

On-Surface Measurements Primer

- *Gas and Liquid Measurement Methods*

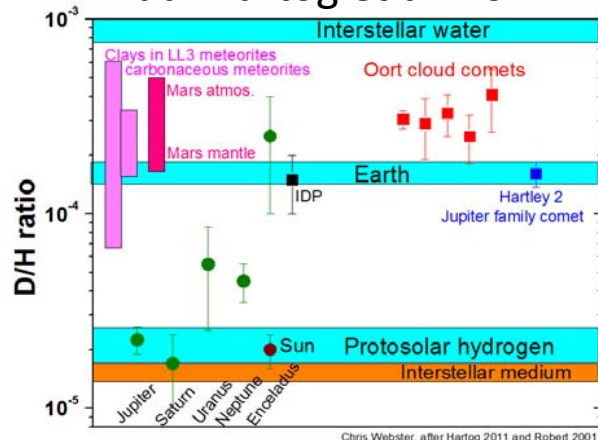
Dr. Chris R. Webster
Jet Propulsion Laboratory

KISS Study on
In Situ Science and Instrumentation for Primitive Bodies
April 30th at 4:15 p.m.

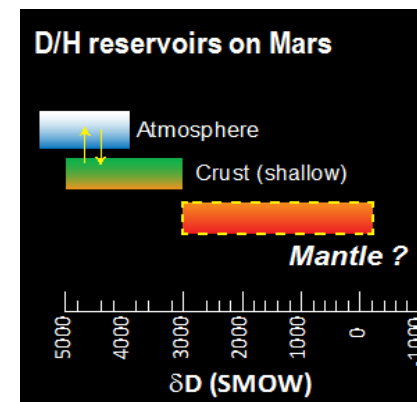
High Science Return -Isotope Ratio Measurements

Ocean-like water in the Jupiter-family comet 103P/Hartley 2

- Paul Hartog et al. 2011



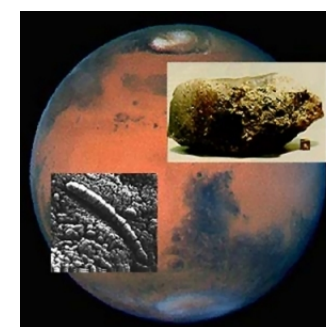
What will MSL-SAM reveal about Mars?



Carbonates in the Martian meteorite Allan Hills 84001 formed at 18 ± 4 °C in a near-surface aqueous environment

- Itay Halevy, Woodward Fischer, John Eiler, 2011

- K-Ar dating says meteorite is 4 billion years old;
- Isotope ratios in ^3He , ^{21}Ne and ^{38}Ar say it was in space (cosmic ray exposure) for 10-20 million years!
- ^{14}C dating says that it sat in Antarctica for 13,000 years;



Basic Requirements

- Carefully identify target body-specific requirements !

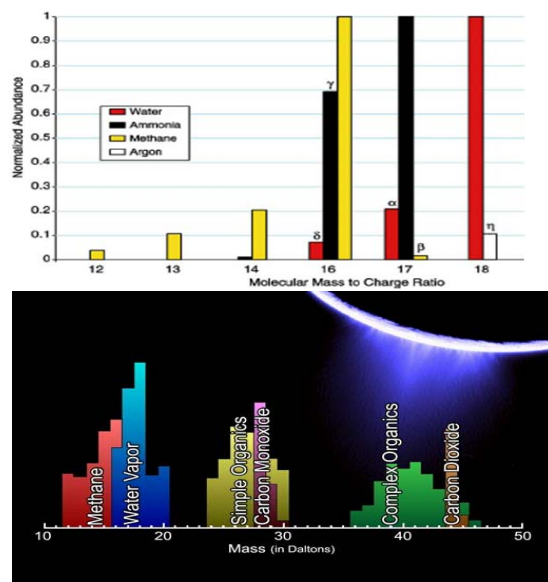
| Measurement | New bodies* | Earth, Mars, meteorites |
|---|-------------|-------------------------|
| Elemental abundances | 10% | 2% |
| Mineralogical components | 10% | 5% |
| Noble gas isotope ratios | 5% | 3% |
| D/H | 30% | 1% |
| $\delta^{13}\text{C}$ | 10 ‰ | 0.1 ‰ |
| $\delta^{13}\text{C}$ biological | 10 ‰ | |
| $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ | 20 ‰ | 0.2 ‰ |
| $\delta^{15}\text{N}$ | 20 ‰ | 0.2 ‰ |
| $\delta^{34}\text{S}$, $\delta^{33}\text{S}$ | 10 ‰ | 0.2 ‰ |

* Inner planets (not Earth), outer planets, satellites, primitive bodies

Comparing Mass Spec and Tunable Laser Spectrometers

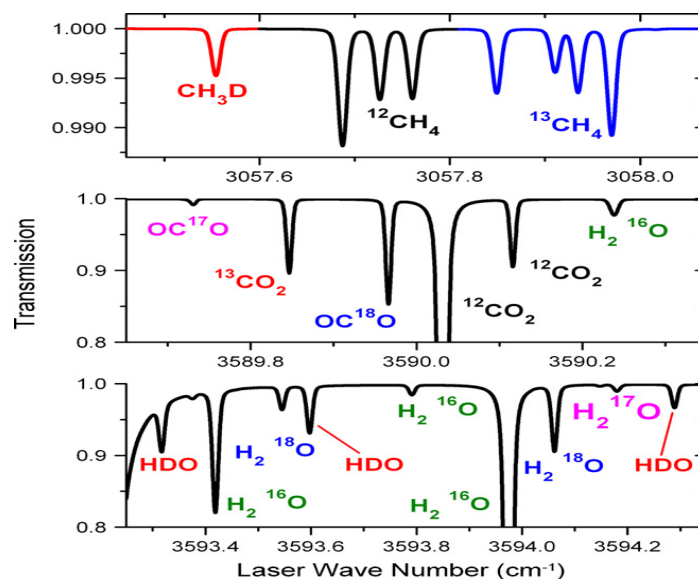
Mass Spectrometer:

- Surveys all gases;
- Essential for noble gases & complex organics;
- High vacuum instrument needing pumps, bakeout
- Mass interferences in D/H, CO/N₂, ¹³CO₂ (Phoenix), methane, ammonia and water.



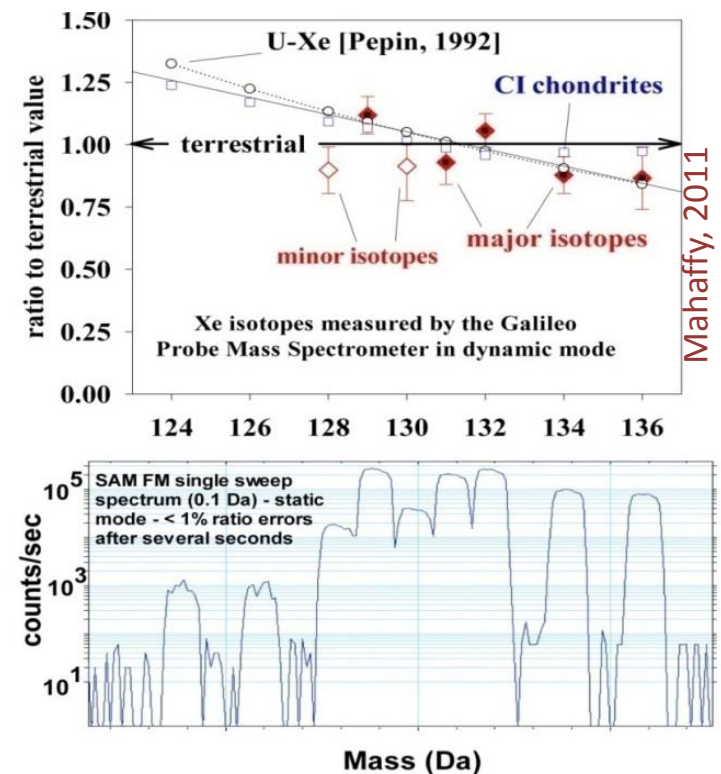
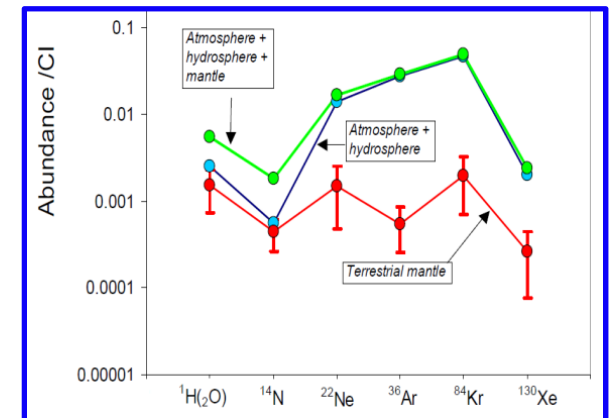
Tunable Laser Spectrometer:

- Targets specific gases- no interference;
- Direct, non-invasive, with high sensitivity to water, methane, other gases;
- Carbonates, hydrates to 10⁻⁹ wt%
- High precision ~0.1% CHNOS isotope ratios without interferences
- “High” pressure (0.1-100 mbar) instrument
- All solid-state with no moving parts.



