Considerations for selection of a mass spectrometer to measure sulfur isotopes at Io

• Environmental models
  • Partitioning between particulates, neutrals, and ions (ion-neutral chemistry)
  • Differences in loss processes (thermal escape, plume eruptions, ion pickup)

• Reactivity of compounds on mass spectrometer surfaces (open versus closed source)

• Required resolution ($^{34}$S$^{16}$O$_2$ versus $^{32}$S$^{18}$O$_{16}$O requires ~8000 M/δM at 10% peak valley with the approximate abundance difference is 22.)

• Required sensitivity (abundance of SO$_2$, SO, etc.)

• Mission resources available (mass, power, and cost available in the mission)
### Table 19.2. Summary of Io atmospheric species.

<table>
<thead>
<tr>
<th>Species</th>
<th>Io Abundance*</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SO₂</strong></td>
<td>(\sim(1-10) \times 10^{16}) in (\pm(30-45)°) latitude band(\sim(2-10?) \times ) higher in active volcanoes</td>
<td>Synthesis of all observations; see Sections 19.2.2, 19.2.3, and 19.2.4; McGrath <em>et al.</em> 2000a; Spencer <em>et al.</em> 2000; Spencer <em>et al.</em> 2002; Jessup <em>et al.</em> 2004</td>
</tr>
<tr>
<td><strong>S₂</strong></td>
<td>(1 \times 10^{16}), Pele plume (t), (\text{SO}_2/\text{S}_2 \sim(3-12))</td>
<td>Spencer <em>et al.</em> 2000</td>
</tr>
<tr>
<td><strong>SO</strong></td>
<td>(\sim(0.03-0.1) \times \text{SO}_2)</td>
<td>Lellouch 1996</td>
</tr>
<tr>
<td><strong>NaCl</strong></td>
<td>((0.003-0.013) \times \text{SO}_2), active volcanoes</td>
<td>Lellouch <em>et al.</em> 2003</td>
</tr>
<tr>
<td><strong>S</strong></td>
<td>(3.6 \times 10^{12} &lt; N_S &lt; 1.3 \times 10^{14}) (t)(\sim 9 \times 10^{12}) at (2 R_{Io}) (t) = (0.1 \times O)</td>
<td>Feaga <em>et al.</em> 2002 (upper limit revised up; see text)</td>
</tr>
<tr>
<td><strong>O</strong></td>
<td>(\sim (4-7) \times 10^{13}), disk average(\sim 1 \times 10^{14}) at (2 R_{Io}) (t) = (11 \times S)</td>
<td>Ballester 1989</td>
</tr>
<tr>
<td><strong>Na</strong></td>
<td>(4 \times 10^{12}), disk average</td>
<td>Bouchez <em>et al.</em> 2000 [see also Burger <em>et al.</em> 2001, Retherford 2002]</td>
</tr>
<tr>
<td><strong>K</strong></td>
<td>((1-10) \times 10^{8}; \text{Na/K} = 10 \pm 5) at ((10-20) R_{Io})</td>
<td>Brown 2001</td>
</tr>
<tr>
<td><strong>Cl</strong></td>
<td>(\sim 1 \times 10^{13}), disk average</td>
<td>Feaga <em>et al.</em> (2004)</td>
</tr>
<tr>
<td><strong>H</strong></td>
<td>(\sim 2 \times 10^{12})</td>
<td>Strobel and Wolven 2001</td>
</tr>
<tr>
<td><strong>CS₂</strong></td>
<td>(&lt; 2 \times 10^{14})</td>
<td>McGrath <em>et al.</em> 2000a; Spencer <em>et al.</em> 2000; Spencer <em>et al.</em> 2002</td>
</tr>
<tr>
<td><strong>CO</strong></td>
<td>(&lt; (3.6-6) \times 10^{17})</td>
<td>Lellouch <em>et al.</em> 1992</td>
</tr>
<tr>
<td><strong>H₂S</strong></td>
<td>(&lt; (0.7-1.2) \times 10^{16})</td>
<td>Lellouch <em>et al.</em> 1992</td>
</tr>
<tr>
<td><strong>OCS, S₂O, ClO, CS, NaOH</strong></td>
<td>Not detected (mm)</td>
<td>Lellouch <em>et al.</em> 1992</td>
</tr>
<tr>
<td><strong>KCl</strong></td>
<td>(&lt; 1 \times \text{NaCl})</td>
<td>Lellouch <em>et al.</em> 2003</td>
</tr>
</tbody>
</table>

* Numbers in vertical column density, cm\(^{-2}\), unless otherwise noted; (t) = tangential.

