Solid Phase Micro Extraction for Organic Contamination Control Throughout Assembly and Operational Phases of Space Missions

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Abstract

Space missions concerned with life detection contain highly sensitive instruments for the detection of organics. Terrestrial contamination can interfere with signals of indigenous organics in samples and has the potential to cause false positive biosignature detections, which may lead to incorrect suggestions of the presence of life elsewhere in the Solar System. This study assessed the capability of solid phase micro extraction (SPME) as a method for monitoring organic contamination encountered by spacecraft hardware during assembly and operation. SPME-gas chromatography-mass spectrometry (SPME-GC-MS) analysis was performed on potential contaminant source materials, which are commonly used in spacecraft

construction. The sensitivity of SPME-GC-MS to organics was assessed in the context of contaminants identified in molecular wipes taken from hardware surfaces on the ExoMars *Rosalind Franklin* rover. SPME was found to be effective at detecting a wide range of common organic contaminants that include aromatic hydrocarbons, non-aromatic hydrocarbons, nitrogen-containing compounds, alcohols and carbonyls. A notable example of correlation of contaminant with source material was the detection of benzenamine compounds in an epoxy adhesive analyzed by SPME-GC-MS and in the ExoMars rover surface wipe samples. The current form of SPME-GC-MS does not enable quantitative evaluation of contaminants, nor is it suitable for the detection of every group of organic molecules relevant to astrobiological contamination concerns, namely, large and/or polar molecules such as amino acids. However, it nonetheless represents an effective new monitoring method for rapid, easy identification of organic contaminants commonly present on spacecraft hardware and could thus be utilized in future space missions as part of their contamination control and mitigation protocols.

Keywords

- Contamination control
- Planetary Protection
- Mars
- ExoMars
- SPME
- Biosignatures

Introduction

1.1. Planetary protection and Organic Contamination Control

The search for life, either extant or extinct, elsewhere in the Solar System represents one of the most significant challenges to modern day science. The forefront of the search has been, and will continue to be for the near future, dominated by unmanned space probes and surface rovers (Klein et al., 1976; Barnes et al., 2006, 2021; Mahaffy et al., 2012; Pappalardo et al., 2013; Lunine et al., 2015; Turtle et al., 2017; Vago et al., 2017; Farley et al., 2020; Beauchamp et al., 2021). These crafts carry payloads that accommodate highly sensitive instruments designed for the detection and characterization of organic molecules (Klein et al., 1976; Barnes et al., 2006; Mahaffy et al., 2012; Brockwell et al., 2016; Rull et al., 2017; Goesmann et al., 2017; Reinhardt et al., 2020; Guzman et al., 2020).

Certain organic molecules, or distributions of organic molecules, are indicative of biological processes and are respectively termed “biomarkers” or “organic biosignatures” (Summons et al., 2008). Alongside other potential biosignatures such as stable isotopes, atmospheric gases, biosedimentary structures, and macrotextures, organic biomarker compounds are a target for both past habitability and extant life detection efforts (Des Marais et al., 2008). Given the potentially small amounts of organics that may provide a biomarker signal, it is essential to ensure all hardware concerned with sampling is organically clean and free from terrestrial contamination to prevent false positive results (Mahaffy et al., 2003; Blakkolb et al., 2014; Neveu et al., 2018).

Planetary protection is the branch of astrobiology concerned with the prevention of both the forward contamination of other planetary bodies with terrestrial biological matter, so as to preserve pristine conditions for future scientific exploration, and the potential backwards

65 contamination of Earth's biosphere with extra-terrestrial microorganisms, if these exist
66 (Rummel and Meyer, 1996). The guidelines surrounding planetary protection policies are set
67 out by the Committee on Space Research (COSPAR) (Rummel et al., 2002; Kminek et al.,
68 2017), with a summary of different mission categories and the required protection for each
69 given in Table 1.

70 Planetary protection and its circumambient body of research has been historically dominated
71 by study into biological contamination of other planetary bodies with terrestrial organisms
72 and vice versa (e.g. Rettberg et al., 2019). A prime example of this is the intensive biological
73 control research related to the Viking Mars missions (Rummel, 2001). Historically, a lesser
74 amount of attention has been given to the identification and monitoring of non-biological
75 organic contamination on space missions.