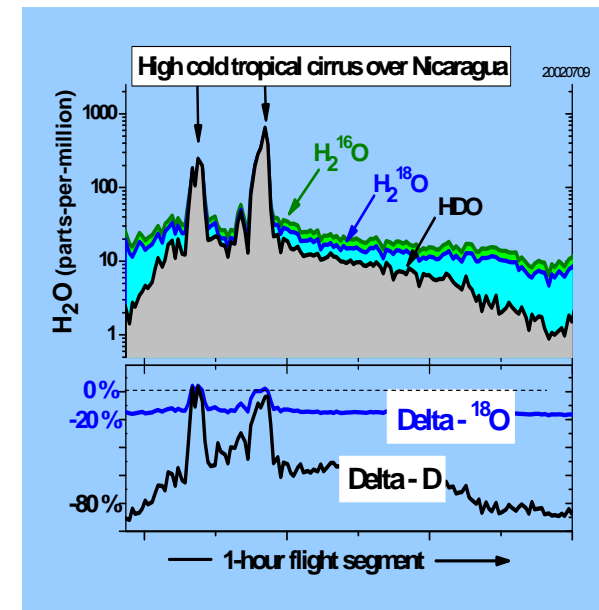
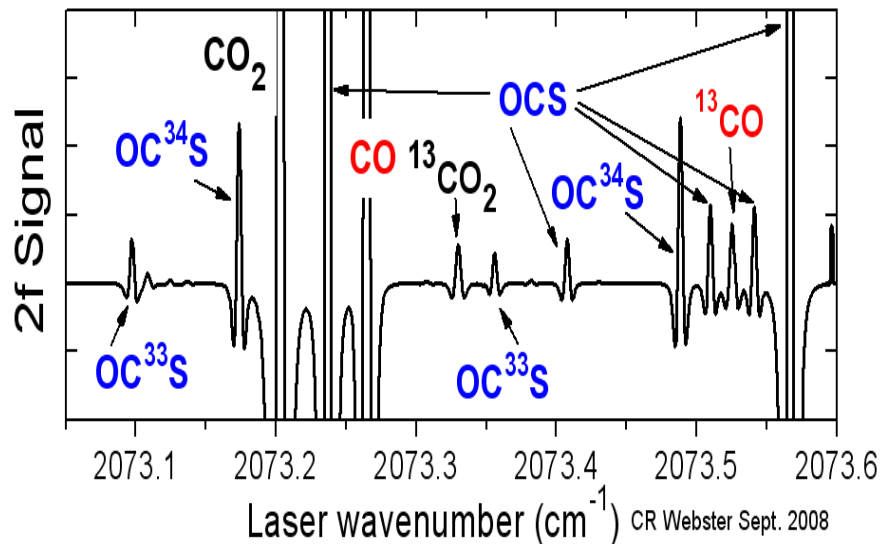
Examples of MS strengths

- Noble gas excess on Earth identifies delivery from icy planetesimals during late heavy bombardment
- Xe isotope anomaly – Earth shows severe mass-dependent Xe isotope fractionation (4% per amu) and has 7% too much ^{129}Xe
- Questions our fundamental understanding of solar system formation and composition

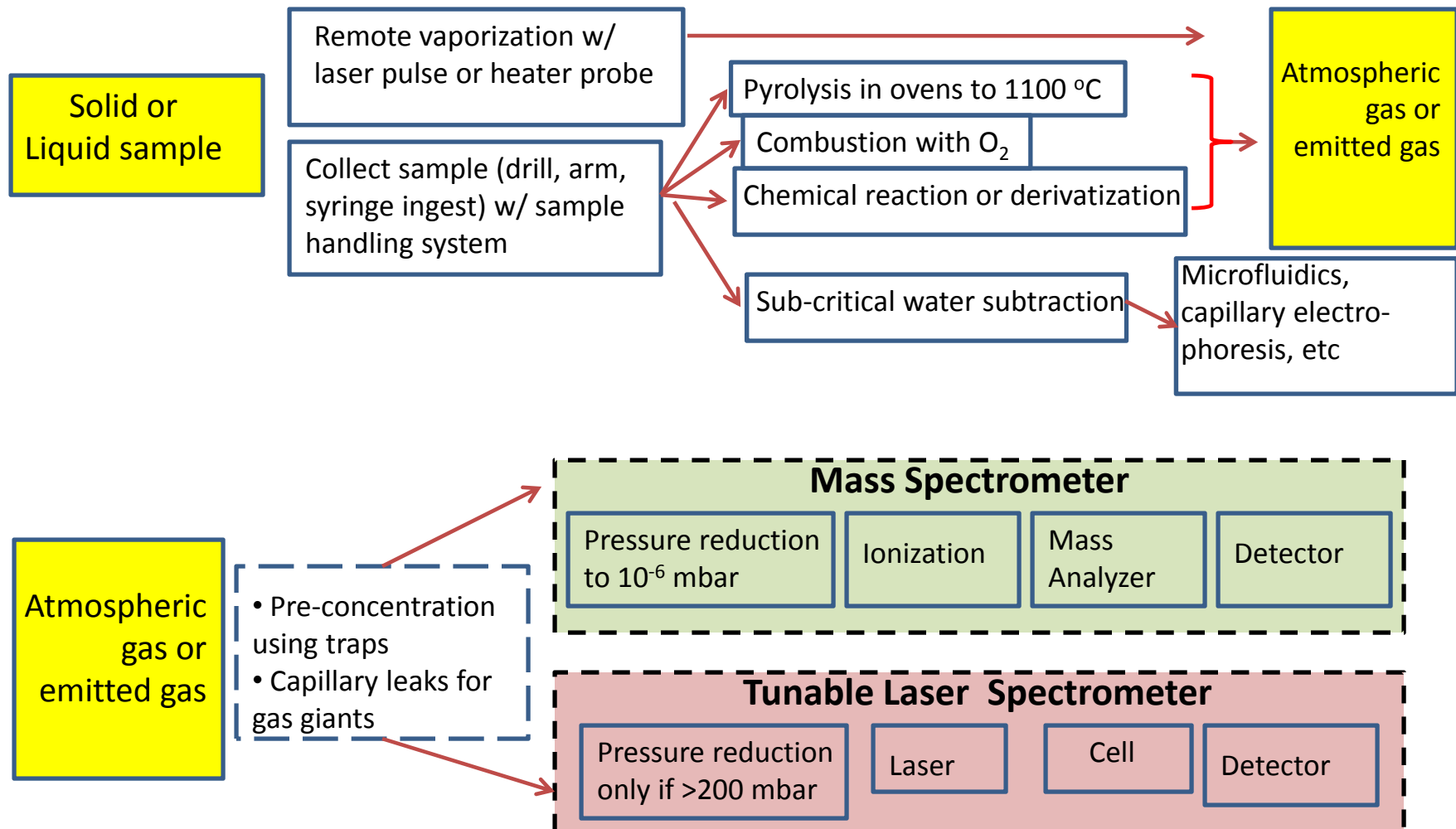


Examples of TLS strengths

- For Mars, TLS can measure water, carbonate content to 10^{-10} wt% in soils, and C, O, H, S, N isotope ratios to 0.1%
- Saturn and Uranus probes: TLS can measure CO without interference, detect low water, discriminate water, ammonia, methane, and measure isotope ratios in all targets;
- Venus: $^{34}\text{S}/^{33}\text{S}/^{32}\text{S}$ in gases for surface-atmosphere exchange;
- Titan: Precursors C_2H_2 , HCN , HC_3N , and isotope ratios.

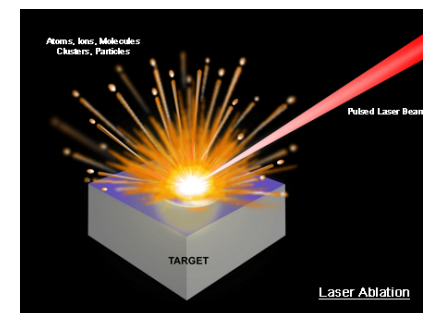


Sample Flow for MS and TLS

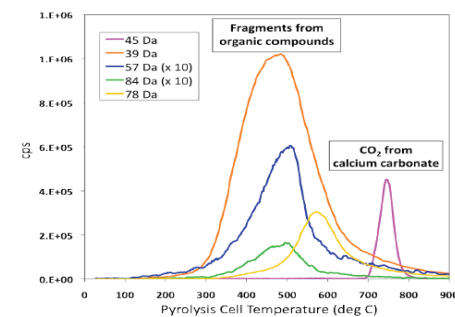


Sample Processing

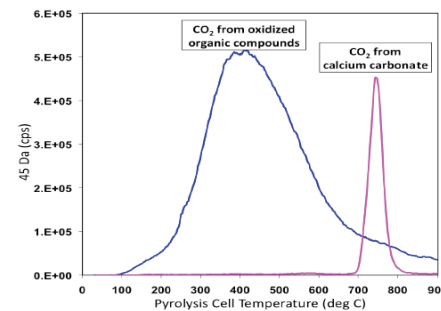
- Drill, grinder, piezoelectric sieve for size filtering
- Surface vaporizer (laser ablation, heater)
- Pyrolysis in oven (to 110°C) to evolve gases (H₂O, CO₂, SO₂, etc.) from clays, carbonates, hydrates, sulfates, etc.
- Combustion with O₂ to produce oxides- transforms macromolecular C into CO₂, CH₄ for isotopic analysis;
- Liquid derivatization by making non-volatile polar compounds volatile (e.g. amines, carboxylic acids, nucleobases) for analysis by GCMS.



Applied Spectra Inc.



