2F) \ln(P(\text{CO}_2))$$

where

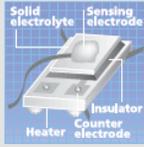
$P(\text{CO}_2)$: Partial pressure of CO₂,

E_c : Constant value R : Gas constant

T : Temperature (K) F : Faraday constant

By monitoring the electromotive force (EMF) generated between the two electrodes, it is possible to measure CO₂.

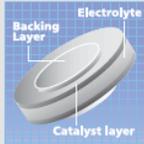
Electrochemical



Solid state electrolyte type

Figaro was the first company to successfully commercialize solid state electrolyte CO₂ sensors by using a Figaro patented technology. This CO₂ sensor has compact size, low power consumption, and has lower cost and longer

life than conventional Infra-red sensor technology.



Liquid electrolyte type

This type of sensor shows good accuracy, linear response, and exhibit excellent selectivity to its target gas. Since liquid electrolyte sensors can be operated without heat, they can be used in the development of battery operated

sensing devices. Unlike traditional electrochemical sensors, Figaro's sensors are designed for environmental safety, using weak alkaline electrolyte.



Catalytic

The catalytic type gas sensor is a long established technology. The principle is based on combustion of the target gas on a heated catalyst, producing heat which is measured in order to determine the presence of gas.

Figaro's 35+ years of experience in catalyst material technology and its advanced micro fabrication technology enable production of the most advanced compact pellistor sensors whose durability, stability, quick response, and linear output make them ideal for detecting many combustible gases.

Matheson: Surface Sensitive Sensors

The Gas Sniper Portable Gas Detector *(continued)*

VOC Leak Detector (EPA Method 21) – Monitors ‘1’ to ‘6’ Gases Simultaneously

Gas Sensor Selection Table		
Model Number	Description	Full Scale Range
STANDARD Confined Space Gases		
SGS-CO2-5K	Carbon Dioxide	0-5000 ppm
SGS-CO2-10K	Carbon Dioxide	0-10,000 ppm
SGS-CO2-20V	Carbon Dioxide	0-20% Vol
SGS-CO2-60V	Carbon Dioxide	0-60% Vol
SGS-CH4-L/P	Hydrocarbons ⁺	0-100% LEL/0-50,000 ppm
SGS-O2	Oxygen	0-40% Vol
TOXIC Gases[▲]		
SGS-NH3-75	Ammonia	0-75 ppm
SGS-ASH3-1	Arsine	0-1 ppm
SGS-ASH3-2	Arsine	0-0.2 ppb
SGS-BR-1	Bromine	0-1 ppm
SGS-CO-150	Carbon Monoxide	0-150 ppm
SGS-CO-500	Carbon Monoxide	0-500 ppm
SGS-CL2-3	Chlorine	0-3 ppm
SGS-CLO2-1	Chlorine Dioxide	0-1 ppm
SGS-B2H6-03	Diborane	0-0.3 ppm
SGS-B2H6-30	Diborane	0-30 ppm
SGS-F2-5	Fluorine	0-5 ppm
SGS-N2H4-5	Hydrazine	0-5 ppm
SGS-HC-L/AR [*]	Hydrocarbons ⁺	100% LEL
SGS-HBR-9	Hydrogen Bromide	0-9 ppm
SGS-HCL-15/R [■]	Hydrogen Chloride	0-15 ppm
SGS-HCL-15	Hydrogen Chloride	0-15 ppm
SGS-HCN-30	Hydrogen Cyanide	0-30 ppm
SGS-HF-9	Hydrogen Fluoride	0-9 ppm
SGS-H2S-1	Hydrogen Sulfide	0-1 ppm
SGS-H2S-30	Hydrogen Sulfide	0-30 ppm
SGS-H2S-100	Hydrogen Sulfide	0-100 ppm
SGS-CH4-L/AR [*]	Methane ⁺	0-100% LEL
SGS-NO2-15	Nitrogen Dioxide	0-15 ppm
SGS-NO-100	Nitric Oxide	0-100 ppm
SGS-O3-1	Ozone	0-1 ppm
SGS-PH3-1	Phosphine	0-1 ppm
SGS-SiH4-15	Silane	0-15 ppm
SGS-SO2-10	Sulfur Dioxide	0-10 ppm

[▲]The Gas Sniper can be configured with up to ‘6’ gas sensors; only a maximum of ‘2’ toxic sensors may be used in the Gas Sniper with any configuration.

⁺Flammable gas

^{*}“AR” denotes gas sensor has “autoranging” capability; the sensor automatically ranges from % LEL to % Vol in concentration.

[■]“R” indicates sensor also has capability to detect CL₂.



Gas Sensors

[R = Cl₂ detection]



Gas Sniper-01 Model for EPA Method 21

utilizes hydrophobic filters to prevent moisture contamination. The Gas Sniper will continuously operate for up to 30 hours on alkaline batteries or 18 hours on Ni-Cad batteries. A maximum of 30 seconds is all that is needed for instrument warm up.

Principle of Operation

Depending on the specific gas being monitored, the Gas Sniper utilizes catalytic combustion, electrochemical cell, galvanic cell and infrared sensor technologies to accurately detect gases within several full scale ranges. These sensors provide accurate measurement for the target gas being monitored and are designed for continuous duty with the following features:

- **Linear Output**
- **High Accuracy; Superior Repeatability**
- **Immune to Ambient Temperature Changes**
- **Low Power Consumption**

An integral, extremely low power suction pump provides a continuous, steady sample flow to provide accurate and repeatable measurements. Sample flow to the gas sensor is regulated and consistently monitored.

Industrial Scientific Corp. [<http://www.indsci.com/default.aspx>] has announced the MX6 iBrid™ Multi-Gas Monitor, an improved, 6-gas version of the existing CSA-CP, [compound specific analyzer-combustion products] that is expected to be available in mid-2011. See http://www.indsci.com/news_releases.aspx?id=2405&terms=CSA “The MX6 is designed to detect from one to six gases including oxygen, combustible gases and up to four toxic gases. With 25 field-replaceable “smart” sensor options, an integrated sampling pump, and interchangeable lithium-ion and alkaline battery packs, the MX6 can be set up in millions of different detection configurations. Such configuration flexibility allows it to measure potential hazards in any industry. The addition of a photo-ionization detector (PID) allows for the detection of the potentially “unknown” toxic hazards or volatile organic compounds that may exist in some applications.”