76 Surfaces determined to be biologically clean are not necessarily organically clean, and
77 common cleaning methods such as thermal bakeout, unless combined with hard vacuums and
78 trapping mechanisms, may destroy microorganisms present but fail to remove residual
79 organic signatures. It is also possible that volatilized contaminants may re-condense on the
80 flight hardware if the bakeout chamber is not clean prior to use or there is an inappropriate
81 set-up without cold traps in place.

82 In addition to biological monitoring, minimizing the contributions of organic and particulate
83 contaminants, termed "contamination control," is required for life detection missions. For the
84 avoidance of false positives, it is essential to ensure the highest levels of organic cleanliness
85 possible, which cannot be achieved with a sole focus on biological contamination (Des
86 Marais et al., 2008). Within planetary protection, organic contamination control has a
87 different focus to biological contamination control because, although it can affect the results

of the individual science mission, the compounds of interest are not required to be self-replicable and capable of widespread proliferation. The documentation of all known potential organic contaminants, for the purpose of ensuring contaminating molecules are not mistaken for compounds of interest during sample analysis, is known as "contamination knowledge."

1.2. **Mars planetary protection and the ExoMars mission**

Since its conception in the late 1950s, planetary protection has been majorly focused on space missions to Mars, given the planet's status in the solar system as a prime potential candidate for harboring past or present life (Klein et al., 1976; Rummel, 2001; Des Marais et al., 2008; Grotzinger et al., 2012). This pre-eminence of focus on Mars is further highlighted by the Mars mission specific planetary protection categories seen in Table 1. So called "Mars special regions" on the planet's surface represent those of most concern in relation to planetary protection, given the belief that, if terrestrial microorganisms were transported to these locations, they would potentially be able to survive and proliferate (Rummel et al., 2014; Rettberg et al., 2016). These regions, therefore, also have the conditions that would give the highest potential for martian life.

ExoMars is a joint European Space Agency and Roscosmos two phase mission consisting of the ExoMars Trace Gas Orbiter, which launched in 2016, and the ExoMars *Rosalind Franklin* rover, now scheduled for launch mid-2022. The primary scientific objective of ExoMars is the detection of evidence for the presence of previous life on Mars (Barnes et al., 2006; Vago et al., 2017). The rover will house the Pasteur payload, which contains a drill capable of sampling to a depth of 2 meters in the subsurface along with a suite of instruments, described in Table 2, for the analysis of potential chemical biosignatures in the martian soil.

Under planetary protection guidelines, the rover phase of the ExoMars mission has been classified as Category 4b. All sampling hardware must be isolated and organically clean during the mission, with the entirety of the rover's Analytical Laboratory Drawer (ALD) sample-handling path contained within a so called ultra-clean zone (UCZ) (Vago et al., 2017).The UCZ will be cleaned to a level on the order of nanograms of contaminants per cm^2, which is commensurate to the Viking lander sample transfer chain cleaning requirements of 1 ng cm^{-2} and considerably more stringent than the requirements for the Mars Science Laboratory (MSL) sample transfer chain of 100 ng cm^{-2} (Mahaffy et al., 2003; Guarnieri et al., 2009). The remainder of the ExoMars rover and lander, which will not come into contact with samples, will only have to follow the less stringent category 4a guidelines, as applied to the MSL and MER rovers (Vago et al., 2017).

1.3. Current monitoring methods and related issues

To achieve these high levels of cleanliness a variety of techniques are employed:

All work is carried out under clean room conditions. A typical aerospace cleanroom is class 100,000 or ISO 8 (i.e., contains 100,000 or fewer particles of 0.5 µm in diameter per cubic foot of air, controlled by High Efficiency Particle Air (HEPA) filters and maintaining a positive air pressure between the inside and the outside environments. For the assembly of the most sensitive flight hardware, class 10 or ISO 4 cleanrooms may be employed, containing less than 10 0.5 µm particles per cubic foot of air, and in these environments, personnel must be isolated by wearing clean suits at all times.