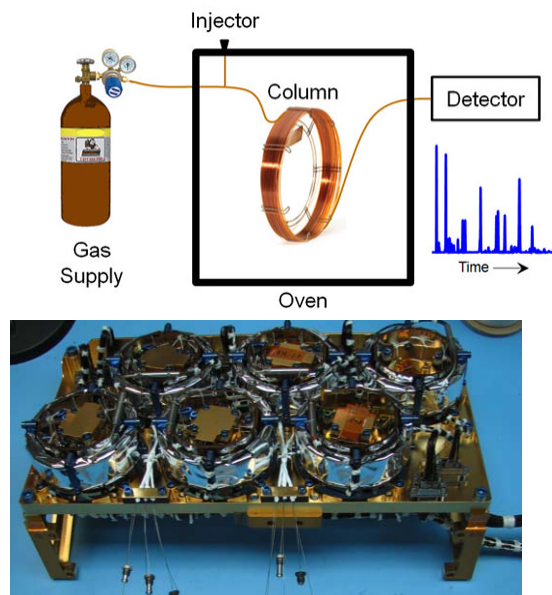
Pyrolysis – EGA



Combustion - EGA

SAM EGA- Paul Mahaffy

Gas Chromatography - GCMS

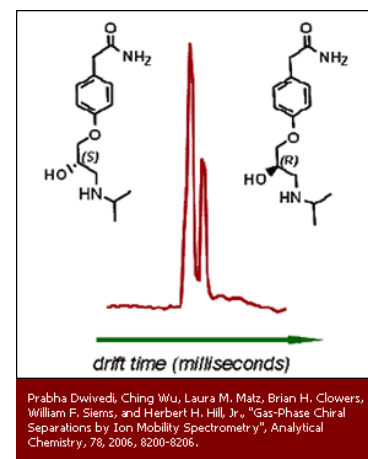


6-column GC on MSL-SAM

- Separation in He gas flowed through temp-controlled (30-250°C) chromatographic columns (CC, metallic capillary tubes).
- Wide variety of organic and inorganic compounds.
- Detection by nano-thermal conductivity detectors (TCD-similar to COSAC Rosetta) with a dynamic and linear response area, suited to melting ratio ranging from a few hundreds to a few.
- Non-destructive detectors allow feed to MS with a lower detection threshold

Ion Mobility Spectrometers (IMS)

- Pre-sorting method in which ions are separated during drift through inert gas using an electric field
- Slow drift allows fast MS to sample over drift time
- Like GC, can separate chiral molecules



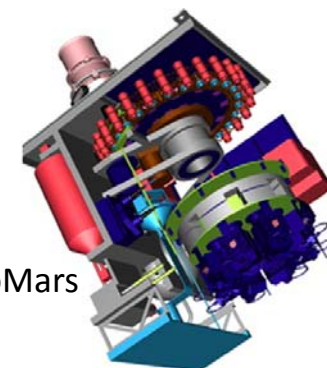
Wet Chemical Methods

- **Wet chemical analytical methods** determine properties of solids (soils) and liquids, including: pH (acid, alkaline), concentration, conductivity, salinity, specific gravity, density, viscosity and moisture content. Dissolution in water or solvent is followed by elemental analysis nitrogen, chloride, bromide, fluoride, nitrates, sulfates, phosphates



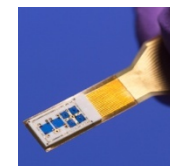
MECA Wet Chemistry Lab on Phoenix Mars Lander:

Conductivity, pH (3 sensors), Cl^- (2 sensors), Br^- (2 sensors), I^- (2 sensors)
 NO_3^- , SO_4^{2-} , K^+ , Ca^{2+} , Mg^{2+} , NH_4^+ , Na^+
 Pb/Cu/Cd/Zn/Fe (ASV)
 Cyclic Voltammetry
 ORP (redox potential)

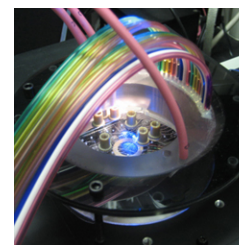


Urey on ExoMars

- **High Purity Liquid Chromatography (HPLC):** Velocity of each component depends on its chemical nature, the nature of the stationary phase (column) and composition of the mobile phase. Widely used for analysis of beverages, forensics, pharmaceuticals and drug testing, environmental, industrial and petrochemical analysis.
- **Microcapillary Electrophoresis (μCE):**
 - Lab-on-a-chip technologies developed at UC Berkeley and JPL
 - Uses LIF and micro-capillary electrophoresis
 - Identifies chirality (handedness)



E-nose
resistive
sensors

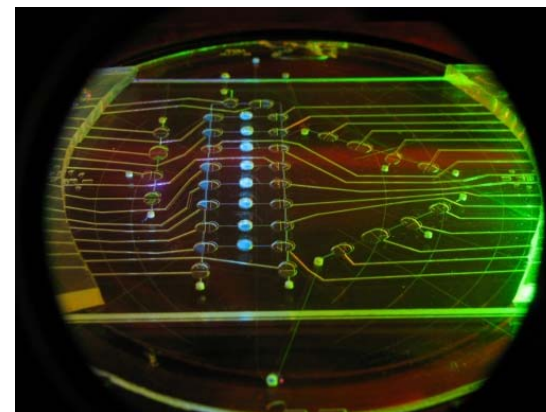
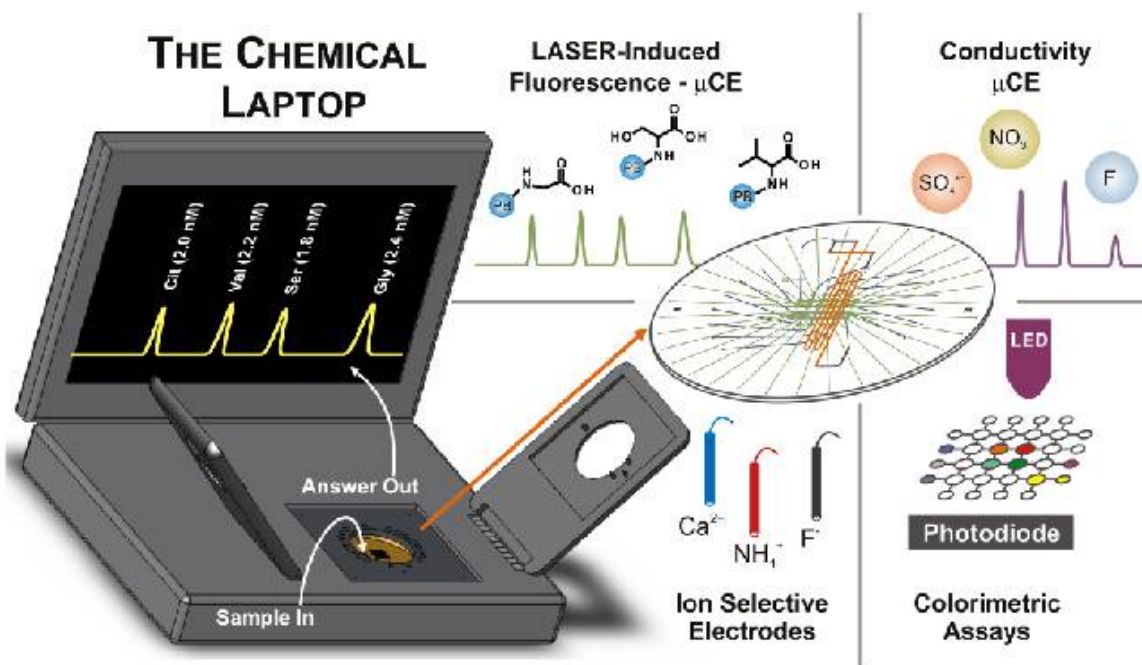


Liquid Chromatography and Microfluidics



- LC usually uses electrospray ionization
- Extremely sensitive chemical analyzer that takes a tiny bit of liquid or solid and automatically performs an analysis using stored liquids;
- Developed in MDL by Peter Willis and Rich Mathies UCB team;
- Demonstrated for chirality determinations
- Can use sub-critical water as solvent

• Applications: **sample handling/analysis for planetary probes**, robotic explosive sniffers for airports and battle zones, water/soil analyzers for environmental studies, handheld health monitors (blood/urine), etc.



The Chemical Laptop was patented by Caltech in June 2011

Ionization methods for MS

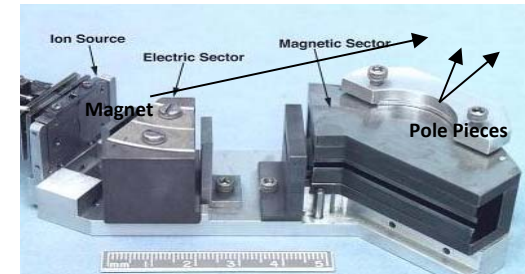
- Not always needed (e.g. in space – INMS)
- Gases: e^- impact, chemical ionization, laser ionization inside ion traps;
- Liquids, solids: electrospray, MALDI, soft laser desorption (SLD), laser ablation/ desorption (LDMS)
- **Matrix-assisted laser desorption/ionization (MALDI)**- soft ionization good for large fragile molecules to avoid fragmentation
 - e.g. organics, sugars, polymers, proteins, etc
 - UV laser pulse, well suited to TOF MS
- **Chemical Ionization MS (CIMS)** for thin films- uses SF_6^- or H_3O^+ to react and produce labeled compounds for MS detection;
- **Secondary-ion MS (SIMS)**- uses focused ion beam (Ar^+ , Xe^+ , O^- , O_2^- , SF_5^+ , C_{60}^+) to probe highly localized areas with microscopic depth penetration, releasing secondary ions fed to sector, quadrupole, or TOF spectrometers (e.g. Cosima on Rosetta).



Caltech ion microprobe
nano-SIMS for isotope
ratios to <0.1 per mil

Mass Discrimination – Magnetic Sector

- Magnetic sectors
 - Double-focus magnetic sectors
 - Heavy magnets, but can be miniaturized for specific capability
- Isotope Ratio MS (IRMS)
 - Continuous flow or dual inlet fast switching with cal gas
 - MS is tailored to specific mass ranges (e.g. 44, 45, 46 for CO₂ isotopes, and 28,29,30 for N₂) with multi-collectors;
 - Good peak shapes for analysis
 - 0.1 per mil precision



< 1kg, mass res 330

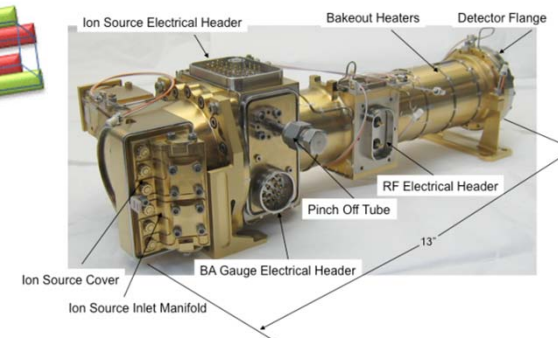
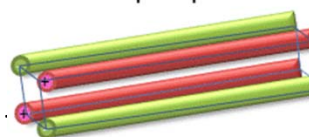


Mass Discrimination – Ion Traps

- **Linear Quadrupole trap**

- Selective mass filter that tunes RF (few MHz) sequentially transmit ions- continuous or in jumps
- Or use as 2-D trap between axial and radial fields;
- Workhorse NASA GSFC for variety of planetary bodies