NOTE: this instrument uses transducing/detecting components that exhibit similar non-specific responses as do all such solid-state components [the “CO” sensor responds to acetylene, unsaturated hydrocarbons, but may have some compensation against H₂; “HCN” sensor has negative response to NO_x, etc.]. photo follows:



The JPL Electronic Nose, now on the ISS



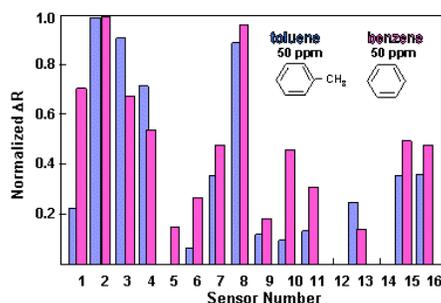
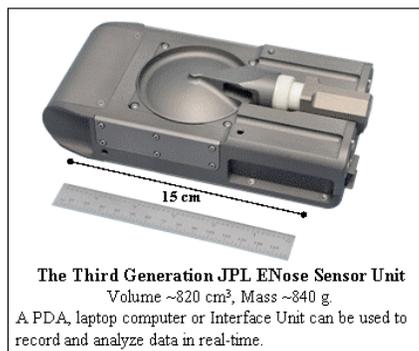
Figure 1: The Third Generation ENose. The Sensor Unit is enclosed in the Interface Unit, which will be connected to the ISS EXPRESS Rack



THE JPL ELECTRONIC NOSE (ENose)



- ◆ The JPL ENose provides rapid, early identification and quantification of target chemical species.
- ◆ An electronic nose is an array of semi-selective chemical sensors. The JPL ENose is 32 sensors which change electrical resistances when environmental composition changes.
- ◆ The sensing array responds in “fingerprint” patterns to a broad suite of target analytes. Fingerprints are deconvoluted for id and quantification.
- ◆ Targets include **leaks or spills** of selected compounds, Hg, SO₂ and possibly heating insulation which signals **electrical fires**.
- ◆ The JPL ENose can be used to **monitor cleanup processes**.



JPL eNose has evolved and has flown, in some configurations^{6,82}

The Third Generation ENose is an air quality monitor designed to operate in the environment of the US Lab on the International Space Station (ISS). It detects a selected group of analytes at target concentrations in the ppm regime at an environmental temperature range of 18 – 30 °C, relative humidity from 25 - 75% and pressure from 530 to 760 torr. This device was installed and activated on ISS on Dec. 9, 2008 and has been operating continuously since activation. Data are downlinked and analyzed weekly. Results of analysis of ENose monitoring data show the short term presence of low concentration of alcohols, octafluoropropane and formaldehyde as well as frequent short term unknown events.

NASA at Kennedy Space Center (KSC) is assessing several commercial and developing electronic noses (E-noses) for these applications. A short series of tests identified those E-noses that exhibited sufficient sensitivity to the vapors of interest. Only two Enoses exhibited sufficient sensitivity for hypergolic fuels at the required levels, while several commercial E-noses showed sufficient sensitivity of common organic vapors. These E-noses were subjected to further tests to assess their ability to identify vapors. Development and testing of E-nose models using vendor supplied software packages correctly identified vapors with an accuracy of 70–90%. In-house software improvements increased the identification rates between 90 and 100%.⁹⁵

Cyrano Sciences now owned by Smiths Detection [UK]



Cyranose 320™

Also:

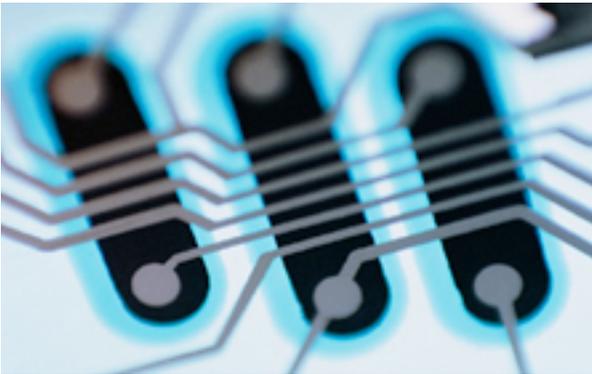
eNose monitor of aroma of Apricots⁹⁶: The objective of this research was to characterize the aroma of two lots of Castlebrite apricots at different stages of initial maturity using gas chromatography–mass spectrometry (GC–MS), electronic nose (e-nose) analysis, and a sensory panel.

The e-nose was able to discriminate between both stages of maturity for all samples regardless of the duration of cold storage.

Black Tea via eNose⁹⁷

Fish freshness⁹⁸

Nate Lewis [CalTech] has formed a new company: **Next Dimension Technologies**
<http://www.nextdimensiontech.com/technology.htm>



The company's core technology is based on a new generation of sensors and sensor array systems. The sensors are designed using nanotechnology-based materials and transducers that exhibit remarkable sensitivity and fast responses towards a broad set of chemical vapors. In addition, the company's patent-protected sensor designs exploit spatial and temporal response patterns that allow for facile detection of chemical vapors in complex environments and also allow for differentiation of both simple and complex vapor mixtures.

Next Dimension Technologies' sensors and sensor array systems can be readily customized to solve even the most demanding application problems. By tailoring sensor responses to the analytes of interest and by selectively rejecting background environments and troublesome interferents that plague conventional sensors, the company's detection systems can offer unprecedented performance in a wide variety of applications.

A5. Optical and Infrared Spectroscopy

See also, p38, Honeywell: BW Technologies America CO₂ detector; same for Industrial Scientific Corp., and others

Yokogawa Tunable-Diode-Laser-based monitors:

GASES MEASURED	
O ₂	0.01% detection limit, Min Range 0-1%
H ₂ O (low range)	0.2 ppm, Min Range 0-20ppm
H ₂ O (high range)	ppm to % levels
CO (low range)	low ppm range
CO (high range)	high-ppm to % levels
CO ₂	low ppm range
CO ₂	high-ppm to % levels
CO + CO ₂	dual gas, % concentrations
NH ₃	Minimum Range 0-30 ppm
H ₂ S	High ppm to % level

Measures O₂, moisture, CO, NH₃, CH and HCN

Interference Free *for most applications*

TruePeak Measurement Capable of measuring under changing pressure, temperature and background

Process Pressures up to 20 Bar

Optical Measurement, no sensor contact with process

Low LTCO (no moving parts, high MTBF for components)

On Board Diagnostics



ATEX Group II for zone 1 (Cat 2G) or 2 (Cat 3G) with purge systems

In addition to operating in conditions of high temperature or pressure, it can be used under difficult conditions including environments involving corrosive, aggressive and *high particulate content materials*.

The TruePeak TDL analyser forms a complementary solution to Yokogawa's ZR Zirconia oxygen analyser, and measures oxygen (O₂) and pressures as high as 20 bar absolute. Measurement span is typically between 1% and 100% oxygen.

Carbon monoxide (CO), from low ppm detection limits to percentage levels and carbon dioxide (CO₂) can also be measured at process temperatures of up to 1500°C. Subject to application we can also offer **HCl, NH₃, HCN, CH₄ and multipoint measurements such as CO₂, H₂O and CH₄ for combustions processes.**

The analyser can also be used for measuring parts per million **moisture content** in corrosive and aggressive process streams including chlorine and hydrocarbons.

TDL Sensors, Ltd. [UK]

A Multi-laser option is available using the same instrument for multi-gas measurements such as NH₃ + moisture + O₂, HCl + moisture + O₂, HF + moisture + O₂, CO + O₂, HCl + HF + moisture.

LEL methane 0-100%

Free from interference by other hydrocarbons

Open-path, perimeter monitoring - up to 500-m path length

Very low maintenance

HF, CO, HCN, H₂S also available



TDL100-P



Photon Machines-Tunable-Diode-Laser [“TDL”] based detection systems

Bloodhound™ TDL instrument

The Bloodhound™ sensors are ruggedized for industrial applications
Simple measurement of multiple gases with high fidelity and fast response is possible
anywhere in your process

Molecular species measurements of O₂, CH₄, CO, CO₂, NH₃, H₂O, and many other
small molecules.