In addition to particles, molecular contaminants are monitored and minimized in cleanrooms used to build "search-for-life" hardware. Contamination control for organics is a complex activity that starts from the building and commissioning of cleanrooms. Construction

materials are scrutinized and chosen based on their compatibility with the overall cleanliness; the vetting includes materials that are not located in highly controlled rooms, but nevertheless are in contact with the air supply (e.g., ducting, filter housings, duct sealants).

Reducing the overall VOC (volatile organic compounds) emissions is critical to maintaining low levels of organic contamination. For this purpose, the Airbus UK (Stevenage) bio-cleanroom used to integrate Rosalind Franklin rover was equipped with broad-spectrum carbon filters upstream of HEPA filters (for intake and recirculation air); materials used for the cleanroom construction were chosen based on a requirement of <5 g/litre; and the environment commissioning included a "bake-out" of the facility for a long duration prior to use (>200 days), with heat vents turned on while the facility was at rest and a limited number of people. Built-in or portable VOC sensors were also used as required and for "live" measurements during critical integration phases.

Precision cleaning is the series of processes targeted at removing both particles and molecular films of organic contaminants. Firstly, visible contamination is wiped from the surface. Secondly, a series of rinses with organic and aqueous solvents of varying polarities is performed, which may be coupled with ultrasonic treatment to liberate any contaminants adhering to the surfaces. Thirdly, Freon vapor is used for degreasing. Fourthly, isopropyl alcohol rinses are performed and analyzed for remaining particulate levels. The overall process of precision cleaning commonly achieves Level 100 cleanliness, which is considered high enough in most cases (Mahaffy et al., 2003).

The use of solvents is not suitable for all materials used in spacecraft assembly. Solvents can dissolve certain polymers and may be adsorbed by certain materials, for example, paints, plastics, glass, or carbon fiber and surfaces to be released later under TVAC test conditions,

potentially causing contamination events if deposition occurs on sensitive/critical surfaces. Other techniques are also employed in these cases, using plasma, accelerated CO_2 snow, radiation, or electron beams to remove organic compounds (National Research Council, 2000, 2006; ten Kate et al., 2008; Dworkin et al., 2018). Repeated wiping of surfaces with clean room cloths saturated with propan-2-ol or ethanol during assembly prevents the re-build-up of certain molecular contaminants, although this does not protect against all species, for example, silicones are unlikely to be removed in this manner.

Thermal vacuum bakeout is the concluding step to both remove surface contaminants and reduce subsequent outgassing of organic impurities within the materials. Vacuum bakeout times and temperatures are dependent on both the material constraints and the predicted in-flight temperatures. To achieve best practice and minimize outgassing products, flight hardware is baked at its maximum possible temperature and at least 10°C higher than its in-flight temperature. On ExoMars, a standard bake-out temperature was 125°C (based on ECSS-Q-ST-70-57 for DHMR - Dry Heat Microbial Reduction) and due to the need of combining measures to minimize both organic and biological contamination; on Solar Orbiter, it was necessary to bake sensitive parts to over 200°C, given the high temperatures experienced by flight hardware (García Marirrodriga et al., 2020).

Monitoring clean room and hardware organic cleanliness is currently a complex process often involving multiple, expensive, and time-consuming techniques. (National Research Council, 2000; Mahaffy et al., 2003; Blakkolb et al., 2014; Li et al., 2015). Effective monitoring is confounded further by the fact that, in contrast to biological contamination, quantitative limits for organic contamination control are highly specific to the type of mission and are instrument specific. The lack of well-defined guidance is partly because the cleanliness level must be appropriate to the sensitivity of the instruments of the specific mission. Initially,

undetectable compounds may be transformed into more problematic species by the harsh environments encountered during the long cruise phase, in-orbit or (if applicable) once landed on the surface. It is also possible that some specific organic contaminants may hinder key measurements such as when deposition occurs on sensitive optical surfaces.

The current ESA molecular procedure ECSS-Q-ST-70-05 has been applied to the frame of the ExoMars rover and widely used in other space applications. Based on ESA ECSS, the so called “indirect method” consists of collecting contaminants on the surface by means of a concentration technique, for example by washing or wiping. The resultant contaminated liquid or tissue is then processed, and finally an IR-transparent or a reflective window containing the contaminants is analyzed with the aid of an IR spectrophotometer. With this current ECSS methodology, only groups of contaminants can be detected (e.g., hydrocarbons, esters, methyl- and phenyl-silicones); the detection limit varies but is about 2×10^{-8} g/cm^2 (with a wiped area of 100 cm^2).