Linear quadrupole

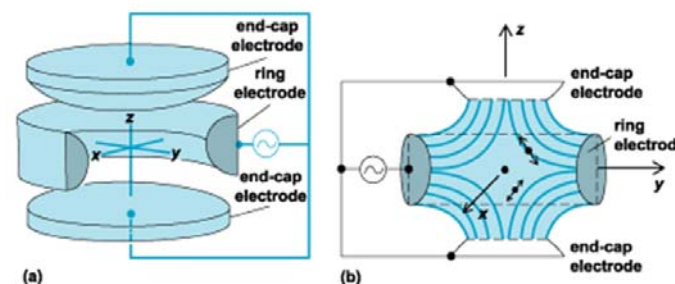


- **Paul Trap**

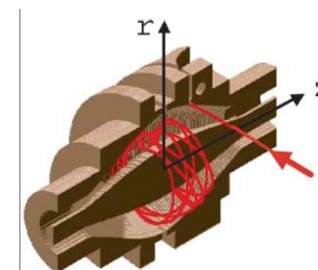
- Static DC and oscillating RF field to trap ions prior to being fed to mass analyzer
- Hyperbolic ring electrode and end caps

- **Orbitrap**

- Outer barrel electrode and coaxial inner spindle
- Electrostatic attraction to inner electrode balanced by centrifugal forces;
- Ion's m/e ratio calculated by FFT of the current induced by ion's oscillation.
- High mass accuracy (1-5-ppm), resolving power (200,000), and dynamic range (5,000)



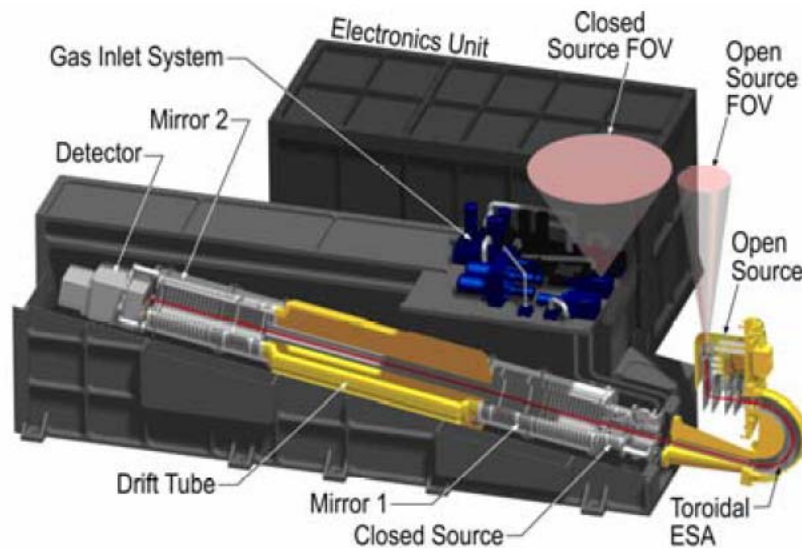
RF Paul trap - Kamas



Orbitrap

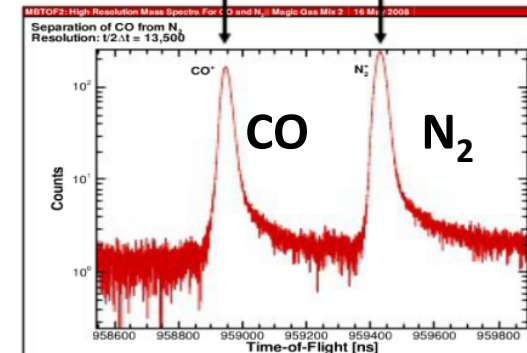
Mass Discrimination – Time-of-flight (TOF)

- TOF and reflectron (multi-bounce) TOF
- Very high resolution (CO, N₂; tholins on Titan)
- Ions accelerated by electric field- heavier ions move slower- mass resolution improved by delaying 100 ns
- Ions equilibrate from MALDI laser pulse in ~100 ns,



MBTOF-I Prototype

$M/\Delta M = 8,500$ at 20%



SwRI's Multibounce TOF
NMS and INMS
Young, Waite, Miller

MS Detectors and Calibration

- Records ion current as m/e scanned
- Electron multiplier, Faraday cups, or microchannel plates
- CCD direct ion detector arrays
- Orbitraps record induced AC current in plate-pair as oscillating ions pass nearby

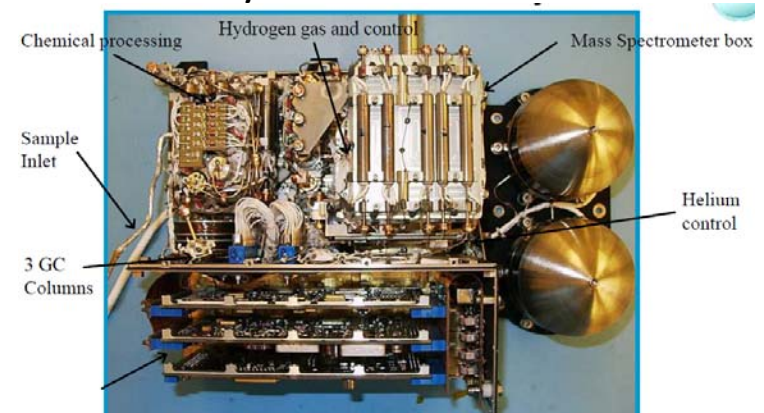
Flight Instrument Examples

SAM suite- MSL



In Situ Science and
Instrumentation for Primitive
Bodies, May 2012

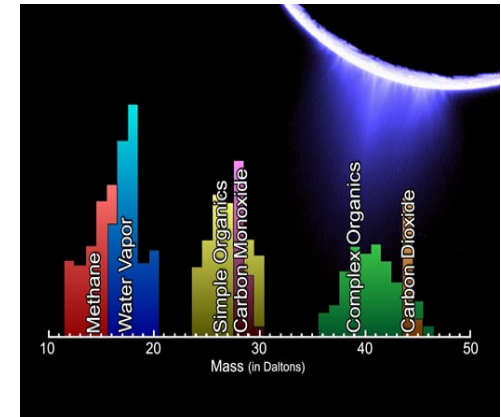
Ptolemy- Rosetta Lander



Chris Webster, JPL

Ion-Neutral Mass Spectrometry (INMS)

- Cassini INMS samples Enceladus plumes;
- Closed source inlet (neutrals) and open source inlet (ions) switched with ES switching lens deflector;
- Single RF QMS with pulse-counting e- multipliers;
- 1-99 amu range with mass ~ 10 kg



Tandem Mass Spectrometry

- Tandem Mass Spectrometer:
 - First mass analyzer isolates target molecule, Second mass analyzer stabilizes ions as they collide with an introduced gas and fragment (variety of fragmentation methods- collision-induced, e-attachment or dissociation, IR multiphoton, etc.); Third mass analyzer record the fragments' m/e
- Tandem TOF-TOF
- Ion traps (e.g. quadrupole) can be selectively tuned to achieve same result

Basic Mass Spectrometers

| <i>Technology</i> | <i>Missions / SOA</i> | <i>Institution</i> | <i>Key Advantages</i> | <i>Key Disadvantages</i> | <i>Resolving Power</i> |
|------------------------|--|---|---|---|----------------------------|
| QMS | <ul style="list-style-type: none"> • MSL, Huygens | <ul style="list-style-type: none"> • GSFC | <ul style="list-style-type: none"> • Sensitive • Small • Continuous injection • Low vacuum ok | <ul style="list-style-type: none"> • Low resolution • One mass at a time | <1000 |
| Magnetic Sector | <ul style="list-style-type: none"> • Viking, Phoenix | <ul style="list-style-type: none"> • JPL (Hoffman at UT now retired) | <ul style="list-style-type: none"> • No RF, low power • Reads many masses simultaneously • Low vacuum OK | <ul style="list-style-type: none"> • Low resolution • Mass of magnet | <1000 |
| Paul Trap | <ul style="list-style-type: none"> • VCAM (ISS), MOMA (ExoMars) | <ul style="list-style-type: none"> • JPL, GSFC, APL | <ul style="list-style-type: none"> • Sensitive • Small • Pulsed injection, reads masses serially | <ul style="list-style-type: none"> • Modest resolution • Low TRL | A few 1000 |
| TOF | <ul style="list-style-type: none"> • In development for planetary | <ul style="list-style-type: none"> • SwRI, GSFC | <ul style="list-style-type: none"> • High resolution • Modest vacuum • Accurate compositions | <ul style="list-style-type: none"> • Large mass & volume • Electron multipliers | ~10,000 |
| Orbitrap | <ul style="list-style-type: none"> • R&D only | <ul style="list-style-type: none"> • Proposed | <ul style="list-style-type: none"> • Very small • No magnet required • Image charge detection | <ul style="list-style-type: none"> • UHV requirement | Up to 600,000; 100,000 typ |

Hecht, Beegle, Neidholdt

Flown Mass Spectrometers

| Missions | Configuration | Mass | m/z range | Resoln m/Δm | Notes |
|------------------------------|--|---------------|------------------|-----------------|---|
| SAM-MSL, (Cassini) | Linear QMS- dynamic or static | 20 kg | 2-535 | 200 | With TLS, 6-col GC, 74 sample cups, pyrolysis to 1100 C, combustion, derivatization |
| Viking-Mars | GCMS- magnetic sector | 15 kg | 12-200 | 200 | 3 sample cups, pyrolysis to 500 C, 1 ppb organics |
| Phoenix TEGA- Mars | Double-focus magnetic sector | 6 kg | 1-40 | 40 | ¹³ CO ₂ , not water |
| Pioneer Venus | Magnetic sector | 11 kg | 1-208 | 150 | Separate GC not feeding MS |
| Rosetta Orb. ROSINA | (i) Reflectron TOF INMS + (ii) double focus DFMS | 15 kg 16kg | 12-150, 1-350 | >500, ~3,000 | Thermal ion source |
| Rosetta Orb. COSIMA | TOF secondary ion MS | 20 kg | 1-1300 | 2,000 | In+ ion beam source Dust collector, microscope and MS |
| Rosetta lander Ptolemy | GC-IRMS w/ quadrup. ion trap | 5 kg | 14-140 | 140 | Fed by 26 sample ovens to 800°C, combustion, fluorination 3-channel GC: (i) composition (ii) CO, CO ₂ , CH ₄ , N ₂ (iii) water from H ₂ ->CO |
| Rosetta lander COSAC | TOF | 5 kg | 1-1500 | 350 | Composition and chirality, uses 2-column GC and pyrolysis ovens, derivatization |

Achievable Sensitivities for a Mass Spectrometer

- Current planetary mass spectrometers (Mars, Venus, primitive bodies)
 - About 20 kg and consume ~10-20 W
 - Measure noble gas abundances 3-20%
 - Measure noble gas isotope ratios to 1% (typical) to 5-10% for light Xe isotopes
 - Interferences limit abundances of CH₄, NH₃, H₂O to 5-20%,
 - Isotope ratio D/H in H₂ to 20%; D/H precision in H₂O, CH₄, NH₃ not useful; ¹⁵N/¹⁴N about 30%; ¹³C/¹²C around 10-100 per mil.
- Enhanced capability mass spectrometers
 - About 30 kg and consume ~20-40 W
 - Measure noble gas abundances
 - Tailored for clumped isotopic analysis?