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### 19

**Satellite Atmospheres**

**Melissa A. McGrath**  
*Space Telescope Science Institute*

**Emmanuel Lellouch**  
*Observatoire de Paris*

**Darrell F. Strobel, Paul D. Feldman**  
*The Johns Hopkins University*

**Robert E. Johnson**  
*University of Virginia*
### TABLE I

Selected Photochemical Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1a. SO$_2$ + hv</td>
<td>SO + O</td>
<td>1.1 (+2) Okabe (1971)</td>
</tr>
<tr>
<td>b</td>
<td>S + O$_2$</td>
<td>6.7 (+7) Drissell &amp; Warneck (1986)</td>
</tr>
<tr>
<td>R2. SO + hv</td>
<td>S + O</td>
<td>1.8 (+6) Phillips (1981)</td>
</tr>
<tr>
<td>R3a. O$_2$ + hv</td>
<td>O + O</td>
<td>1.8 (+10) Bohm (1971)</td>
</tr>
<tr>
<td>b</td>
<td>O$_2$ (O(1D)) + O</td>
<td>9.4 (+8)</td>
</tr>
<tr>
<td>R5a. Na$_2$O + hv</td>
<td>Na + Na +</td>
<td>6.0 (+6) see below</td>
</tr>
<tr>
<td>b</td>
<td>Na + O$_2$</td>
<td>1.0 (+5) 0.1 branching assumed</td>
</tr>
<tr>
<td>R7a. Na$_2$O + hv</td>
<td>Na + Na +</td>
<td>9.0 (+5) like Na$_2$O + hv</td>
</tr>
<tr>
<td>b</td>
<td>Na + S$_2$</td>
<td>1.0 (+5) 0.1 branching assumed</td>
</tr>
<tr>
<td>R8. NaO + hv</td>
<td>NaO + Na</td>
<td>1.0 (+5) assumed</td>
</tr>
<tr>
<td>R9. Na$_2$S + hv</td>
<td>Na$_2$S + Na</td>
<td>1.0 (+5) assumed</td>
</tr>
</tbody>
</table>

