

PLANETARY ORGANICS DETECTOR (POD): A HIGH RESOLUTION MASS SPECTROMETER SYSTEM TO DETERMINE COMPOSITION AND STRUCTURE. P. M. Beauchamp¹, S. M. Hörst², R. V. Yelle³, M. L. Cable¹, E. L. Neidholdt¹, J. L. Beauchamp⁴, R. Hodyss¹, C. Briois⁵, L. Thirkell⁵, P. A. Willis¹, G. Nellis⁶, Y. Gianchandani⁷, M. Choukroun¹, R. Thissen⁸, P. Coll⁹, N. Carrasco¹⁰, A. Makarov¹¹

¹ Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109

(pbeauch@jpl.nasa.gov)

² Department of Earth and Planetary Sciences 3400 N. Charles St., Baltimore, MD 21218 (sarah.horst@jhu.edu)

³ Department of Planetary Sciences and the Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721 (yelle@lpl.arizona.edu)

⁴ Department of Chemistry, California Institute of Technology, 1200 E. California Blvd. MS 127-72, Pasadena, CA 91125 (jlbechamp@caltech.edu)

⁵ LPC2E, UMR6115-CNRS-Universite of Orléans, 3A Avenue de la Recherche Scientifique, 45071 Orléans, Cedex 2, France (Christelle.Briois@cnrs-orleans.fr)

⁶ Kaiser Professor of Mechanical Engineering and Associate Chair for Academic Affairs, University of Wisconsin, 1500 Engineering Drive, Madison, WI 53706 (gfnellis@engr.wisc.edu)

⁷ Director, Center for Wireless MicroSensing and Systems, University of Michigan, Ann Arbor 1301 Beal Ave., Ann Arbor, MI 48109-2122 (yogesh@umich.edu)

⁸ Institut de Planetologie et d'Astrophysique de Grenoble, CNRS UJF, Bâtiment D de physique - BP 5338041 Grenoble cedex 9, France (Roland.thissen@ujf-grenoble.fr)

⁹ Paris Diderot University, Laboratoire Interuniversitaire des Systèmes Atmosphériques LISA UMR 7583, France, (Patrice.Coll@lisa.u-pec.fr)

¹⁰ University of Versailles Saint-Quentin, LATMOS, Office 1219, 11 bld d'Alembert, 78280 Guyancourt, France (nathalie.carrasco@latmos.ipsl.fr)

¹¹ Director of Research, Life Science Mass Spectrometry, Thermo Fisher Scientific, Bremen, Germany (alexander.makarov@thermofisher.com)

Introduction: The Planetary Organics Detector (POD) is an instrument **system** with tandem mass spectrometers (MS/MS) and a cryogenic-capable sample handling system for the analysis of gas, liquid, and solid samples. Solid samples and aerosols are sampled via a soft ionization source. This system will leapfrog current capabilities and is intended to be the highest performing mass spectrometer system available for

spaceflight applications. The use of a rectilinear ion trap (RIT) mass spectrometer coupled to an Orbitrap™ Mass Spectrometer enables ultra-high resolution measurements ($m/\Delta m > 50,000$ for 50-200 Da) over a wide mass range (12-800 Da) (Figure 1). Importantly, the concomitant use of high resolution and of MS/MS enables the POD to distinguish structural isomers and isobars, i.e. molecules that have the same nominal mass