Mass Specs Under Development

| Configuration | Example | m/z range | Resolution at m/z=x | Complexity | Notes |
|---------------------|---------------|------------|---------------------|------------|---|
| Multibounce TOF | SwRI MBTOF | Very large | >20,000 | High | High sensitivity, duty cycle, with ultra-high resolution |
| Orbitrap | GSFC, Caltech | Large | 200,000 | High | High mass accuracy to 1 ppm, |
| Miniature EM sector | Sinha | 9-166 | 300 | Low | K, Si isotopes to 5-10% K-Ar geochron. Isotope ratios to 30 per mil |

Titan tholins are “greasy” polymeric C,H,N compounds that require very high mass resolution

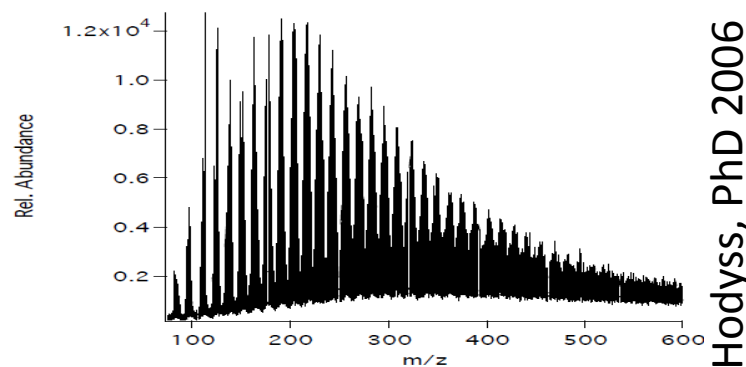
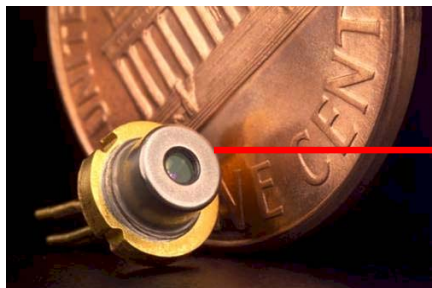
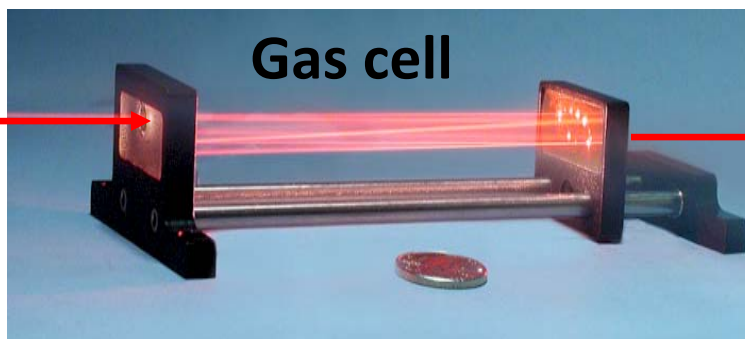


Figure 1.1 Laser desorption ionization mass spectrum of CH₄ + N₂ tholins.

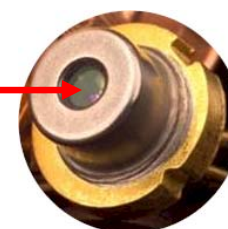
Tunable Laser Absorption Spectroscopy



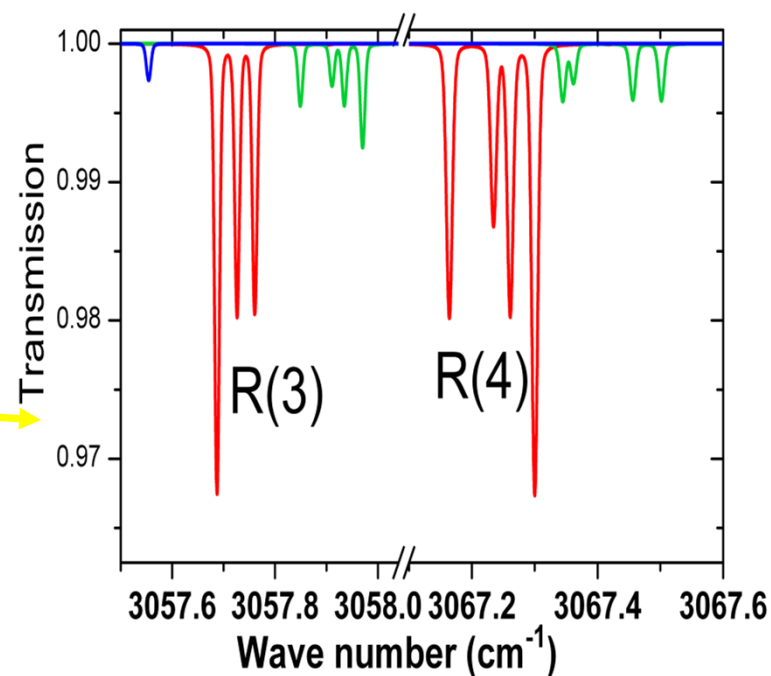
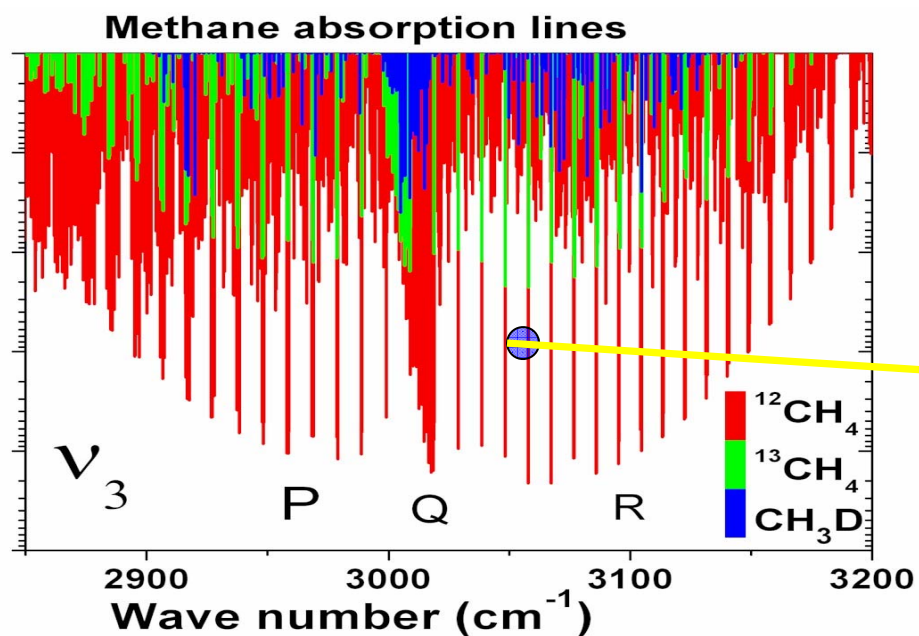
Tunable laser
1-12 μm



Gas cell



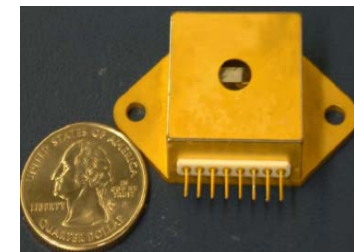
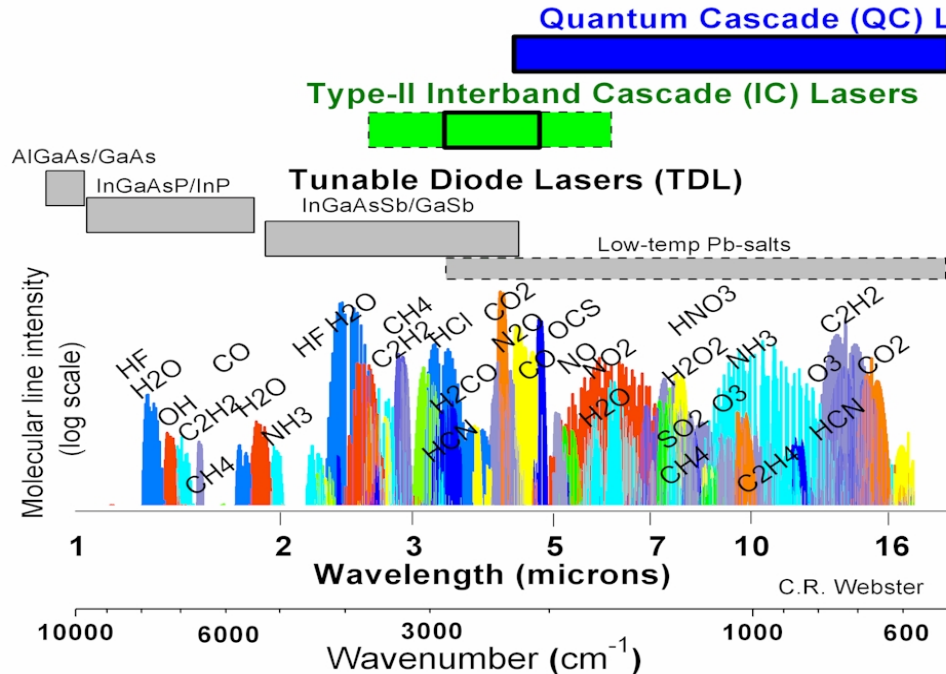
Detector