**SOURCES:** 210, 594 (1986)  
**ARTICLES:** 851

### TABLE II

Isonospheric Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficients</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>R10. S + O$_2$</td>
<td>SO + O</td>
<td>2.3 (+12) JPL92</td>
</tr>
<tr>
<td>R11. SO + SO</td>
<td>5.8 (+7) 1540177 RB90</td>
<td></td>
</tr>
<tr>
<td>R12. SO + O$_2$</td>
<td>SO$_2$ + O</td>
<td>2.9 (+13) 1400177 JPL92</td>
</tr>
<tr>
<td>R13. O + S$_2$</td>
<td>S + O$_2$</td>
<td>7.2 (+11) 1607675 Yang &amp; DeMichel (1992)</td>
</tr>
<tr>
<td>R14. SO + O$_2$</td>
<td>2SO$_2$</td>
<td>7.6 (+15) Yang &amp; DeMichel (1992)</td>
</tr>
<tr>
<td>R15. O + O + M</td>
<td>O + M</td>
<td>1.0 (+20) 1197654 NIST (1994)</td>
</tr>
<tr>
<td>R16. SO + O + M</td>
<td>SO$_2$ + M</td>
<td>7.7 (+11) Yang &amp; DeMichel (1992)</td>
</tr>
<tr>
<td>R17. SO + O + M</td>
<td>SO$_2$ + M</td>
<td>8.4 (+12) 1108765 Yang &amp; DeMichel (1992)</td>
</tr>
<tr>
<td>R18. S + S + M</td>
<td>S$_2$ + M</td>
<td>1.0 (+20) 1197654 Bush &amp; Dydek (1973)</td>
</tr>
<tr>
<td>R19. NaO + O</td>
<td>Na + O$_2$</td>
<td>1.7 (+10) JPL92</td>
</tr>
<tr>
<td>R20. NaO + O</td>
<td>Na + O$_2$</td>
<td>5.0 (+13) Phase (1991)</td>
</tr>
<tr>
<td>R21a. NaO + O</td>
<td>NaO + O</td>
<td>1.0 (+5) assumed</td>
</tr>
<tr>
<td>b</td>
<td>Na$_2$ + O$_3$</td>
<td>#Na$_2$O$_3$ removed</td>
</tr>
<tr>
<td>R22 NaO + S</td>
<td>NaO + NaS</td>
<td>1.0 (+2) assumed</td>
</tr>
<tr>
<td>b</td>
<td>Na$_2$ + SO</td>
<td>#Na$_2$O$_3$ removed</td>
</tr>
<tr>
<td>R23. NaO + O$_2$ + M</td>
<td>NaO + O$_2$ + M</td>
<td>1.0 (+10) assumed</td>
</tr>
<tr>
<td>R24. NaO + O$_2$ + M</td>
<td>NaO$_2$ + M</td>
<td>2.2 (+27) 217703 JPL92</td>
</tr>
<tr>
<td>R25. NaO + O$_2$ + M</td>
<td>NaO$_2$ + M</td>
<td>3.1 (+12) 1570704 JPL92</td>
</tr>
<tr>
<td>R26. NaS + O</td>
<td>Na + SO</td>
<td>8.7 (+10) like NaO + O</td>
</tr>
<tr>
<td>R27. NaS + O</td>
<td>Na + SO</td>
<td>8.4 (+13) like NaO$_2$ + O$_2$</td>
</tr>
<tr>
<td>R28. NaS + O</td>
<td>Na + SO</td>
<td>1.8 (+12) assumed</td>
</tr>
<tr>
<td>R29. Na$_2$S + O</td>
<td>Na$_2$O + SO</td>
<td>#Na$_2$O$_3$ removed</td>
</tr>
<tr>
<td>R30a. Na$_2$S + S</td>
<td>Na$_2$S + Na</td>
<td>1.6 (+12) assumed</td>
</tr>
<tr>
<td>R30b. Na$_2$S + S</td>
<td>Na$_2$S + Na</td>
<td>1.6 (+12) assumed</td>
</tr>
<tr>
<td>R31. Na$_2$S + O</td>
<td>2NaS</td>
<td>1.6 (+12) assumed</td>
</tr>
</tbody>
</table>

**Photochemistry and Vertical Transport in Io's Atmosphere and Isonosphere**

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AND

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Photochemistry and Transport in Io’s Atmosphere and Isonosphere

1 Photoassociation coefficients for zero optical depth, hemispheric average, with units of sec$^{-1}$. Binomial and tomospheric rate coefficients have unit of cm$^3$ sec$^{-1}$, and cm$^2$ sec$^{-1}$, respectively.
Sulfur Compounds are Reactive

To MEASURE IONS AND REACTIVE NEUTRALS AN OPEN SOURCE IS NEEDED
What lessons have we learned from Cassini?
**Enceladus The Cryo-Geyser**

Volatile composition like a comet?

Nano ice grains that contain water cluster ions and carbonates?
Ion Neutral Mass Spectrometer
Instrument Configuration

During the Enceladus flybys:

- Neutral densities from closed source
- Ion densities from open source

**Note:** Dissociative ionization helps determine the mass deconvolution.

For example, a molecule of $N_2$ penetrating inside the closed source can be ionized and dissociated into $N_2^+$ and $N^+$ and be observed in the detector on mass channels 28 and 14.
Decoding Enceladus with High Resolution MS

A dynamic range of $\sim 10^8$ and mass resolution on the order of 17,000 ($M/\Delta M$) at 1% peak height is necessary to settle the most important current questions about the composition of Enceladus’ plume:

- direct measurement of all $H_2O$ isotopes
- determine C, N, O content via numerous separations ($N_2$ vs. CO, HCN vs. $C_2H_4$, $H_2CO$ vs. $C_2H_6$, etc.)
- determination of noble gases such as Ar

$H_2O$ isotopes
$\sim 16,300$ (28 bounces)
$CO, N_2, C_2H_4$
$\sim 10,900$ (15 bounces)
$C_3H_4, C_2H_2N, 40Ar$
$\sim 8,750$ (10 bounces)

December 3, 2018 KISS Conference on Io’s Sulfur Isotopes
The Mass Spectra Vary with Flyby Velocity

- **Mass Spectra**

- **Elemental Composition**

Velocity varies from 7.7 km s\(^{-1}\) (E14, E17, E18) to 17.7 km s\(^{-1}\) (E5)
Plume Signal versus Time from Closest Approach

Several features are seen
Large spikes are likely ice grain impacts

Signal for M/Z = 44, (CO₂)
is proxy for plume density
MASS SPECTROMETER OPTIONS

Consideration of mass resolution and sensitivity versus mass and power resources
How does Time of Flight (TOF) work?
TOF Concept

• A packet of ions is accelerated to a defined kinetic energy and the time required to move through a fixed distance is measured.

• As KE = mv²/2 then lighter ions travel faster than heavier ones → mass separation.

• The greater the distance between source and detector the smaller the mass difference that can be seen (resolution).
NIM/PEP/JUICE prototype
NIM /PEP /JUICE Prototype: Dynamic range

Mass spectrum acquired in th-mode, showing almost 5 decades of dynamic range with 8 bit ADC card.
Prototype Results: Mass Resolution

PEP / NIM prototype

Krypton at $2 \cdot 10^{-9}$ mbar

$m/\Delta m = 780$

$m/\Delta m = 1100$

MASPEX: Unique Capabilities

• What uniquely enables MASPEX to accomplish these objectives?
  A. Mass Resolution
  B. Sensitivity
Resolution: Multi-Bounce Time-of-Flight

Mass Resolution = 10,800 in 12 bounces

Detector

Ion source

3rd Generation Prototype

[Diagram of a multi-bounce time-of-flight mass spectrometer with labeled parts: Mirror 1, Lens 1, Drift Region, Lens 2, Mirror 2.]

[Graph showing mass resolution for Xenon isotopes with 2, 6, and 12 bounces.]
MBTOF principle
Studies of the Enceladus plume hint at the presence of a large number of possible organic compounds whose identification is hindered by the low resolution of Cassini INMS. The simulation (left) demonstrates how increasing resolution enables the individual fragment ions (created by electron impact ionization within the source) of parent organic molecules to be fully separated and quantified. The spectrum (right) shows how the peak shape used in the simulation derived from MASPEX laboratory data.

A comprehensive simulation of the expected Europa environment was performed in the same way to identify the optimum analyte fragments and the resolution necessary for full separation. This information is used to define MASPEX’s science operation modes.
Sensitivity

• Ion storage source
  • $10^5$ ions per extraction leading to.........................

• Cryotrap
  • Concentrates the sample to give an effective sensitivity of..............................

0.02 counts s$^{-1}$ per molecule cm$^{-3}$

or

8 x $10^{-5}$ A per mbar @ 8 x $10^{-7}$ mbar source pressure

2000 counts s$^{-1}$ per molecule cm$^{-3}$
High Performance Open Ion Source for Exploration (High-POISE)

A Bundt pan Electrostatic Analyzer (ESA) with reflectron for coaxial ion injection to mass spectrometers

High-POISE enables:
- Increased accuracy in abundance measurements for neutrals and reactive neutrals versus closed ion source.
- Analysis of ions that are excluded (neutralized) in antechamber/gas inlet system of closed ion source.
- Analysis of larger molecular weight species (organics, amino acids, etc.) without worry of fragmentation
  - Debated that larger molecular weight species fragment in closed ion source systems due to their increased kinetic energy from space craft velocity
- Coaxial or orthogonal ion injection into a variety of mass spectrometers, including MASPEX (coaxial injection)

Photographs of the prototype Bundt pan ESA open ion source.
BACKUP SLIDES
Mass resolution examples

• $^{1}H_{2}^{32}S$ versus $^{34}S$ requires $\sim 1800$ M/$\delta M$ at 10% peak valley and the approximate abundance difference is 23.