Similarly, multi-stepped solvent extraction, followed by pre-concentration of analytes (by evaporation) and analysis by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, Fourier transform infrared (FTIR) spectroscopy and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) techniques were carried out on swabs from surfaces of the MSL sample transfer chain hardware at various stage of construction (Blakkolb et al., 2014). The use of multiple solvents, however, complicated the analysis of the data and diluted the contaminants of interest, reducing sensitivity of the detection. The whole process of extraction, concentration, and analysis was also very time consuming and therefore costly. A similar process to that employed for MSL was proposed for Mars 2020 (Table 2, Summons et al., 2014).

Inventories of materials used during construction of spaceflight hardware and their potential for contamination are also required to be stored for potential future testing to allow for identification of suspected contaminants in experimental results from spacecraft instruments (Mahaffy et al., 2003). Such a materials database was created for monitoring during the ongoing MSL mission (ten Kate et al., 2008). Potential materials for use in the most contamination sensitive parts of the ExoMars rover were thoroughly tested to determine their appropriateness for use and to calculate contamination budgets (Guarnieri et al., 2009).

Various culture-dependant assays (Benardini III et al., 2014b, 2014a) and culture-independent methods (La Duc et al., 2004, 2009; Nellen et al., 2006; Probst et al., 2012) have been used to track the microbial bioburden present on flight instrument surfaces. While the NASA/ESA standard assay technique (Morris et al., 2010) is a good example of a standardized planetary protection contamination control method, these techniques give no indication of the non-biological organic contamination present.

A diagnostic organic contamination monitoring process is needed. While useful, witness plates (ten Kate et al., 2008) can only show what is condensing/falling onto clean metal surfaces at the specific time of exposure. As such, they are not representative of the whole contamination history of flight hardware. They also cannot show transfer from hands/gloves as they are not handled in the same way as the actual flight hardware. A standardised technique to directly sample the flight hardware surfaces in addition to the atmosphere itself, which is rapid, inexpensive, and easy to use, would be very useful (alongside the use of witness materials) for monitoring clean room and flight hardware cleanliness.

1.4. **SPME as a new monitoring method for planetary protection**

The monitoring method explored in this study is solid phase micro-extraction (SPME), a technique developed by Arthur and Pawliszyn (1990), involving the use of fused silica fibers coated with a liquid organic polymer or solid sorbent onto which the analyte is absorbed. SPME combines sampling and pre-concentration into a single step (Harper, 2000) and removes the need for additional solvents. The SPME fiber can be inserted directly into the inlet port of a GC, where the analytes can be thermally desorbed and analyzed by MS.

Although not discussed in detail here, SPME fibers may also be used for passive atmospheric sampling (Li et al., 2001; Isetun et al., 2004; Tuduri et al., 2012). Therefore, SPME-GC-MS has the potential to monitor organic contamination present on the surfaces of spacecraft along with the surrounding environmental atmosphere, thus providing an extremely useful dual application few other current monitoring methods can provide.

The study builds on the proof of concept study performed by Royle et al. (2019), which demonstrated that the SPME-GC-MS method is suitable for the monitoring of organic cleanliness of spacecraft surfaces. However, the previous study was limited to testing the technique on individual standard compounds in isolation, rather than a complex mixture of organic contaminants, which would resemble a situation more akin to real-world spacecraft surfaces.

The present study aimed to evaluate the potential for the application of SPME as a monitoring method for organic contamination of spacecraft throughout both the assembly and operational phases of space missions. Standard materials used in construction and assembly of the ExoMars rover were analyzed using a modified version of the SPME-GC-MS method set out by Royle et al. (2019). These materials have the potential to outgas complex mixtures

of organic molecules, which could, if transported to the sampling instruments in a spacecraft payload, lead to false positive detections of organics. Molecular wipes, taken from surfaces on the ExoMars rover during assembly (ESA 2009), were solvent extracted and analyzed by GC-MS to allow for the identification of any contaminants present on the rover's surfaces. Organic molecules detected by the SPME method were compared against the ExoMars rover molecular wipes data to match up any common contaminants present to try and identify reasonable sources of the contamination present on the ExoMars rover. The same potential contaminant source materials were also analyzed using a more conventional thermal desorption technique to allow for comparison with the less well studied SPME method.