Measurements from parts-per-million to percent concentrations.

Large dynamic range configured for your application.

Temperature to within ± 15 K.

The Vaisala SPECTRACAP® Sensor

The SPECTRACAP® Sensor is based on Tunable Diode Laser (TDL) technology, tuned to a characteristic and unique wavelength of the oxygen molecule in the near infrared (NIR) region, see Figure 1 below. Consequently, there are no direct cross sensitivities with other gases, and the measured absorption is proportional to the oxygen concentration in the gas sample

Power supply

input range 11 ... 36 VDC

Power consumption

Maximum 6W

Typical 3W

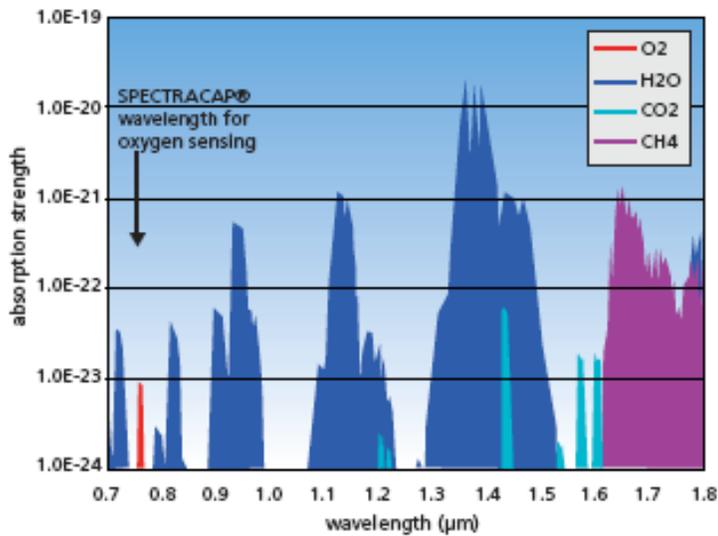


Figure 1: Absorption wavelengths of some common gases. Note how the oxygen absorption does not overlap with other atmospheric gases.

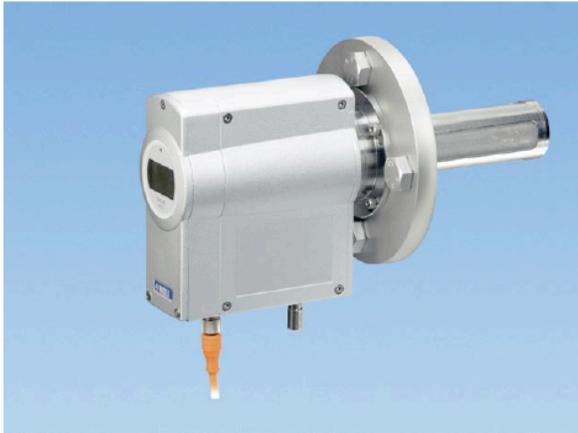


© Fondriest Environmental, Inc.

Vaisala: GMP343 carbon dioxide sensor, diffusion aspiration, 0-2% CO₂, 0-5 VDC & RS-232 output IP67-classified and suitable for harsh environments.

Single-beam, dual-wavelength CO₂ measurement with no moving parts
 Compensation options for temperature, pressure, humidity, and oxygen

OMT355 Oxygen Transmitter Process Measurements



The Vaisala SPECTRACAP[®] Oxygen Transmitter.

Performance

Measurement range	0 ... 25 % O ₂
Accuracy (including noise, linearity, and repeatability)	±0.2 % O ₂
Temperature dependence over T range	±2 % of reading
Stability	±1 % of reading/yr
Zero drift	±0.1 % O ₂ /yr
Response time of measurement	3 s
Diffusion limited response in still air	T ₆₃ /T ₉₀
without filters	10 s / 20 s
with stainless steel mesh filter	10 s / 25 s
with stainless steel mesh and PTFE filters	30 s / 70 s
Pressure dependence without pressure compensation	
0.8 ... 1.2 bar	-2 % of reading
1.2 ... 1.4 bar	-5 % of reading
Accuracy of pressure compensation	±0.25 % of reading
Background gas effects for CO ₂ and H ₂ O, uncompensated	<1 % of reading for <6 vol-% CO ₂
	<1 % of reading for gas dewpoint < 30 °C
Accuracy of background gas compensation	
0 ... 50 vol-% CO ₂	±0.5 % of reading
0 ... 300 g/m ³ H ₂ O (T ₄ = 80 °C)	±1 % of reading

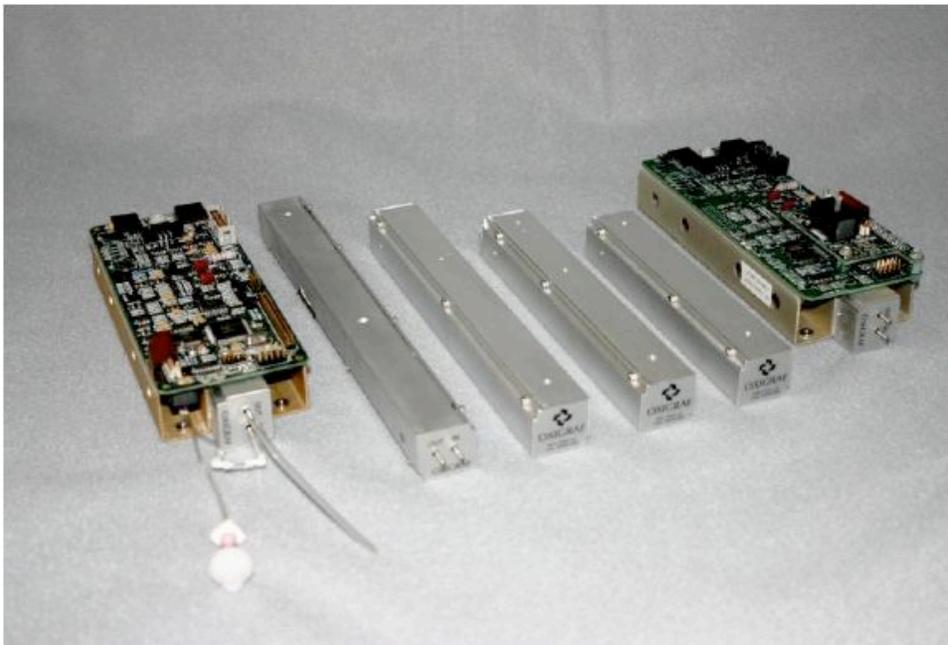
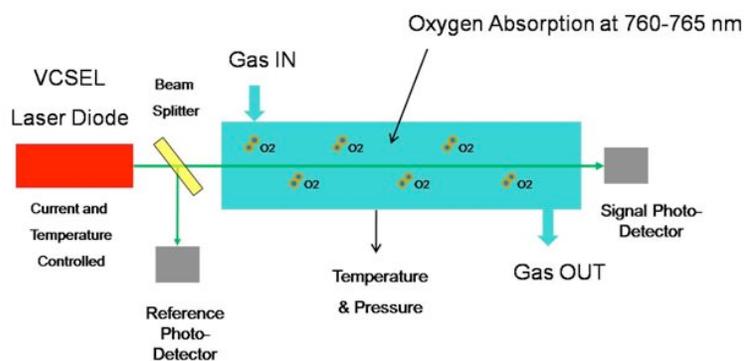
Operating Environment

Operating temperature range	
for probe (in-line installation)	-20 ... +80 °C
for electronics (housing)	-40 ... +60 °C
for transmitter (ambient gas measurement)	-20 ... +60 °C
Storage temperature range	-55 ... +80 °C
Operating pressure range	0.8 ... 1.4 bar
Maximum pressure range for probe	up to 10 bar

Oxigraph OEM O2 sensors

Oxigraf oxygen sensor uses absorption spectroscopy to measure the concentration of oxygen molecules in a gas sample.

