AN UPDATE ON THE MASPEX INSTRUMENT: NEW CAPABILITIES FOR PLANETARY CHEMISTRY AND HABITABILITY. K. E. Miller^{1*}, G. P. Miller¹, K. Franke¹, P. Hoeper¹, J. H. Waite, Jr.¹, T. Brockwell¹, R. S. Perryman¹, G. Dunn¹, J. Hanley¹, B. Magee², C. R. Glein¹, J. L. Burch¹, and the MASPEX team. ¹Southwest Research Institute, San Antonio, TX; ²Southwest Research Institute, Boulder, CO; *kmiller@swri.edu.

Introduction: The MAss Spectrometer for Planetary EXploration (MASPEX) instrument is a multi-bounce time-of-flight (MBTOF) mass spectrometer designed for quantitative measurement of planetary volatiles with adaptive mass resolution and high sensitivity [1-3]. MASPEX-Europa is part of NASA's Europa Clipper payload, and will measure volatile and organic molecules in the Europan environment to constrain composition, chemical processes, and habitability. Here, we present early results from performance characterization during ground calibration of the Flight Model (FM) instrument.

Overview of Instrument: MASPEX-Europa uses a closed source with electron impact ionization for analysis of volatiles (Fig. 1).

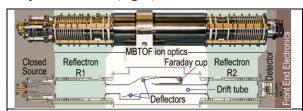


Fig. 1. Overview of major components of the MASPEX analyzer. Figure from [1].

Analyte ions are extracted via electrostatic lenses into the instrument drift tube, where velocity differences between ions lead to mass separation. Electrostatic mirrors (reflectrons R1 and R2) at either end of the drift tube can be "closed" to bounce the ions and extend their flight path. Longer flight paths increase the separation between masses, leading to higher mass resolution. When R2 is opened, the ions pass through to the microchannel plate (MCP) detector and their arrival time is measured. With calibration against known masses, flight times can be converted to mass-to-charge (m/z) values, and the ions can be identified. MCP gain is calibrated via an off-axis Faraday cup in the drift tube.

Mass Range: Planetary volatiles are dominated by low-mass compounds such as N₂ (28 u), CH₄ (16 u), CO₂ (44 u), and H₂O (18 u). Organic compounds, and especially many of the targets of astrobiological interest, have higher masses. These include a rich variety of compound classes such as alcohols, ketones, and amines, which can easily reach masses of several hundred u. The ability to measure across a broad mass range is therefore critical for astrobiological research, as well as general characterization of complex organics.

Operating in "survey" mode with both mirrors open, the MASPEX FM detected common background peaks (including H₂O, N₂, and O₂) plus fragment peaks from the calibrant material FC-43 up to 614 u in a single spectrum (Fig. 2).

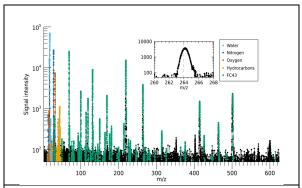


Fig. 2. FM data demonstrating mass range. Mass calibration is performed via best fit to masses 16, 17, 18, 28, 32, 69, 131, 219, 264, 414, and 464 u. Points within 0.5 u of integer masses corresponding to NIST ion fragments for water, nitrogen, oxygen, propane (hydrocarbons) and FC43 are overplotted in color. The exact mass for the FC43 264 u peak is shown as the vertical line in the inset.

Mass Resolution: Measurement of the exact mass of an unknown ion peak provides strong constraints on compositional identity. Common mass interferences in planetary environments include CO and N₂, which both have a unit mass of 28 u, and hydrocarbons versus O- or N- bearing organics [4]. Unambiguous identification and quantitation of such compounds can be accomplished with increased mass resolution.

The MASPEX instrument has variable mass resolution depending on the number of laps ions make through the drift tube before detection. An example of high mass resolution measurement with the FM is shown in Fig. 3, where peaks from $C_6H_4^{13}CH_3^+$ (from isotopically labeled o-xylene; exact mass = 92.058 u) and $C_6H_5CH_3^+$ (from toluene; exact mass = 92.062 u) are separated from each other. Fitted peak shapes shown have a resolution at full width at half maximum (FWHM) of 34,956.