The current study coincides with a wave of life detection missions to Mars over the coming years, namely, the aforementioned rover phase of the ExoMars mission as well as NASA's Mars 2020 *Perseverance* rover and future Mars Sample Return campaign (Mattingly and May, 2011; Farley et al., 2020). The significance of the findings of this study will not be limited to those concerned with life detection on Mars, but will also be of great relevance to numerous future astrobiological space missions throughout the solar system where organic cleanliness will be crucial to their success, such as those looking at the putative prebiotic chemistry of icy bodies (National Research Council, 2000; Pappalardo et al., 2013; Turtle et al., 2017).

2. Methodology

2.1. **ExoMars contamination sampling**

2.1.1. **Molecular wipes**

Airbus Defence and Space UK provided this study with 8 molecular wipe samples taken from different surfaces of the ExoMars rover during its construction. Molecular wipes (tissues wet

with spectral grade isopropyl alcohol, IPA) were taken per ESA ECSS-Q-ST-70-05 protocol (ESA 2009). The surfaces on the ExoMars rover from which the molecular wipe samples were taken are as follows: A, from gold plated carbon fibre reinforced plastic (CFRP); B, from a Kapton (polyimide) substrate; C and D, from an electrolytic-gold coated aluminium surface; E, from CRFP populated with solar cells; and F, G and H, from unspecified locations.

2.1.2. **Solvent Extraction**

Each molecular wipe was first weighed and then placed into a test tube. The following solvent order was used for the extractions: water, acetonitrile, and toluene. A total of 4 ml of solvent was added to the test tube and then sonicated for 3 minutes. The supernatant was then pipetted off into a clean test tube, with this process being performed 3 times for each solvent. These extracts were evaporated under a nitrogen stream and transferred to vials; they were then further evaporated to dryness. Following this, 25 µl of an internal standard solution (1.158 mg ml^{-1} pyrene/dichloromethane) was syringed into each vial.

The water and acetonitrile extracts were derivatized by the addition of N, O-(bis-trimethylsilyl) trifluoroacetamide (BSTFA) followed by heating for 45 minutes at 85 °C, with this step not being required for the toluene extract. BSTFA is a silylation reagent that replaces labile hydrogens on a wide range of polar compounds with a $-Si(CH_3)_3$ group, making these polar compounds more amenable to GC separation.

Procedural blanks were performed with a clean, empty test tube and following the same sampling method as for the molecular wipes.

GC-MS analysis was performed using an Agilent Technologies 7890 GC coupled to a 5975 MS. Injection was split with a 10:1 split ratio and the injector temperature held at 270 °C.

Helium was used as the carrier gas with a constant column flow rate of 1.1 ml min^{-1}. Separation was performed on a J&W DB-5MS UI column (30 m × 0.25 mm × 0.25 µm). The oven temperature was held at 40 °C for 2 minutes and then ramped up at 5 °C min^{-1} to a final temperature of 310 °C, where it was held for 14 minutes. The scan range for mass spectra acquisition was 45–550 m/z, with peaks identified using the NIST mass spectral library in tandem with retention order comparisons to published data.

2.2. **Potential contaminant source materials**

A detailed list of construction materials for the ExoMars rover was provided by Airbus Defence and Space UK. Material selection was then made from this list; however, due to a lack of easily available highly specialized aerospace materials, those tested in this study were not specifically the same as the materials used for the rover. This is not deemed problematic as this is a proof of concept/method development study rather than a specific review of sources of contamination onboard the ExoMars rover. Due to uncertainty over the surface cleanliness of materials, from transport and storage, they were rinsed with pentane before sampling where possible. It was not possible to analyze all materials by thermal desorption as some were not amenable to insertion into narrow thermal desorption tubes. Details of chosen materials and analytical techniques applied are provided in Table 4.