The O2Cap family integrates an **Oxigraf oxygen sensor** with a CO₂ sensor for dual gas measurements for research, industrial and laboratory measurements. Measure Oxygen concentrations from 5-100% and CO₂ from 0-10%. Perform capnography tests with fast breath-by-breath measurement. The units come with a pump or pressure regulated gas sampling system, bright vacuum fluorescent alphanumeric display (VFD), touch panel keypad, a rear 0-1VDC analog output for O₂ readings, rear terminal strip with limit detection relays and 4 – 20 mA analog outputs, and a RS232 digital interface.



Cavity-ringdown spectroscopy⁹⁹ is not high TRL, yet.

Because cavity-ringdown spectroscopy [“CRS”] requires a very high-Q optical cavity [extremely high-reflectance mirrors and very low losses, overall, aside from the absorption of the gaseous molecules of interest], any mechanism that degrades the Q also concomitantly degrades the performance of the CRS instrument. This can include “errant” aerosol particles and films that gradually build up on the surfaces of the optics, etc. Other issues to be addressed would be evaluation of possible cross-signals from multiple species and the tradeoff between narrowing the bandwidth of the excitation light source to reduce or eliminate such cross-signals and the accompanying tradeoffs of signal strength and rapidity with which a mixture of many gases at widely-differing concentrations can be monitored.

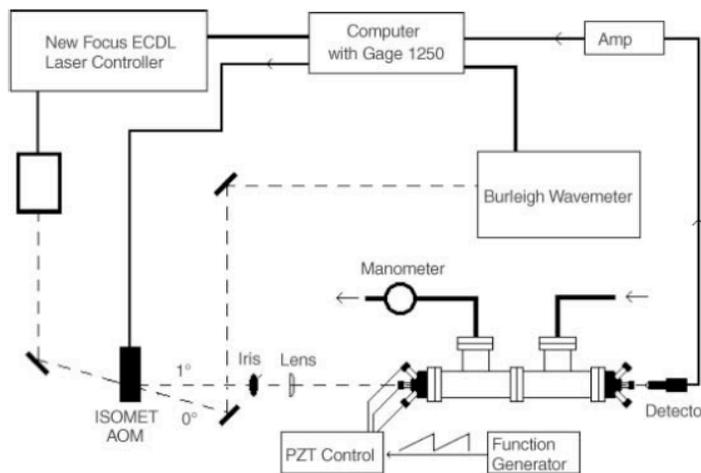
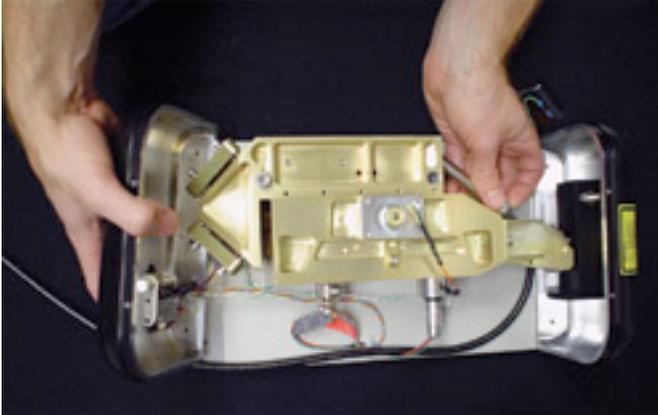


FIGURE 1 Schematic layout of the experimental set-up

Nonetheless, this technique can certainly be kept on NASA’s “watch list,” since the limiting sensitivities are attractive:

A continuous-wave (cw), external-cavity tunable diode laser centered at 1.55 μm is used to pump an optical cavity absorption cell in cw-cavity ringdown spectroscopy (cw-CRDS). Preliminary results are presented that demonstrate the sensitivity, selectivity and reproducibility of this method. Detection limits of 2.0 ppm for CO, 2.5 ppm for CO₂, 1.8 ppm for H₂O, 19.4 ppb for NH₃, 7.9 ppb for HCN and 4.0 ppb for C₂H₂ are calculated. [From the abstract of Awtry&Miller⁹⁹]

An article in Photonics Spectra also reviewed the tunable, mid-IR laser absorption spectroscopy¹⁰⁰ collaboration between Aculight and Prof. JH Miller, at GWU.



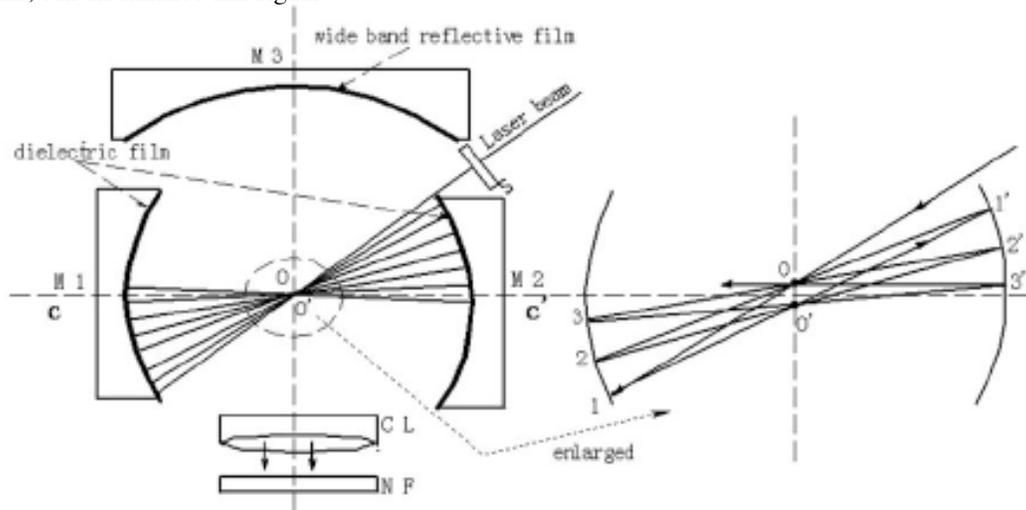
Aculight Argos OPO modules consist of a quasi-monolithic resonant OPO cavity mounted on a pump laser-pointing unit. Here the fiber laser collimator is shown being inserted into the pointing unit.