• $^{34}S^{16}O_{2}$ versus $^{32}S^{18}O^{16}O$ requires $\sim 8000$ M/$\delta M$ at 10% peak valley and the approximate abundance difference is 22.

• Organic molecules could further complicate this identification and they may arise from the ambient environment or spacecraft contamination.
Simulations of the required measurements identify the key and driving requirements for the mass resolution.
A block diagram of the instrument showing the major subsystems:
Gas inlet system (GIS)
Mass spectrometer (MS).
High Performance Open Ion Source for Exploration (High-POISE) – more info

SIMION ray trace showing ion transmission through the entire device (top left).

SIMION simulation results displaying the Weene plot (bottom left), counts/bin versus azimuthal angle (angular resolution), and counts/bin versus energy (energy resolution) of the device.
MASPEX Performance

Ability to separate similar mass molecules (MBTOF)

Ability to measure trace quantities (cryotrap)

ScTM requirements
COSMIC DUST ANALYZER

• Analysis of salty ice grains in the plume (Postberg et al., Nature 2009 & 2011)
  • Presence of an ocean plume-source & ocean in contact with rock

• Constrained ocean salinity and alkaline pH:
  • NaC~ 0.5 – 1%, NaHCO3~ 0.2 - 0.5%, and ~ 8.5 – 9

• Detection of nano-phase silica emitted by Enceladus (Hsu et al., Nature 2015)
  • Presence of alkaline hydrothermal systems (T ≥ 90°C)
  • Fast transport of material from core to plume
The Neutral Gas and Ion Mass Spectrometer of the PEP Experiment on the JUICE Mission

Peter Wurz, Stefan Meyer, André Galli, Marek Tulej, Audrey Vorburger, Davide Lasi, Daniele Piazza, and Matthias Lüthi

Physikalisches Institut, Universität Bern, 3012 Bern, Switzerland

Pontus Brandt

The Johns Hopkins University, Applied Physics Laboratory, Laurel, MD, USA

Stas Barabash

Swedish Institute of Space Physics, S-981 28 Kiruna, Sweden
Particle Environment Package (PEP) Instrument

• PEP includes 6 sensors
  • JDC: Ion spectrometer and mass analyzer (electron capabilities)
  • JEI: Electron spectrometer (ion capabilities)
  • JoEE: Energetic electrons spectrometer
  • JENI: Energetic ion spectrometer and ENA imager (electron capabilities)
  • JNA: Low energy ENA imager
  • NIM: Neutral gas and ion mass spectrometer

• Seven mechanical units arranged in two groups PEP-Lo and PEP-HI, located on the nadir and zenith plane of the spacecraft
Sensitivity: Cryo-trapping

- Flight heritage Ricor cryocooler
- Sintered 316L SS absorber
- Quantitative absorption and release of Argon
- Increases sensitivity by a factor of >10,000
Ambient analytes that fall below the radiation noise line or require integration in excess of a single flyby must be measured by cryotrapping.
Contamination Control

• Why is contamination control so important?
Origins of SMOG

• Desorption
  • All surfaces have a covering of physisorbed material that will outgas
• Decomposition
  • Breakdown of solids to produce more volatile molecules
• Diffusion
  • Gas dissolved in solids diffuses to the surface
• Permeation
  • Trapped gas permeates through solids to the surface
• Thrusters
  • Designed to ‘outgas’ material rapidly
The green horizontal line is the limit of detection of Cassini INMS as determined from the dark counts in mass channels where no signal is observed and attributed to radiation and cosmic rays.

The data is derived from the majority of Titan flybys, inbound between CA-3500 sec and CA–950 seconds.