Selection of the chemical adsorbents and operating conditions for the injection traps onboard the Dragonfly Mass Spectrometer Gas Chromatograph

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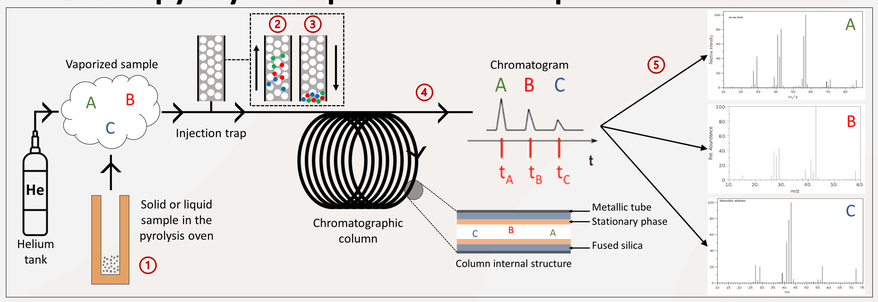
1. Exploring Titan's surface with the Dragonfly mission

- Rich atmospheric organic chemistry, formation of aerosols [1]
- Contact between organics and transitory liquid water in impact craters [2]
- Suspected cryovolcanism [3]

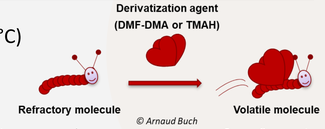
- ✓ 2019 : selection of Dragonfly by NASA
- ❑ **2028 : launch**
- ❑ 2034 : landing at Titan
- ❑ 3.3 years nominal exploration

- Analyses carried out on the ground, with air travel between site (several hundred kilometers in total)
- 4 instruments, including **DraMS**: *Dragonfly Mass Spectrometer*. Two modes: gas chromatography (GC-MS) and laser desorption-ionization (LD-MS)
- DraMS objectives: [4]
  - ➢ **Quantify the organics** and identify prebiotic molecules
  - ➢ Look for potential molecular **biosignatures** (e.g. an enantiomeric excess)

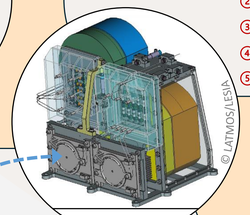
2. The pyrolysis-trap-GC-MS technique used on DraMS



① Sample vaporization in the pyrolysis oven (600°C)
  - ➢ For non-volatile molecules, a preliminary **derivatization** step is carried out

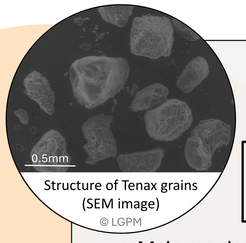


② **Adsorption** of molecules in the chemical injection trap (reconcentrating & refocusing)
③ **Desorption** by heating the trap for a punctual injection into the column
④ Chromatographic **separation**
⑤ **Identification** of molecules *via* their retention time and mass spectrum



DraMS-GC

3. DraMS injection traps



Structure of Tenax grains (SEM image)
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Goal of this study: selecting the best adsorbent(s) for DraMS and optimizing the desorption parameters

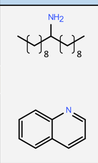
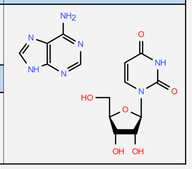
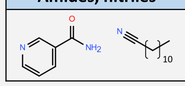
- Main requirements for the adsorbents:
  - ➢ **Desorption efficiency** for target molecules at the operating temperature (see *§ 5.1*)
  - ➢ Preservation of the enantiomeric excess for chiral molecules (see *§ 5.2*)
  - ➢ Resistance to **mechanical stress** during launch
  - ➢ Compatibility with derivatization agents

Name	Particles size	Optimum temperature for desorption	Comments
Tenax TA	35-60 mesh 250-500 µm	280 – 300°C	⊕ **Heritage** : successfully used for the Huygens, Mars Science Laboratory (Curiosity rover) and Rosetta missions ⊖ Constraining **contamination** of analyses by aromatic compounds [6]
Carbotrap C	20-40 mesh 420-840 µm	330 – 360°C	Never used in a space mission