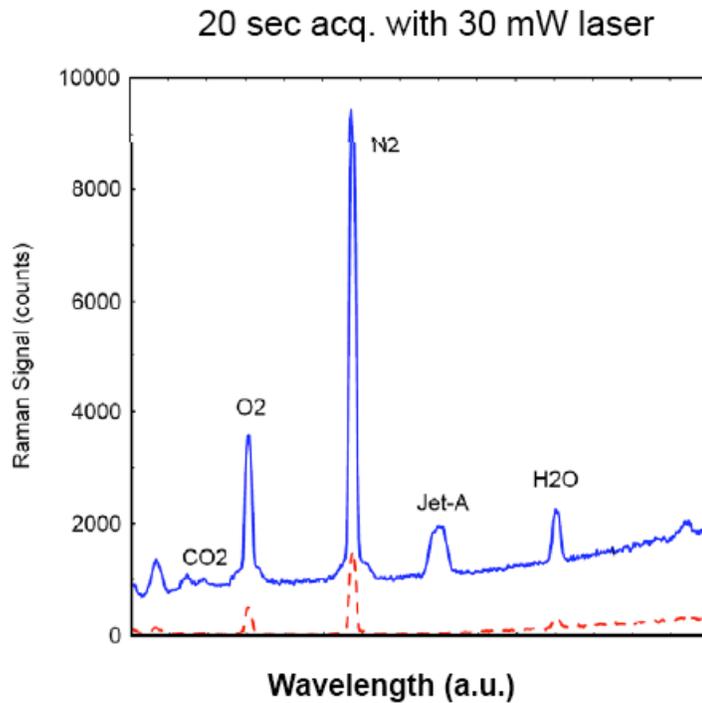
Raman Spectroscopy¹⁰¹

Potentially a major constituent analyzer that includes N_2 , O_2 , CO_2 , H_2O [maybe, CO , too]
 Raman scattering cross sections: $N_2 = 4.3$, $O_2 = 5.2$, $CO_2 = 11$, $H_2O = 12$, $CH_4 = 34$ all in units of 10^{-31} $cm^2/molecule/steradian$

[all 3-D space surrounding a molecule is covered by 4π steradians; for a lens with off-paraxial angle of θ , then steradians = $4\pi(1-\cos(\theta))$]

Ignoring any enhancements, such as resonant cavities, multipass systems, etc., and the use of shorter wavelength light that would increase the scattering cross sections, a 1-W laser in the blue wavelength region produces about 2.4×10^{18} photons/s and a less-than-0.5-NA lens might only intercept ≈ 0.8 steradians of angular space. Thus, the Raman scattering from one molecule of N_2 would be $\{2.4 \times 10^{18} * 0.8 * 4.3 \times 10^{-31}\} \approx 8 \times 10^{-13}$ photons/s. One atmosphere at room temperature is $\approx 2.4 \times 10^{19}$ molecules/cm³, of which 80% might be N_2 and the laser beam can be expected to excite only about .001 cm³ that is imaged by the lens, or 2×10^{16} N_2 molecules, thus, scattering 1.6×10^4 photons/s through the lens. Although not a huge number, this is pretty easy to detect, particularly if one collects for many seconds or for one minute with a low-noise photomultiplier or cooled solid-state detector. Using shorter-wavelength laser light, multipass configurations¹⁰², higher-NA or even non-imaging optical detection systems, can all enhance this signal.





Raman spectra showing N_2 , O_2 , CO_2 , and H_2O taken using a single-pass, fiber-optic system by Q-V Nguyen, of NASA GRC⁸⁵

Potentially a major constituent analyzer that includes N_2 , O_2 , CO_2 – demonstrated since 1968 with Raman¹⁰¹

Intra-cavity configurations enhance Raman sensitivity¹⁰³⁻¹⁰⁵

Pixelated cytological Raman analysis of Bioaerosols has been reported⁶⁴

A6. Spacecraft Maximum Allowable Concentrations List from the National Academies' Press 2008

1 Acrolein
2. C3 to C8 Aliphatic Saturated Aldehydes
3 Ammonia
4 Benzene
5 n-Butanol
6 C2-C9 Alkanes
7 Carbon Dioxide
8 Carbon monoxide
9 1, 2-Dichloroethane
10 Dimethylhydrazine
11 Ethanol
12. Formaldehyde
13 Limonene
14 Methanol
15 Methylene Chloride
16 Propylene Glycol
17 Toluene
18 Trimethylsilanol
19 Xylenes

VII. Acknowledgements

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VIII. References

1. Snyder, A.P., *et al.* Orthogonal analysis of mass and spectral based technologies for the field detection of bioaerosols. *Anal. Chim. Acta* 513, 365-377 (2004).
2. Zhou, H.Y., Homer, M.L., Shevade, A.V. & Ryan, M.A. Nonlinear least-squares based method for identifying and quantifying single and mixed contaminants in air with an electronic nose. *Sensors* 6, 1-18 (2006).
3. Quinn, J.C., Bryant, P.H., Creveling, D.R., Klein, S.R. & Abarbanel, H.D.I. Parameter and state estimation of experimental chaotic systems using synchronization. *Phys. Rev. E* 80, 17 (2009).
4. Vollmer, M.K., Reimann, S., Folini, D., Porter, L.W. & Steele, L.P. First appearance and rapid growth of anthropogenic HFC-245fa (CHF₂CH₂CF₃) in the atmosphere. *Geophysical Research Letters* 33, - (2006).
5. Limero, T., Reese, E. & Cheng, P. Demonstration of the microAnalyzer's Measurement of Common Trace Volatile Organic Compounds in Spacecraft Atmospheres. *International Conference on Environmental Systems 2008*, 2128 (2008).
6. Ryan, M.A., *et al.* Operation of Third Generation JPL Electronic Nose on the International Space Station. *Proceedings of the 2009 International Conference on Environmental Systems 2009*, 2522 (2009).
7. A. Chutjian, M.R.D., B. J. Bornstein, A. P. Croonquist, E. Edgu-Fry, D. J. Fry,, V. Garkanian, M.A.G., V. R. Haemmerle, W. M. Heinrichs, R. D. Kidd, S. Lee,, J. A. MacAskill, S.M.M., L. Mandrake, T.M. Rust, R. T. Schaefer, & J. L. Thomas, N.T., and M. J. Walch,M. Christensen, A. Dawson, D. Demonbrun, R. Vanholden,P. M. Holland,B. J. Shortt. Results from the Vehicle Cabin Atmosphere Monitor: A Miniature Gas