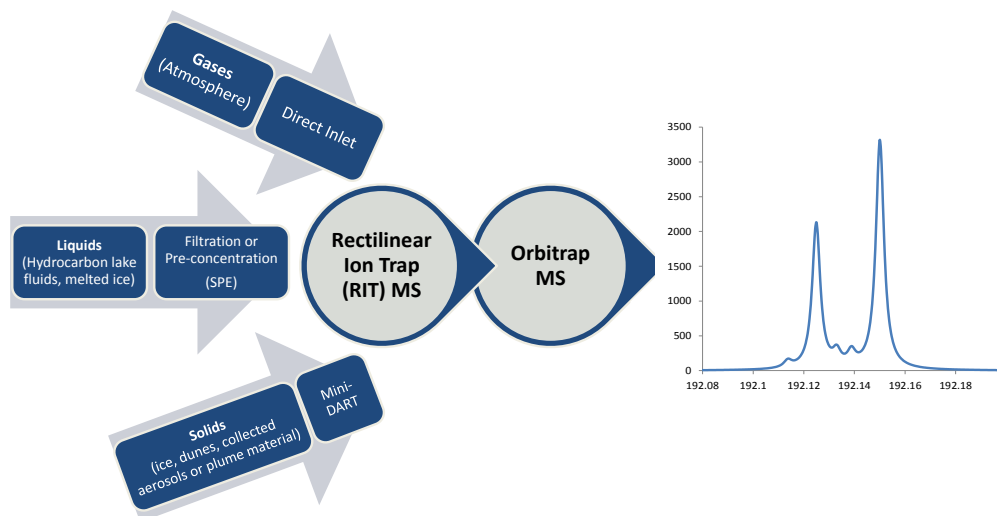


Figure 1: Flow diagram of POD. Resolution of 50,000 $m/\Delta m$ allows discrimination of species with the same nominal mass.

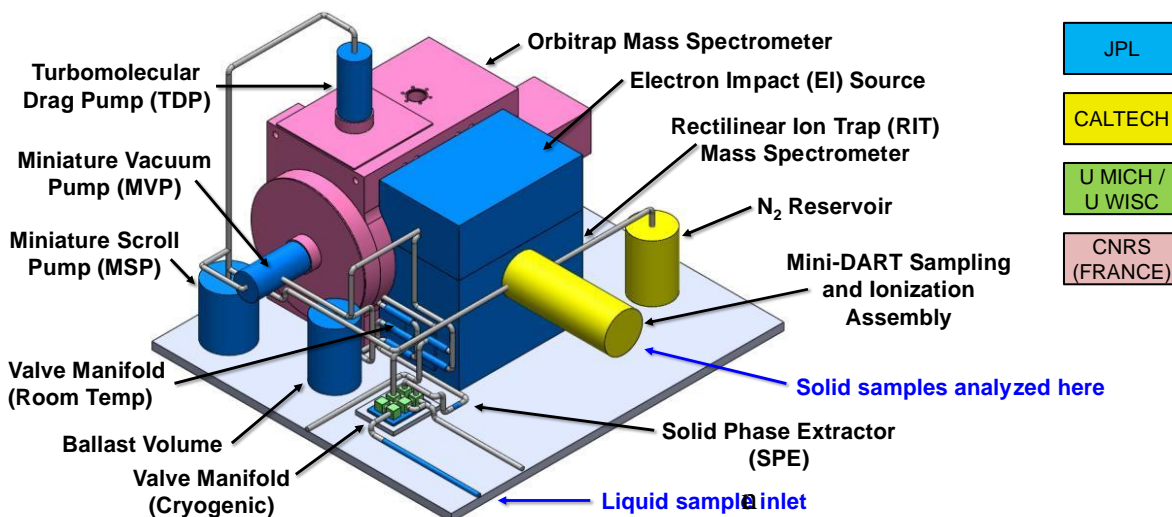


Figure 2: POD TRL 6 instrument concept (14.5 kg, 44.5 cm x 40.0 cm x 33.0 cm). The miniature direct analysis in real time (mini-DART) assembly and the liquid sample handling (SPE, cryogenic valve manifold) subsystem are mission-specific. Colors denote contributors.

mass. These capabilities are not only key for environments with an abundance of organics such as Titan, but also for those with chemical inventories like Enceladus and comets, where distinguishing between compounds such as N_2 , CO, and C_2H_4 (all nominal mass 28) [1], for example, is critical.