Sensitivity: Mass spectrometers excel at measurement of trace compounds present in planetary environments. Higher instrument sensitivity enables measurement of less abundant compounds by increasing

ion production. However, ion flux must be optimized, as coalescence effects in mass spectrometers can degrade quantitative capabilities if the ion packet sizes are too large [5,6].

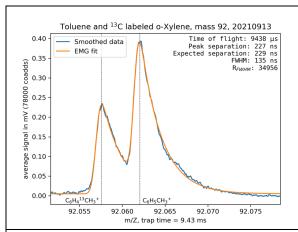


Fig. 3. Separation by the MASPEX FM instrument of peaks that differ in mass by 0.004 u. EMG = Exponentially Modified Gaussian

To enhance measurement of trace compounds, MASPEX has been designed with two innovative features: a storage source, and a cryotrap. Ions are produced in the source continuously between extractions, and stored via an electrostatic potential well so that the ion production duty cycle of the instrument is close to 100%. The approximate number of ions per second produced in the N₂⁺ peak with an N₂ partial pressure of 3×10^{-5} Pa is shown in Fig. 4, which combines data from the EM and FM instruments. The cryotrap can be used to further optimize measurement by physically collecting neutral sample molecules over an extended time period for later measurement.

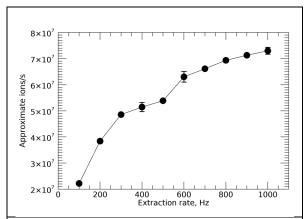


Fig. 4. Ion flux can be scaled on MASPEX using the storage source to optimize measurement parameters.

Dynamic Range: Geochemical characterization of natural mixtures frequently relies on comparison of trace and major constituents, such as measurement of

the ⁴⁰Ar/H₂O ratio or measurement of isotopic ratios [7]. Calculating such comparisons requires simultaneous or near-simultaneous measurement of peaks with many ions without saturating the detector; and with few ions while maintaining sufficient signal/noise. Dynamic range, which describes the magnitude of difference in peak integrals that can be measured by the instrument, is therefore an important performance characteristic for analysis of planetary environments. Fig. 5 shows calculation of MASPEX dynamic range based on EM noise characterization.

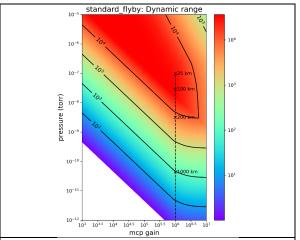


Fig. 5. MASPEX dynamic range is shown by the color bar, and varies with pressure and detector gain. Dynamic range will increase as flyby altitude above Europa decreases (altitudes along dashed line), and is expected to exceed 5,000.

Conclusions: Mass range, mass resolution, sensitivity, and dynamic range are all critical to instrument performance with respect to measurement of planetary volatiles and organics. Here, we highlight calibration data from the MASPEX-Europa FM instrument relative to these four parameters. These data demonstrate a mass range greater than 500 u, mass resolution greater than 30,000 FWHM, sensitivity exceeding 0.02 ions/second/molecule/cm⁻³, and dynamic range exceeding 5,000.

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References: [1] Brockwell T. G. et al. (2016) 2016 IEEE Aerospace Conference. [2] Hässig M. et al. (2015) Planet. & Space Sci., 117, 436. [3] Waite, J. H. et al. (2019) EPSC-DPS Joint Meeting 2019. [4] Waite, J. H. et al. (2009) Nature, 460, 487. [5] Eiler, J. et al. (2017) International Journal of Mass Spec., 422, 126. [6] Kaufmann, A. and Walker, S. (2018) Rapid Commun. Mass Spec., 32, 503. [7] Miller, K. E. et al. (2019) ApJ, 871.