- Chromatograph/Mass Spectrometer for Trace Contamination Monitoring on the ISS and Orion. *ICES 2008* 01-2045, 0321 (2008).**
- 8. Martin, P.M. & Mills, A.A. Does Lunar Regolith Follow Rosins Law. *Moon* 16, 215-219 (1977).**
 - 9. Greenberg, P.S. & Hyatt, M.J. Instrumentation and sensor technologies for the measurement and detection of Lunar Dust. in *Aerospace conference, 2009 IEEE* 1-10 (2009).**
 - 10. Richard, D.T. & Davis, S.S. Lunar dust characterization by polarimetric signature. *Astronomy & Astrophysics* 483, 643-649 (2008).**
 - 11. Madl, A.K. & Pinkerton, K.E. Health effects of inhaled engineered and incidental nanoparticles. *Crit. Rev. Toxicol.* 39, 629-658 (2009).**
 - 12. Keck, L., Spielvogel, J. & Grimm, H. From nanoparticles to large aerosols: ultrafast measurement methods for size and concentration. *J. Phys., Conf. Ser.* 170, 012007 (012005 pp.)-012007 (012005 pp.) (2009).**
 - 13. Schleh, C., *et al.* The effect of titanium dioxide nanoparticles on pulmonary surfactant function and ultrastructure. *Respir. Res.* 10, 11 (2009).**
 - 14. El-Gendy, N., Gorman, E.M., Munson, E.J. & Berkland, C. Budesonide Nanoparticle Agglomerates as Dry Powder Aerosols With Rapid Dissolution. *J. Pharm. Sci.* 98, 2731-2746 (2009).**
 - 15. Bosch, H.W., Ostrander, K.D. & Cooper, E.R. Dry powder aerosols of nanoparticulate drugs. (Elan Pharma International Ltd, 2009).**
 - 16. Klingler, C., Muller, B.W. & Steckel, H. Insulin-micro- and nanoparticles for pulmonary delivery. *Int. J. Pharm.* 377, 173-179 (2009).**
 - 17. Hopkins, R.J., Jones, J.W., Barrington, S.J., Foot, V. & Baxter, K.L. Introducing depolarisation into an inexpensive, simple cloud sensor for standoff aerosol detection - art. no. 697212. in *Polarization: Measurement, Analysis, and Remote Sensing Viii*, Vol. 6972 (eds. Chenault, D.B. & Goldstein, D.H.) 97212-97212 (Spie-Int Soc Optical Engineering, Bellingham, 2008).**
 - 18. Foot, V.J., Clark, J.M., Baxter, K.L. & Close, N. Characterising single airborne particles by fluorescence emission and spatial analysis of elastic scattered light. in *Optically Based Biological and Chemical Sensing for Defence*, Vol. 5617 (eds. Carrano, J.C. & Zukauskas, A.) 292-299 (Spie-Int Soc Optical Engineering, Bellingham, 2004).**
 - 19. Hirst, E., Kaye, P.H., Foot, V., Clark, J.M. & Withers, P.B. An instrument for the simultaneous acquisition of size, shape, and spectral fluorescence**

- data from single aerosol particles. in *Optically Based Biological and Chemical Sensing for Defence*, Vol. 5617 (eds. Carrano, J.C. & Zukauskas, A.) 416-423 (Spie-Int Soc Optical Engineering, Bellingham, 2004).
20. Kaye, P.H., Aptowicz, K., Chang, R.K., Foot, V. & Videen, G. Angularly resolved elastic scattering from airborne particles - Potential for characterizing, classifying, and identifying individual aerosol particles. in *Optics of Biological Particles*, Vol. 238 (eds. Hoekstra, A., Maltsev, V. & Videen, G.) 31-61 (Springer, Dordrecht, 2007).
 21. Ferge, T., *et al.* Fast determination of the relative elemental and organic carbon content of aerosol samples by on-line single-particle aerosol time-of-flight mass spectrometry. *Environmental Science & Technology* 40, 3327-3335 (2006).
 22. Martin, A.N., Farquar, G.R., Frank, M., Gard, E.E. & Fergenson, D.P. Single-particle aerosol mass spectrometry for the detection and identification of chemical warfare agent simulants. *Analytical Chemistry* 79, 6368-6375 (2007).
 23. Steele, P.T., *et al.* Autonomous, broad-spectrum detection of hazardous aerosols in seconds. *Analytical Chemistry* 80, 4583-4589 (2008).
 24. Goddard, G. & Kaduchak, G. Ultrasonic particle concentration in a line-driven cylindrical tube. *J. Acoust. Soc. Am.* 117, 3440-3447 (2005).
 25. Kaduchak, G. & Sinha, D.N. Cylindrical acoustic levitator/concentrator. (The Regents of the University of California, 2001).
 26. Kaduchak, G. & Sinha, D.N. Cylindrical acoustic levitator/concentrator having non-circular cross-section. (The Regents of the University of California, 2002).
 27. Kaduchak, G., Sinha, D.N. & Lizon, D.C. Novel cylindrical, air-coupled acoustic levitation/concentration devices. *Review of Scientific Instruments* 73, 1332-1336 (2002).
 28. Martinez, R., *et al.* Ion cluster desorption from frozen NH₃ induced by impact of fast multi-charged ions. *International Journal of Mass Spectrometry* 253, 112-121 (2006).
 29. Farenzena, L.S., *et al.* Electronic sputtering analysis of astrophysical ices. *Earth Moon and Planets* 97, 311-329 (2005).
 30. Rokushika, S., Hatano, H. & Hill, H.H. Ion Mobility Spectrometry In Carbon-Dioxide. *Analytical Chemistry* 58, 361-365 (1986).

31. Johnson, P.V., Beegle, L.W., Kim, H.I., Eiceman, G.A. & Kanik, I. Ion mobility spectrometry in space exploration. *International Journal of Mass Spectrometry* 262, 1-15 (2007).
32. Krylov, E.V. Comparison of the planar and coaxial field asymmetrical waveform ion mobility spectrometer (FAIMS). *International Journal of Mass Spectrometry* 225, 39-51 (2003).
33. Fox, J., Saini, R., Tsui, K. & Verbeck, G. Microelectromechanical system assembled ion optics: An advance to miniaturization and assembly of electron and ion optics. *Review of Scientific Instruments* 80, 6 (2009).
34. Song, Y.S., *et al.* Novel linear ion trap mass analyzer composed of four planar electrodes. *Journal of the American Society for Mass Spectrometry* 17, 631-639 (2006).
35. Ouyang, Z., Noll, R.J. & Cooks, R.G. Handheld Miniature Ion Trap Mass Spectrometers. *Analytical Chemistry* 81, 2421-2425 (2009).
36. Gao, L., Song, Q.Y., Patterson, G.E., Cooks, R.G. & Ouyang, Z. Handheld rectilinear ion trap mass spectrometer. *Analytical Chemistry* 78, 5994-6002 (2006).
37. Keil, A., *et al.* Monitoring of toxic compounds in air using a handheld rectilinear ion trap mass spectrometer. *Analytical Chemistry* 80, 734-741 (2008).
38. Keil, A., *et al.* Ambient mass spectrometry with a handheld mass spectrometer at high pressure. *Analytical Chemistry* 79, 7734-7739 (2007).
39. Cooks, R.G., *et al.* Ambient Ionization and Miniature Mass Spectrometry: Biomedical Applications. *Biopolymers* 92, 297-297 (2009).
40. Cooks, R.G., Ouyang, Z., Takats, Z. & Wiseman, J.M. Ambient mass spectrometry. *Science* 311, 1566-1570 (2006).
41. Burchfield, D.E., Niu, W., Steiner, G. & Lewis, J.F. The Orion Air Monitor; an Optimized Analyzer for Environmental Control and Life Support. *Proceedings of the 2008 International Conference on Environmental Systems 2008*, 2046 (2008).
42. Holland, P.M., Chutjian, A., Darrach, M.R. & Orient, O.J. Miniaturized GUMS instrumentation for in situ measurements: micro gas chromatography coupled with miniature quadrupole array and Paul ion trap mass spectrometers. in *First Jet Propulsion Laboratory in Situ Instruments Workshop*, Vol. 4878 (eds. Bearman, G.H. & Beauchamp, P.M.) 1-7 (Spie-Int Soc Optical Engineering, Bellingham, 2003).