Lasers and Detectors for a TLS

Solid-state miniature devices available at room temperature (TEC stabilized)

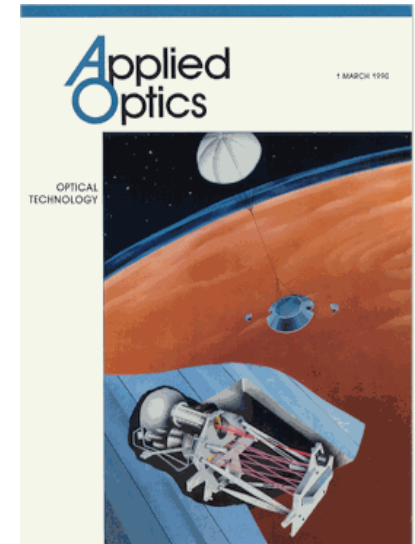
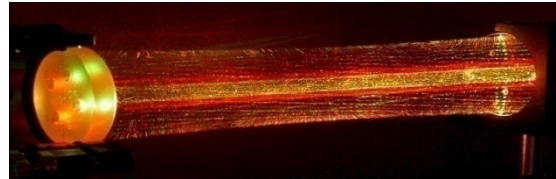
Tunable Laser Sources for Gas Measurements



TLS laser –
100 g

Cell configurations for TLS

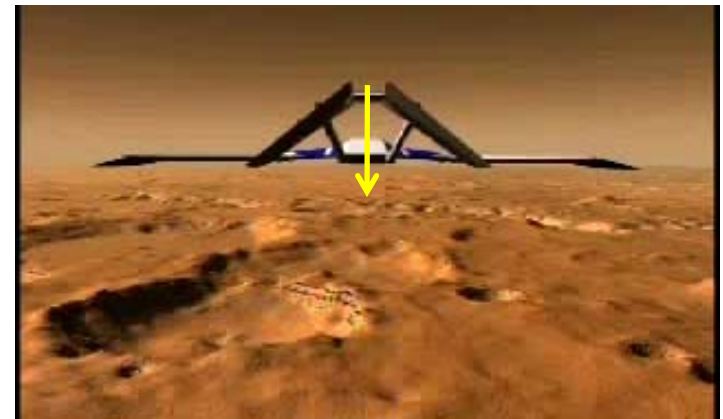
- Closed Herriott cell
 - MSL-TLS
 - Best precision isotope ratios
- Open path Herriott cell or to reflector
 - Cassini Huygens, Mars 98 MVACS, atmospheric probes
 - Temperature dependence of isotopic lines reduces precision
- Open path to surface (topographic)- Mars airplane



Mars Probe Hygrometer

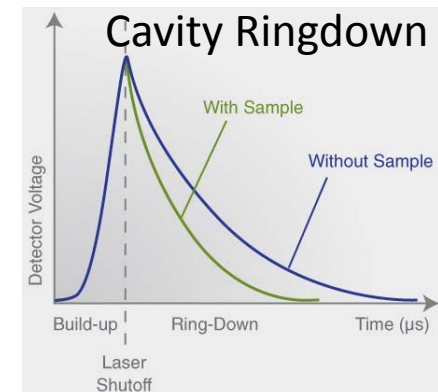
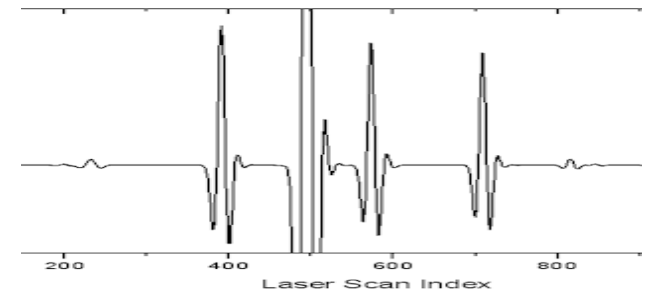
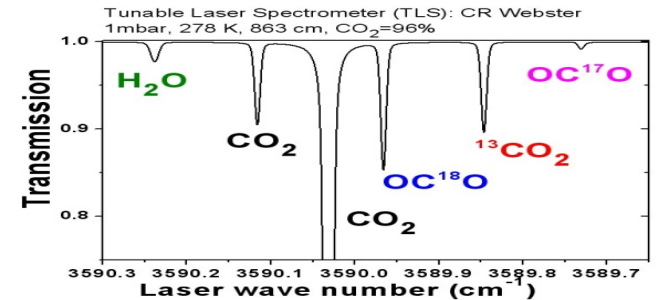


Mars 98 TLS



TLS Detection Methods and Calibration

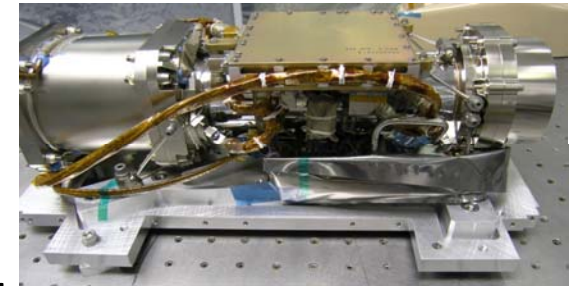
- Direct absorption
 - For stronger absorptions
 - Use Beer's law with HITRAN database
- 2f detection
 - Enhanced sensitivity but needs transfer gain factor calibration
- Cavity ring down
 - Measure decay time of cavity on and off line
 - Single mirror set (>99.99% reflectivity) for each wavelength channel
 - Increases effective pathlength to 1-10 km
- Calibration
 - In Therm-vac and on-surface using gas mixes and isotope calibration gases (NIST traceable).



Picarro

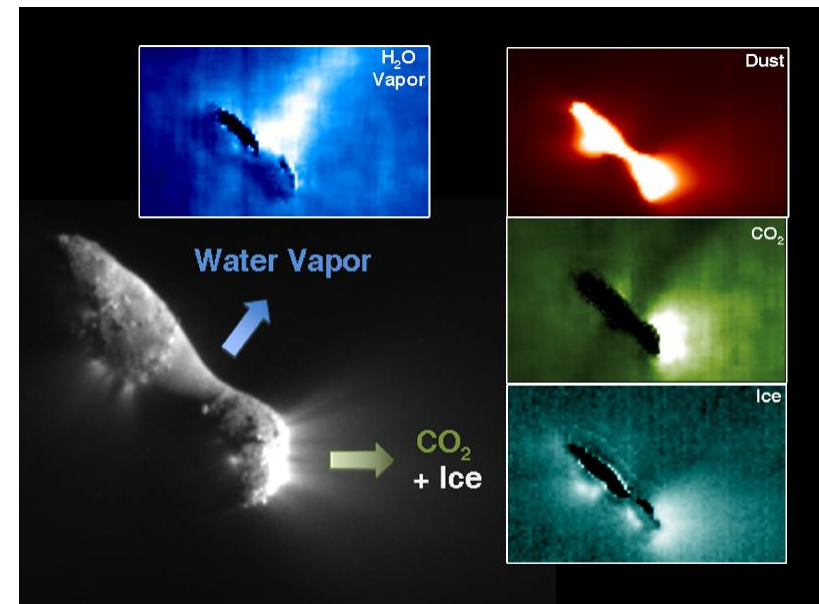
Achievable sensitivities for a TLS

- Current (TLS on MSL, 4 kg):
 - Abundances to 2-5%
 - Isotope ratios in C, H, N, O, S to 1-5 per mil using current capability
 - Wt% for water, carbonates to 10^{-10} wt% from evolved gas
- Enhanced capability (5-10 kg):
 - Abundances to 2%
 - Isotope ratios in C, H, N, O, S to 0.1 per mil using stabilized systems with concurrent calibration gases have been demonstrated commercially
 - Tailored for clumped isotope analysis?



Accessing Primitive Body Composition

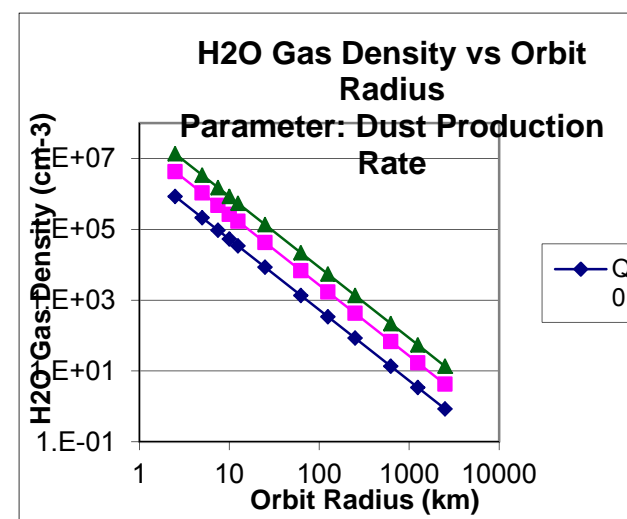
- Compositional measurements must be made within geological context;
- Projectiles (Deep Impact, LCROSS) can vaporize volatiles for direct sampling;
- Touch-and-go (Hayabusa, OSIRIS-Rex) can grab samples for return or for in-situ analysis
- For comets, coma and tail can be directly sampled (see next slide).