The POD concept originated from the Keck Institute for Space Studies (KISS) “Future Missions to Titan: Science and Engineering Challenges” Study [2]. Its development (to ~ TRL 3) was funded by a KISS grant and JPL internal research and technology funds to: (1) advance the liquid and solid cryogenic sample handling sub-system, (2) develop a mini-DART (Direct Analysis in Real Time) ion source for solid sample analysis, and (3) demonstrate the digital ion trap drive to operate the RIT [3]. We are in the process of developing these subsystems and maturing the interfaces between them as well as interfacing the RIT to an Orbitrap Mass Spectrometer, whose development is funded by the Centre National d'Etudes Spatiales (CNES) and developed concurrently in France by a consortium of five laboratories, in direct collaboration with Dr. A. Makarov (Thermo Fisher Scientific) [4]. The resulting MS/MS instrument with a mass resolving power of $\geq 50,000$ $m/\Delta m$ FWHM (50-200 Da), will be capable of handling and ionizing multiple sample types, and of identifying organics, including structural isomers, in the range of m/z 12 to 800.

Instrument Description: The POD instrument system (Figure 2) comprises the following subsystems:

1. Sample Handling Subsystem – cryogenic fluidic sample acquisition, sample manifold with miniature cryovalves [5, 6], miniature Direct Analysis in Real Time (mini-DART) to desorb and ionize solids, and Solid Phase Extractor (SPE) to pre-concentrate liquid samples.

2. Rectilinear Ion Trap (RIT) Mass Spectrometer–equipped with Atmospheric Pressure Ionization (API) inlet source and the capability for in-trap electron impact (EI) ionization of vapors, mass spectrometer with charged particle detector, and digital drive electronics.
3. Orbitrap Mass Analyzer – under development by the French Orbitrap Consortium.
4. POD Integration Subsystems – RIT-Orbitrap control electronics and integrated vacuum system.

The Orbitrap subsystem is based on a patented commercial instrument, which has recently achieved in the laboratory [7, 8] a mass resolution of $m/\Delta m \sim 1,000,000$ at m/z of 400 Da and obtains a complete mass spectrum in less than 1 second. The laboratory prototype developed by the French Orbitrap Consortium to produce a robust flight instrument is currently able to reach $m/\Delta m = 360,000$ at m/z for ^{12}C , and $m/\Delta m = 105,000$ for adenine [9]. High-resolution mass spectrometry (HRMS) allows resolution of isobars by measuring the precise mass of the ions, which is related to the sum of the nuclear mass defect of the constituent atoms. Exact mass must be resolved to better than 0.01 Da. Hence, the increase of the mass resolving power gives access to degrees of chemical information [10]:

1. $m/\Delta m < 500$ allows separation of peaks of different nominal mass (e.g., 325 Da versus 326 Da).
2. $3,000 < m/\Delta m < 10,000$ allows separation of peaks for nominally isobaric species (N_2 / CO at 28 Da) but only for species below m/z 50 (i.e. major constituents in the solar system that can be accessed by other spectroscopic methods).
3. $10,000 < m/\Delta m < 100,000$ provides separation of isobaric species up to 800 Da (i.e. it allows unequivocal identification of the molecular formula).

Applications: Titan and Enceladus scientific and measurement goals and objectives relevant to POD are provided in several recent Science Traceability Matrices (STMs) e.g., TandEM: Titan and Enceladus mission the Joint NASA/ESA Titan Saturn System Mission as well as the NASA Titan Lander study, performed for the Decadal Survey. These STMs were based on the mass spectrometers and gas chromatography systems available at the time. POD meets or exceeds the resolution requirements in these STMs, enabling more definitive identification of the organic species. In addition, POD is designed to be used in MS/MS mode, one of the most powerful tools available in mass spectrometry.

From a sample, the first mass analyzer (RIT) generates a spectrum of ions and detects them with an electron multiplier detector. An ion of interest is isolated and selectively interacts with an inert gas (N_2), which fragments the ion by collision-induced dissociation (CID). The second mass analyzer (Orbitrap) detects the resulting ions and the fragmentation pattern from MS/MS can be used to elucidate the structure of a variety of small- to medium-sized molecules, such as amino acids [11], peptides, carbohydrates, lipids, fatty acids, oligonucleotides, and even DNA/RNA adducts. Using MS/MS, POD will more readily identify the type and distribution of all the species found on planetary surfaces or atmospheres. Of particular interest for Titan, POD can identify the structures of oxygenated species, which is necessary to detect evidence of (1) prebiotic chemistry, (2) chemical interaction of aerosols with the (water ice) surface, and/or (3) cryovolcanism. With the addition of a noble gas enrichment cell, POD could also measure noble gases and isotopes to constrain the evolution of Titan's interior.