43. Orient, O.J. & Chutjian, A. A compact, high-resolution Paul ion trap mass spectrometer with electron-impact ionization. *Review of Scientific Instruments* 73, 2157-2160 (2002).
44. Palmer, P.T. & Limer, T.F. Mass spectrometry in the U.S. space program: past, present, and future. *Journal of the American Society for Mass Spectrometry* 12, 656-675 (2001).
45. Lammert, S.A., *et al.* Miniature Toroidal Radio Frequency Ion Trap Mass Analyzer. *Journal of the American Society for Mass Spectrometry* 17, 916-922 (2006).
46. Eiceman, G.A., Krylov, E.V., Nazarov, E.G. & Miller, R.A. Separation of ions from explosives in differential mobility spectrometry by vapor-modified drift gas. *Analytical Chemistry* 76, 4937-4944 (2004).
47. Eiceman, G.A., *et al.* Differential mobility spectrometry of chlorocarbons with a micro-fabricated drift tube. *Analyst* 129, 297-304 (2004).
48. Eiceman, G.A., Nazarov, E.G., Miller, R.A., Krylov, E.V. & Zapata, A.M. Micro-machined planar field asymmetric ion mobility spectrometer as a gas chromatographic detector. *Analyst* 127, 466-471 (2002).
49. Eiceman, G.A., *et al.* Miniature radio-frequency mobility analyzer as a gas chromatographic detector for oxygen-containing volatile organic compounds, pheromones and other insect attractants. *Journal of Chromatography A* 917, 205-217 (2001).
50. Krylov, E., Nazarov, E.G., Miller, R.A., Tadjikov, B. & Eiceman, G.A. Field dependence of mobilities for gas-phase-protonated monomers and proton-bound dimers of ketones by planar field asymmetric waveform ion mobility spectrometer (PFAIMS). *Journal of Physical Chemistry A* 106, 5437-5444 (2002).
51. Miller, R.A., Eiceman, G.A., Nazarov, E.G. & King, A.T. A novel micromachined high-field asymmetric waveform-ion mobility spectrometer. *Sensors and Actuators B-Chemical* 67, 300-306 (2000).
52. Miller, R.A., Zapata, A., Nazarov, E.G., Krylov, E. & Eiceman, G.A. High performance micromachined planar field-asymmetric ion mobility spectrometers for chemical and biological compound detection. *Biomems and Bionanotechnology* 729, 139-147 (2002).
53. Nazarov, E.G., Coy, S.L., Krylov, E.V., Miller, R.A. & Eiceman, G.A. Pressure effects in differential mobility spectrometry. *Analytical Chemistry* 78, 7697-7706 (2006).

54. Krylov, E.V. & Nazarov, E.G. Electric field dependence of the ion mobility. *International Journal of Mass Spectrometry* 285, 149-156 (2009).
55. Krylov, E.V., Coy, S.L. & Nazarov, E.G. Temperature effects in differential mobility spectrometry. *International Journal of Mass Spectrometry* 279, 119-125 (2009).
56. Krylov, E.V., Nazarov, E.G. & Miller, R.A. Differential mobility spectrometer: Model of operation. *International Journal of Mass Spectrometry* 266, 76-85 (2007).
57. Buryakov, I.A., Krylov, E.V., Nazarov, E.G. & Rasulev, U.K. A New Method of Separation of Multi-Atomic Ions by Mobility at Atmospheric-Pressure Using a High-Frequency Amplitude-Asymmetric Strong Electric-Field. *International Journal of Mass Spectrometry and Ion Processes* 128, 143-148 (1993).
58. Buryakov, I.A., *et al.* Ion Division by Their Mobility in High Tension Alternating Electric-Field. *Pisma V Zhurnal Tekhnicheskoi Fiziki* 17, 60-65 (1991).
59. Limero, T., Cheng, P. & Boyd, J. Evaluation of Gas Chromatography-Differential Mobility Spectrometry for Measurement of Air Contaminants in Spacecraft. *International Conference on Environmental Systems* 2006, 2153 (2006).
60. Limero, T., Galen, T. & Pierson, D. In-Flight Environmental Monitoring of Nasa Spacecraft. *Abstracts of Papers of the American Chemical Society* 198, 143-ENVR (1989).
61. Matney, M.L., Beck, S.W., Limero, T.F. & James, J.T. Multisorbent tubes for collecting volatile organic compounds in spacecraft air. *American Industrial Hygiene Association Journal* 61, 69-75 (2000).
62. Lancaster, P.A., Leslie, D.R. & Tantaro, V. Sensitivity and operating characteristics of the Graesby Ionics Otto Fuel Monitor (OFM MK2). *Defense Science and Technology Organisation Technical Reports* AR-009-436, 1-36 (1995).
63. Snyder, A.P., Maswadeh, W.M., Tripathi, A., Ho, J. & Spence, M. Field detection and identification of a bioaerosol suite by pyrolysis-gas chromatography-ion mobility spectrometry. in *Chemical and Biological Sensing Iii*, Vol. 4722 (ed. Gardner, P.J.) 121-132 (Spie-Int Soc Optical Engineering, Bellingham, 2002).
64. Tripathi, A., *et al.* Bioaerosol Analysis with Raman Chemical Imaging Microspectroscopy. *Analytical Chemistry* 81, 6981-6990 (2009).

65. Dworzanski, J.P., Tripathi, A., Snyder, A.P., Maswdeh, W.M. & Wick, C.H. Novel biomarkers for Gram-type differentiation of bacteria by pyrolysis-gas chromatography-mass spectrometry. *J. Anal. Appl. Pyrolysis* 73, 29-38 (2005).
66. Hirschfeld, T. Hy-Phen-Ated Methods. *Analytical Chemistry* 52, A297-& (1980).
67. Hirschfeld, T. Instrumentation in the Next Decade. *Science* 230, 286-291 (1985).
68. Kusz, P., Andrysiak, A. & Bobinski, J. SEPARATION OF MIXTURES OF PERMANENT GASES AND LIGHT-HYDROCARBONS ON SPHERICAL CARBON MOLECULAR-SIEVES BY GAS-SOLID CHROMATOGRAPHY. *Chromatographia* 15, 297-300 (1982).
69. Contreras, J.A., *et al.* Hand-Portable Gas Chromatograph-Toroidal Ion Trap Mass Spectrometer (GC-TMS) for Detection of Hazardous Compounds. *Journal of the American Society for Mass Spectrometry* 19, 1425-1434 (2008).
70. Leonhardt, J.W. A new ppb-gas analyzer by means of GC-ion mobility spectrometry (GC-IMS). *Journal of Radioanalytical and Nuclear Chemistry* 257, 133-139 (2003).
71. Sahner, K., *et al.* CO₂ selective potentiometric sensor in thick-film technology. *Sensors* 8, 4774-4785 (2008).
72. Lang, T., Wiemhöfer, H.-D. & Göpel, W. Carbonate based CO₂ sensors with high performance. *Sensors and Actuators B: Chemical* 34, 383-387 (1996).
73. Hong, H.S., Kim, J.W., Jung, S.J. & Park, C.O. Suppression of NO and SO₂ cross-sensitivity in electrochemical CO₂ sensors with filter layers. *Sensors and Actuators B-Chemical* 113, 71-79 (2006).
74. Raj, E.S., Pratt, K.F.E., Skinner, S.J., Parkin, I.P. & Kilner, J.A. High conductivity La_{2-x}Sr_xCu_{1-y}(Mg, Al)(y)O-4 solid state metal oxide gas sensors with the K₂NiF₄ structure. *Chem. Mat.* 18, 3351-3355 (2006).
75. Portnoff, M., Grace, R., Guzman, A. & Hibner, J. Measurement and Analysis of Adsistor and Figaro Gas Sensors Used for Underground Storage Tank Leak Detection. *EPA Technical Report EPA/600/SR-92/219*(1993).
76. Bermudez, J.A. Investigation of electrochemical carbon monoxide sensor monitoring of anesthetic gas mixtures. *Anesthesiology* 99, 1233-1235 (2003).