Sampling Cometary Coma and Tails (Ion, Dust) with MS, TLS

Collection during flyby or station-keeping

| Sample Collection and feed to TLS cell | Expected measurement |
|---|---|
| Limit of detection (LOD) for water in TLS cell | 1×10^8 molecules/cm ³ |
| Gas density at 50 km | 1×10^5 molecules/cm ³ |
| Gas outflow speed compared to almost stationary (2 m/sec) spacecraft | 500 m/sec |
| Volume swept in 1 second | 4×10^5 cm ³ in 1 second |
| # molecules collected at 50 km with 3 cm diameter orifice if only 60% efficient | 9×10^{13} molecules per hour collected |
| Cell density achieved if warmed into cell that is 0.3 liters | 3×10^{11} molecules/cm ³ per hour collected |
| SNR of water line after <u>one hour collection</u> followed by 5 minute measurement | 3,000 (!) – excellent. Will allow D/H determination to <1% |



Rosetta Payload Composition Instruments



ORBITER:

| | | | | |
|---------------|--|---|-----------------------|--|
| COSIMA | Cometary Secondary Ion Mass Analyser | TOF-SIMS | Grains of the coma | Martin Hilchenbach, Max-Planck-Institute for Solar System Research, Katlenburg- Lindau, Germany |
| ROSINA | Rosetta Orbiter Spectrometer for Ion & Neutral Analysis | Double Focus MS + INMS reflectron TOF | Gas of the coma | Hans Balsiger, University of Bern, Switzerland |

LANDER (Philae):

| | | | | |
|----------------------------|---|-----------------------------------|-----------------------------|---|
| COSAC | Evolved gas analyser - elemental and molecular composition | TOF | Nucleus surface material | F. Goesmann , MPI, Germany |
| MODULUS Ptolemy | Evolved gas analyser - isotopic composition | GC-IRMS with quad. ion trap | Nucleus surface material | Ian Wright, Andy Morse , Open University, UK |
| SD2 | Drilling and sample retrieval | | Sample production | A. Ercoli-Finzi , Politecnico of Milan, Italy |

Comparison of Gas Phase Techniques

| Technique | Noble gases & their isotope ratios | Gas Abundances | Stable isotope ratios in CHNOS | Low H ₂ O, NH ₃ , CH ₄ | Complex Organics | Chirality | pH, ions, salinity, conductivity, etc |
|---------------|------------------------------------|----------------|--------------------------------|---|------------------|-----------|---------------------------------------|
| TLS | ✗ | ✓ | ✓ No interferences | ✓ | ✗ | ✗ | ✗ |
| Mass Spec | ✓ | ✓ | ✓ Mass interferences | ✗ | ✓ | ✗ | ✗ |
| GC | ✗ | (✓) | ✗ | ✗ | ✓ | ✓ | ✗ |
| Wet Chemistry | ✗ | ✗ | ✗ | ✗ | ✓ | ✓ | ✓ |

TUNABLE LASER SPECTROSCOPY

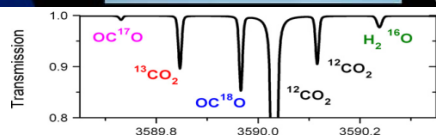
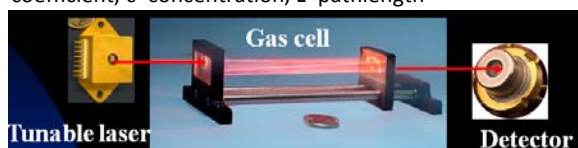
IR ABSORPTION IN GASES AND VAPORIZED LIQUIDS AND SOLIDS

Basic Technique

- Optical depth of IR absorption lines (individual vibration-rotation transitions) give abundances according to Beer's law:

$$T = I/I_0 = 10^{-\epsilon c L}$$

I = transmitted intensity, I_0 = initial intensity, ϵ = absorption coefficient, c = concentration, L = pathlength

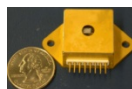


- IR light (1-30 μm) in the form of narrow-band scanning tunable laser is absorbed by IR-active molecules in gas phase;
- Ultra-high spectral resolution provides high sensitivity (deep lines) that is enhanced by detection techniques (second-harmonic for SNR and cavity-ringdown for extended path);
- Good for all IR-active molecules (including weak transitions in N_2 and O_2), but cannot be used for atoms nor for noble gases;
- Especially good at high-precision isotope ratios in CHNOS without interferences of mass spec;
- Gas phase detection of gases directly or produced from liquid or solid pyrolysis or combustion;
- Targets specific spectral lines in narrow scan with resulting limited survey capability;
- Absorbing path can be in sealed cell (Herriott cell or cavity ringdown cell) or open atmospheric path.

Measurement Capability

Typical Laboratory Specifications

- Herriott multipass cells of typically 50 m path;
- Cavity ringdown detection extends path to km;
- Absolute gas abundances to 2% with calibration gases; 20-50 kg field-portable systems;
- Picarro single isotope ratio cavity-ringdown precisions for 15 mins:
 - $\delta^{13}\text{C}$ in CO_2 to 0.1 per mil
 - $\delta^{13}\text{C}$ in CH_4 to 0.5 per mil for 1800 ppb

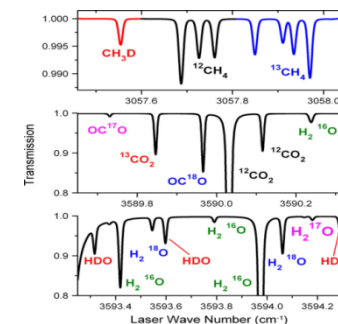
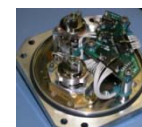
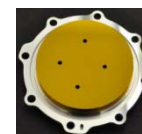
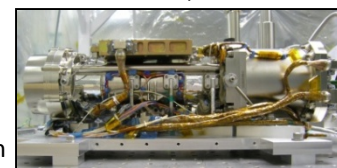


- Extensive use in Earth balloon, aircraft missions to study ozone photochemistry, heterogeneous (aerosol, polar cloud) chemistry, cloud physics
- Typical gases: HCl , HF , NO , NO_2 , HNO_3 , CO , CO_2 , NH_3 , CH_4 , SO_2 , OCS , H_2S , HCN , C_xH_x ;
- Laser sources operating at room temperature are now available: tunable diode lasers, quantum-cascade lasers, interband-cascade lasers.
- Because laser power is high (>1 mW cw), room-temperature detectors (e.g. InAs) are used, and system sensitivity is limited by optical interference fringes, not detector noise;
- Traditional Herriott cell can accommodate up to 6 laser channels with one set of mirrors, whereas cavity ringdown needs one (highly reflective) set of mirrors for each wavelength.

On-Surface Versions

FLIGHT INSTRUMENTS

- Flown on Mars 98 lander and DS-2 probe that both crashed
- TLS in SAM on MSL – tunable laser spectrometer for gas detection in Mars atmosphere or evolved from solid pyrolysis and combustion;
 - 5 mW lasers
 - Two-channels
 - 3.7 kg, 10 W
 - CH_4 to 1 ppb or much less with pre-concentration
 - Isotope ratios in H, C, O to 2-5 per mil
 - C and H_2O in rocks to $10^{-10}\text{wt}\%$



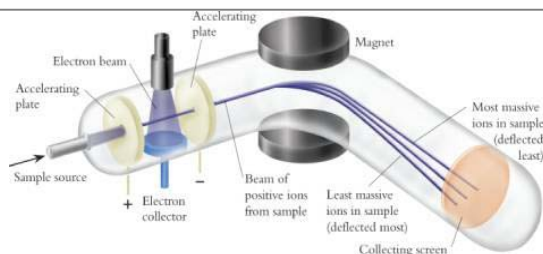
FUTURE INSTRUMENTS

- Mars aircraft (long path to ground) NH_3 , CH_4 , SO_2
- Venus, Saturn, Uranus entry probes to profile gases and isotope ratios on descent;
- Primitive bodies on-surface analysis;

MASS SPECTROMETRY

IDENTIFYING MASS/CHARGE for ATOMS and MOLECULAR FRAGMENTS

Basic Technique



- Gas sampled is produced from a variety of techniques including direct atmosphere, GC, LC, ion traps, pyrolysis, combustion, laser ablation, derivatization, wet chemical and microfluidics;
- Gas sample is ionized by a variety of methods including electron impact, laser ionization, chemical ionization (CIMS), MALDI, secondary ion MS (SIMS);
- Mass discrimination is based on m/z dispersion in a variety of basic methods:
 - Magnetic sectors including IRMS
 - Ion traps, such as the linear quadrupole mass spectrometer (QMS), Paul trap, and Orbitrap
 - Time of Flight (TOF) and reflectron- or multi-bounce- TOF
- Detection is continuous or sequential using electron multipliers, Faraday cups, micro-channel plates, CCD direct ion detector arrays, or as induced AC current in orbitrap plate pairs.

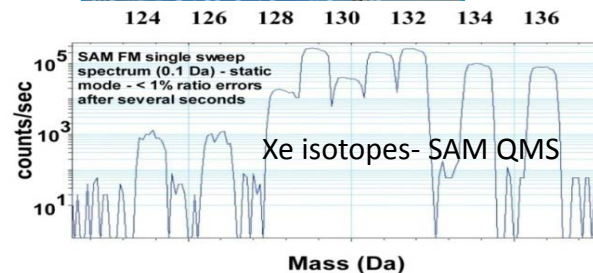
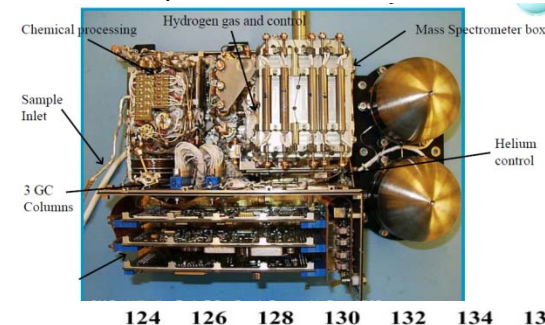
Measurement Capability

- Surveys all gases over wide mass range
- Records m/z spectra for neutrals (NMS) or ions (INMS)
- Essential for noble gases and noble gas isotope ratios
- Suffers from mass interferences in water, methane, ammonia, and stable isotopes:
 - $N_2 = 28 = CO$
 - $HDO = 19 = H_2^{17}O$
 - $^{13}CO_2 = 45 = ^{17}OCO$
 - $^{18}OCO = 46 = ^{17}O^{13}CO$
 - $^{13}CH_4 = CH_3D$ (diff. = 0.003 amu)
 - $^{15}N^{14}NO = 45 = ^{14}N^{15}NO$ $N_2O = 44 = CO_2$
 - $^{34}SOO = 66 = ^{32}SO^{18}O$ so need $^{18}O/^{16}O$
- Current planetary mass spectrometers (Mars, Venus, primitive bodies):
 - Measure noble gas abundances 3-20%
 - Measure noble gas isotope ratios to 1% (typical) to 5-10% for light Xe isotopes
 - Interferences limit abundances of CH_4 , NH_3 , H_2O to 5-20%,
 - Isotope ratio D/H in H_2 to 20%; D/H precision in H_2O , CH_4 , NH_3 not useful; $^{15}N/^{14}N$ about 30%; $^{13}C/^{12}C$ around 10-100 per mil.
- Enhanced capability mass spectrometers:
 - Measure noble gas abundances
 - Tailored for clumped isotopic analysis?