Summary: POD has many advantages over existing instrumentation. In addition to the high mass resolution capability, the sample handling system enables analysis of multiple sample types while minimizing the number of valves. The use of MS/MS technology obviates the need for a complex chromatography system that can clog with repeated ingestion of organics that are likely found on Titan [12]. By reducing heating of the sample through Direct Analysis in Real Time (DART), vital chemical and structural information is preserved. The sample handling subsystem of POD can also provide liquids to other instruments. We also note that POD's vacuum subsystem will be versatile, able to operate over a wide pressure regime (from space vacuum to 1.5 bar) that would be advantageous for other *in situ* or orbital applications requiring low operating pressure ($\leq 10^{-9}$ torr).

References:

[1] Eberhardt P. et al., (1987). *A&A* **187**, 481-484.

[2] <http://www.kiss.caltech.edu/search-results.html?q=Titan>.

[3] Zimmerman, W. F., P. Beauchamp, R. Hodyss, S. S. Kim, E. Neidholdt, and S. Sherrit (2013). Development of technologies for cryogenic in-situ chemical analysis on Titan. Annual Report, JPL Task #01STCR-r.12.136.030.

[4] Briois, C., and 22 colleagues (2013). Dust Orbitrap Sensor (DOTS) for In-Situ Analysis of Airless Planetary Bodies. *Lunar and Planetary Institute Science Conference*, Abstracts 44, 2888.

[5] J.M. Park, R.P. Taylor, A.T. Evans, T.R. Brosten, G.F. Nellis, S.A. Klein, J.R. Feller, L. Salerno, and Y.B. Gianchandani, (2008). "A Piezoelectric Microvalve for Cryogenic Applications," *IOP Journal of Micromechanics and Microengineering*, 18, 1, 015023 (10 pp.).

[6] T.R. Brosten, J.M. Park, A.T. Evans, K. Rasmussen, G.F. Nellis, S.A. Klein, J.R. Feller, L. Salerno, and Y.B. Gianchandani, (2007). "A Numerical Flow Model and Experimental Results of a Cryogenic Microvalve for Distributed Cooling Applications," *Cryogenics*, 47, 9-10, 501-509.

[7] Makarov, A. (2000). Electrostatic Axially Harmonic Orbital Trapping: A High-Performance Technique of Mass Analysis. *Analytical Chemistry*, 72 (6), 1156-1162.

[8] Denisov, E., E. Damoc, O. Lange, and A. Makarov (2012). Orbitrap Mass Spectrometry with Resolving Powers above 1,000,000. *International Journal of Mass Spectrometry*, 325-327, 80-85.

[9] Briois, C., Thirkell, L., Thissen, R. and Makarov, A. (2014). In situ Exploration of Solar System Bodies: the Potential of an Orbitrap Based Mass Analyser, IMSC2014, 24-29 August, Geneva, Suisse.

[10] Marshall, A. G. and C. L. Hendrickson (2008). High-resolution mass spectrometers. *Annual Review of Analytical Chemistry*, 1, 579-599.

[11] M.P. Callahan et al. (2014). Amino acid analysis in micrograms of meteorite sample by nanoliquid chromatography-high-resolution mass spectrometry, *Journal of Chromatography A*, 1332, 30-34.

[12] Professor Mark Smith (2011). Univ. of Houston, private communication.

Acknowledgements: JPL authors gratefully acknowledge the support of JPL Research and Development Funds in conjunction with the Keck Institute of Space Studies, which supported JLB at Caltech. This work was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with NASA. Government sponsor-ship gratefully acknowledged. Copyright 2014, California Institute of Technology. CNRS authors acknowledge the excellent support and funding provided by CNES through its R&T

programme. HR salary and the funding support to the French Orbitrap Consortium is also provided by ESEP and Région Centre.