77. Zuba, D. Accuracy and reliability of breath alcohol testing by handheld electrochemical analysers. *Forensic Science International* 178, e29-e33 (2008).
78. Maniscalco, M., Laurentiis, G.d., Weitzberg, E., Lundberg, J.O. & Sofia, M. Validation study of nasal nitric oxide measurements using a hand-held electrochemical analyser. *European Journal of Clinical Investigation* 38, 197-200 (2008).
79. Arumugam, P.U., *et al.* Wafer-scale fabrication of patterned carbon nanofiber nanoelectrode arrays: A route for development of multiplexed, ultrasensitive disposable biosensors. *Biosensors & Bioelectronics* 24, 2818-2824 (2009).
80. Lu, Y.J., Partridge, C., Meyyappan, M. & Li, J. A carbon nanotube sensor array for sensitive gas discrimination using principal component analysis. *J. Electroanal. Chem.* 593, 105-110 (2006).
81. Martinez, H.M., Rincon, N.E., Torres, J. & Alfonso, J.E. Porous silicon thin film as CO sensor. *Microelectron. J.* 39, 1354-1355 (2008).
82. Ryan, M.A., *et al.* Monitoring space shuttle air quality using the jet propulsion laboratory electronic nose. *IEEE Sens. J.* 4, 337-347 (2004).
83. McAlpine, M.C., *et al.* Peptide-nanowire hybrid materials for selective sensing of small molecules. *Journal of the American Chemical Society* 130, 9583-9589 (2008).
84. Fenaille, F., Visani, P., Fumeaux, R., Milo, C. & Guy, P.A. Comparison of mass spectrometry-based electronic nose and solid phase MicroExtraction gas chromatography mass spectrometry technique to assess infant formula oxidation. *Journal of Agricultural and Food Chemistry* 51, 2790-2796 (2003).
85. Quang-Viet, N. Intrinsically-Safe Fiber Optic Gas Vapor Sensor for Aircraft Fuel Tank Fire-Safety. *NASA Technical Report LEW-17826-1*(2009).
86. Audran, M., *et al.* Determination of perfluorodecalin and perfluoro-N-methylcyclohexylpiperidine in rat blood by gas chromatography-mass spectrometry. *Journal of Chromatography B* 745, 333-343 (2000).
87. Ouyang, Z. & Cooks, R.G. Miniature Mass Spectrometers. *Annual Review of Analytical Chemistry* 2, 187-214 (2009).
88. Xu, W., Chappell, W.J., Cooks, R.G. & Ouyang, Z. Characterization of electrode surface roughness and its impact on ion trap mass analysis. *Journal of Mass Spectrometry* 44, 353-360 (2009).

89. Manicke, N.E., Kistler, T., Ifa, D.R., Cooks, R.G. & Ouyang, Z. High-Throughput Quantitative Analysis by Desorption Electrospray Ionization Mass Spectrometry. *Journal of the American Society for Mass Spectrometry* 20, 321-325 (2009).
90. Gao, L., Cooks, R.G. & Ouyang, Z. Breaking the pumping speed barrier in mass spectrometry: Discontinuous atmospheric pressure interface. *Analytical Chemistry* 80, 4026-4032 (2008).
91. Song, Q.Y., *et al.* Rectilinear ion trap mass spectrometer with atmospheric pressure interface and electrospray ionization source. *Analytical Chemistry* 78, 718-725 (2006).
92. Ouyang, Z., *et al.* A multiquadrupole tandem mass spectrometer for the study of ion/surface collision processes. *Review of Scientific Instruments* 73, 2375-2391 (2002).
93. Kovacs, G.J. & Oppelt, E.T. ETV Joint Verification Statement for RAID-M. *THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM* (2004).
94. Shortt, B.J., Darrach, M.R., Holland, P.M. & Chutjian, A. Miniaturized system of a gas chromatograph coupled with a Paul ion trap mass spectrometer. *Journal of Mass Spectrometry* 40, 36-42 (2005).
95. Young, R.C., Buttner, W.J., Linnell, B.R. & Ramesham, R. Electronic nose for space program applications. *Sensors and Actuators B-Chemical* 93, 7-16 (2003).
96. Defilippi, B.G., *et al.* The aroma development during storage of Castlebrite apricots as evaluated by gas chromatography, electronic nose, and sensory analysis. *Postharvest Biology and Technology* 51, 212 - 219 (2009).
97. Bhattacharyya, N., Tudur, B., Bandypadhyay, R., Bhuyan, M. & Mudi, R. Aroma characterization of orthodox black tea with electronic nose. *Tencon 2004 - 2004 IEEE Region 10 Conference, Vols a-D, Proceedings*, B427-B430 (2004).
98. Masot, R., *et al.* Design and Implementation of an Electronic Nose System for the Determination of Fish Freshness. *Olfaction and Electronic Nose, Proceedings* 1137, 531-532 (2009).
99. Awtry, A.R. & Miller, J.H. Development of a cw-laser-based cavity-ringdown sensor aboard a spacecraft for trace air constituents. *Applied Physics B-Lasers and Optics* 75, 255-260 (2002).
100. Henderson, A. Mid-IR Tunable Lasers Probe Hydrocarbon Molecules. *Photonics Spectra* 43, 72-75 (2009).

101. Barrett, J.J. & Adams, N.I. Laser-Excited Rotation-Vibration Raman Scattering in Ultra-Small Gas Samples. *J Opt Soc Am* 58, 311-& (1968).
102. Li, X.Y., Xia, Y.X., Zhan, L. & Huang, J.M. Near-confocal cavity-enhanced Raman spectroscopy for multitrace-gas detection. *Optics Letters* 33, 2143-2145 (2008).
103. Siebert, D.R., West, G.A. & Barrett, J.J. Gaseous Trace Analysis Using Pulsed Photoacoustic Raman-Spectroscopy. *Applied Optics* 19, 53-60 (1980).
104. Barrett, J.J. Photoacoustic Raman-Spectroscopy of Gases. *Applied Spectroscopy Reviews* 21, 419-464 (1985).
105. West, G.A. & Barrett, J.J. Pure Rotational Stimulated Raman Photoacoustic-Spectroscopy. *Optics Letters* 4, 395-397 (1979).