On-Surface Versions

| Technology | Planetary Missions |
|------------------------|---|
| QMS | <ul style="list-style-type: none"> MSL, Huygens Ptolemy GC-IRMS on Rosetta Lander |
| Magnetic Sector | <ul style="list-style-type: none"> Viking, Phoenix ROSINA on Rosetta |
| Paul Trap | <ul style="list-style-type: none"> VCAM on ISS, MOMA on ExoMars |
| TOF | <ul style="list-style-type: none"> ROSINA, COSIMA on Rosetta |
| Orbitrap | <ul style="list-style-type: none"> Under development |

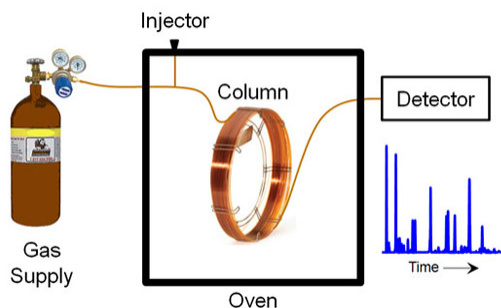
Ptolemy on Rosetta Lander



GAS CHROMATOGRAPHY (GC)

SEPARATING OUT LARGE MOLECULES AND FRAGMENTS

Basic Technique

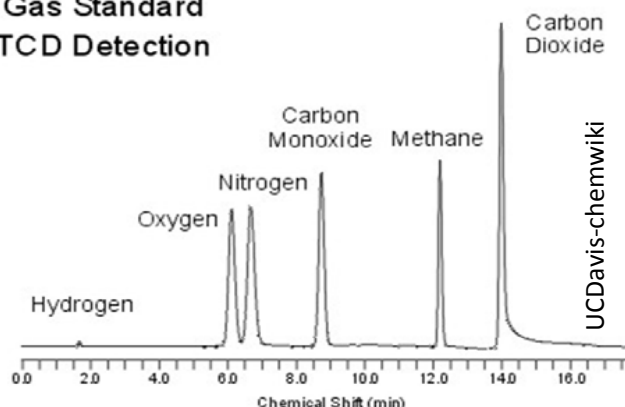


- Used to separate volatiles that can be vaporized without decomposition;
- Mobile phase is carrier gas like He
- Stationary phase is microscopic layer of polymer on inside of column
- Separation in He gas flowed through temp-controlled (30-250°C) chromatographic columns (CC, metallic capillary tubes).
- Column polarity should match sample;
- Detectors are flame ionization detectors (FIDs- destructive) or thermal conductivity detectors (TIDs- non-destructive);
- Detection by nano-thermal conductivity detectors (TCD- similar to COSAC Rosetta) with a dynamic and linear response area, suited to melting ratio ranging from a few hundreds to a few.
- Non-destructive detectors allow feed to MS with a lower detection threshold

Measurement Capability

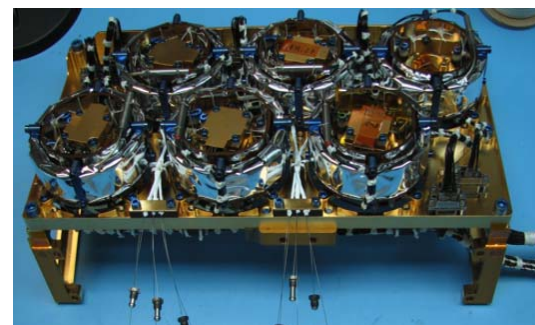
- Wide variety of organic and inorganic compounds.
- Relative concentrations (abundances) to typically 10%
- SAM's GC on MSL has six columns:
- **Column 1** : devoted to "atmospheric gases", as rare Gases (Kr, Ar...) + N₂ + O₂ + CO + CO₂ + H₂O + CH₄;
- **Column 2** : devoted to low molecular weight VOC (C1-C3) and sulfur compounds (SO₂...);
- **Columns 3 and 4** : Classical or "universal" columns that give access to a wide range of products- devoted to pyrolysis products and lighter derivatized products ;
- **Column 5** : devoted to products of derivatization (they are heavy after this sample preparation and need a specific column);
- **Column 6** : devoted to chiral compounds, could be also a backup if one of the (3+4 columns) couple fails.

Gas Standard TCD Detection

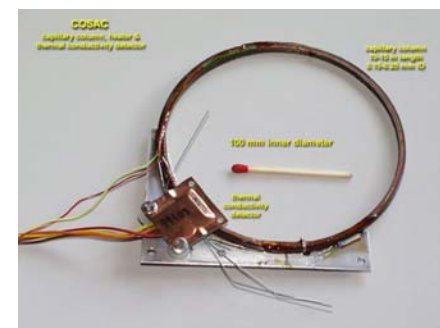


On-Surface Versions

- COSAC on Rosetta has 2-column GC and includes chirality
- SAM on MSL has 6-column GC including chirality



MSL-SAM 6 column GC- M.Cabane



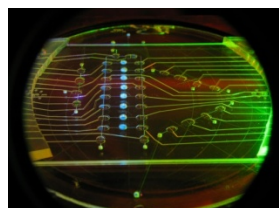
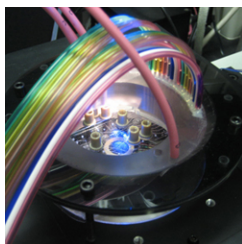
COSAC on Rosetta 2-column GC- Goesmann , MPI

MICROFLUIDICS and WET CHEMISTRY

IDENTIFYING COMPONENTS AND CHEMICAL PROPERTIES BY LIQUID ADDITION

Basic Technique

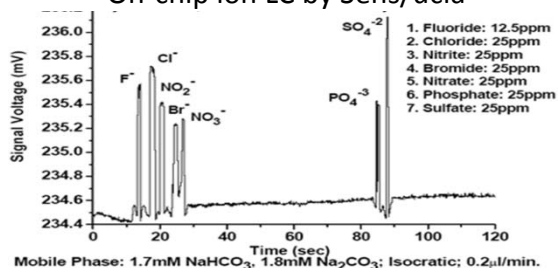
- **Wet chemical analytical methods** determine properties of solids (soils) and liquids, including: pH (acid, alkaline), concentration, conductivity, salinity, specific gravity, density, viscosity and moisture content.
- Dissolution in water or solvent is followed by elemental analysis nitrogen, chloride, bromide, fluoride, nitrates, sulfates, phosphates
- **High Purity Liquid Chromatography (HPLC):**
 - Velocity of each component depends on its chemical nature, the nature of the stationary phase (column) and composition of the mobile phase.
 - Widely used for analysis of beverages, forensics, pharmaceuticals and drug testing, environmental, industrial and petrochemical analysis.
- **Microcapillary Electrophoresis (μ CE):**
 - Lab-on-a-chip technologies developed at UC Berkeley and JPL
 - Identifies chirality (handedness)



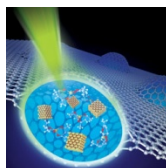
Measurement Capability

- Liquid chromatography and microcapillary electrophoresis allow separation, identification and analysis of chirality in large molecules like amines;
- MECA Wet Chemistry Lab:
 - Conductivity, pH (3 sensors), Cl^- (2 sensors), Br^- (2 sensors), I^- (2 sensors)
 - NO_3^- , SO_4^{2-} , K^+ , Ca^{2+} , Mg^{2+} , NH_4^+ , Na^+
 - Pb/Cu/Cd/Zn/Fe (ASV)
 - Cyclic Voltammetry
 - ORP (redox potential)

On-chip ion LC by Sens/ucla



± 1. On-chip ion liquid chromatography separation result of seven common anions.



Graphene cover slip allows observation of wet chemistry in progress -LBNL

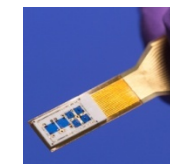
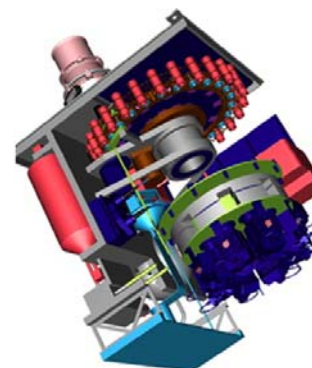
On-Surface Versions

- MECA characterizes the soil of Mars. By dissolving small amounts of soil in water, the wet chemistry lab (WCL) determines the pH, the abundance of minerals such as magnesium and sodium cations or chloride, bromide and sulfate anions, as well as the conductivity and redox potential.

MECA- Soil is delivered through funnel and added to water stored in a metal tank. The bottom section contains electrochemical sensors.



- UREY on ExoMars (cancelled) would have combined lab-on-a-chip organic analysis (LIF, μ CE) with soil reactivity sensors to characterize the biotic capacity of Martian



LASER-Induced Fluorescence - μ CE

