**PLANT DE 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. Hodys5, C. Briois6, L. Thirkell7, P. A. Willis8, G. Nel- lis8, Y. Gianchandani7, M. Choukroun1, R. Thissen8, P. Coll9, N. Carrasco10, A Makarov11

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**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/Δm > 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.

![Flow diagram of POD](image.png)

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


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/Δm~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/Δm = 360,000 at m/z for $^{12}$C, and m/Δm = 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 0.01Da. Hence, the increase of the mass resolving power gives access to degrees of chemical information [10]:

1. m/Δm < 500 allows separation of peaks of different nominal mass (e.g., 325 Da versus 326 Da).
2. 3,000 < m/Δm < 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/Δm < 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 (N₂), 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 (≤10⁻⁵ torr).

**References:**


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