- Two options for the DraMS traps : (2 Tenax TA) or (1 Tenax TA + 1 Carbotrap C)
  - ➢ **Comparison of performances** of Tenax TA and Carbotrap C is needed

4. Experimental method

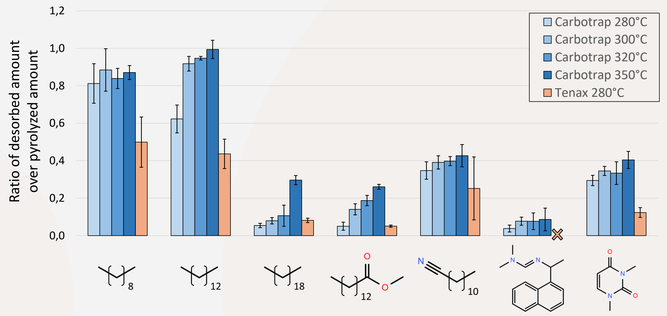
- **Reproduction of the DraMS traps conditions** on a commercial pyrolyzer
- Experimental variables:
  - ➢ Adsorbent: Tenax TA or Carbotrap C
  - ➢ **Desorption temperature**: 280°C, 300°C, 320°C or 350°C (only 280°C on Tenax TA), maintained for 40s except at 350°C (55s) which is the optimum for Carbotrap
  - ➢ Target compounds: from **various chemical families**, to reflect the chemical diversity expected to be found in Titan surface samples and that DraMS must be able to identify [4]

Linear alkanes	Amines	Fatty acid methyl esters (FAMEs)	Nucleobases & nucleosides
			
Amides, nitriles		**Amino acids**	
			

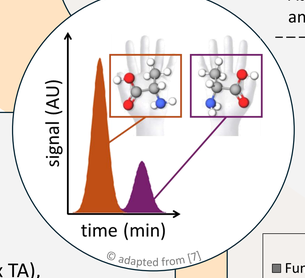
- For a given compound, the amount desorbed (ie. the area of the chromatographic peak) is measured relatively to the amount detected with pyrolysis alone (steps 2 and 3 skipped in *§ 2*)

5. Results

5.1. Comparison of desorption efficiency for Carbotrap C and Tenax TA



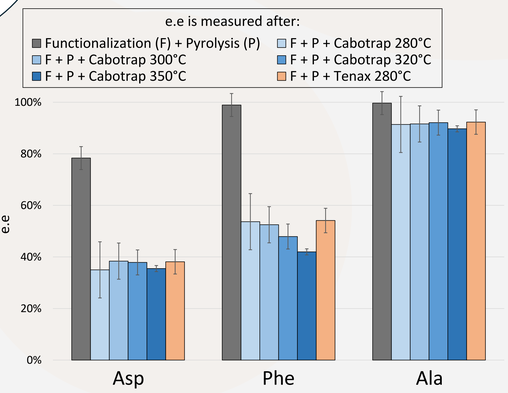
- **Desorption efficiency is better with Carbotrap C than with Tenax TA**, even at 280°C, for almost all compounds tested
- When the optimum is not reached at 280°C, heating at 300°C could significantly improve the desorption for some of them (see C_{14} alkane, C_{14} FAME)
  - At 280°C, alkanes are desorbed from Carbotrap C up to C_{27} and Tenax TA up to C_{24} (resp. C_{18} and C_{22} for FAMEs)



5.2 Preservation of chirality

- Detection of a significant **enantiomeric excess** (e.e) for some molecules (e.g. amino acids) may be a bioindicator
- DraMS chiral column gives the ability to measure the e.e.

$$\text{e.e.} = 100 \cdot \frac{Area_{major} - Area_{minor}}{Area_{major} + Area_{minor}}$$



- Adsorption/desorption **contributes to racemization** of amino acids, just like derivatization [8] and pyrolysis
- Desorption from **Carbotrap C up to 320°C does not racemize amino acids significantly more** than desorption from Tenax TA at 280°C

6. Conclusion and perspectives

- It would be **relevant to include a Carbotrap C trap on DraMS** considering desorption performances alone
- Desorption performances are mostly **limited by the desorption flow** on DraMS (1.2 mL/min)
- Upcoming Carbotrap C vibration tests results will help conclude before final integration

References

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