2.3 **Solid Phase Micro Extraction**

The selection of 75 µm coating thickness Carboxen—polydimethylsiloxane (PDMS) coated SPME fibers (Supelco, USA)—was based on their suitability for the detection of the low molecular weight organic compounds, which are common contaminants found on spacecraft surfaces. The coating also allowed for the monitoring of volatiles, which is important for consideration of SPME-GC-MS as a suitable contamination monitoring method for both the

spacecraft itself and the environment in which it is constructed. Other recommended fiber coatings and thicknesses for alternate types of analytes are provided in Table 5.

A manual SPME holder was used to house the SPME fiber, with the fiber being conditioned before sampling by insertion into the gas chromatograph injection port for 45 minutes at 300 °C.

Samples were weighed and sealed in clean 10 ml headspace vials (Chromacol). The vials were heated at 100 °C for 1 hr for equilibrium to be reached between solid and vapor phases. The SPME fiber was inserted into the headspace above the sample for 5 minutes, allowing time for vapor phase and fiber coating phase to equilibrate. The fiber was retracted back into the holder and immediately analyzed by GC-MS. A procedural blank was performed by preparing an empty headspace vial and sampling under the same conditions as a standard SPME run.

Analysis of the volatiles adsorbed onto the SPME fiber was carried out via SPME-GC-MS analysis. The SPME fiber was inserted directly into the injection port of a Perkin Elmer Clarus 580 GC coupled to a Clarus SQ85 MS. Analytes were desorbed from the fiber for 5 minutes before the fiber was withdrawn. Injection was split with a 20:1 split ratio and the injector temperature held at 300 °C. Helium was used as the carrier gas with a constant column flow rate of 1.1 ml min^{-1}. Separation was performed on a J&W DB-5MS UI column (30 m × 0.25 mm × 0.25 µm). The GC oven temperature was held at 60 °C for 2 minutes and then ramped at 10 °C min^{-1} to a final temperature of 310 °C, where it was held for 11 minutes. The scan range for mass spectra acquisition was 45–550 a.m.u., with peaks identified using the NIST mass spectral library in tandem with retention indices.

Analytical blanks were performed by the insertion of the SPME fiber into the injector of the GC-MS directly after activation.

2.4 Thermal extraction

Material samples were weighed and loaded into clean borosilicate tubes (15 cm, 6 mm o.d., 4 mm i.d.). Clean quartz wool was inserted into the end of the tube to hold the sample in place. naphthalene-d8 dissolved in pentane (which was allowed to evaporate prior to analysis) was added to the sample 30 minutes prior to sampling as an internal standard.

The tubes were then loaded into a CDS 5200 HPR Pyroprobe interface and heated at 300 °C for 5 mins. The products were transferred to a Tenax thermal adsorption tube, which was then thermally desorbed for 5 minutes at 300 °C via a heated transfer line to the injection port of an Aligent Technologies 6890 GC coupled to a 5973 MS. Injection was split with a 50:1 split ratio, and the injector temperature was held at 270 °C. Helium was used as the carrier gas with a constant column flow rate of 1.1 ml min^{-1}. Separation was performed on a J&W DB-5MS UI column (30 m × 0.25 mm × 0.25 µm). The oven temperature was held at 40 °C for 2 minutes and then ramped up at 5 °C min^{-1} to a final temperature of 310 °C, where it was held for 10 minutes. The scan range for mass spectra acquisition was 45–550 m/z, with peaks identified using the NIST mass spectral library in tandem with retention time comparison. A procedural blank was carried out using a clean empty tube stoppered with quartz wool, prepared under the same conditions as the material test sample tubes.

Cleaning runs with a clean, empty tube were performed between each sample run to prevent organic material carry over from the previous sample.

3. Results

The collection of contaminants from surfaces on the ExoMars rover (ESA 2009), their isolation by solvent extraction, and analysis by GC-MS allowed comparison with the SPME and thermal desorption methods and, thereby, identification of potential sources of the contaminants detected.

3.1. **Molecular wipes, ExoMars contamination sampling**

GC-MS data for all wipe samples was highly similar regardless of the sampled location on the rover. Therefore, only the representative ExoMars molecular wipe sample A total ion count (TIC) chromatograms are presented in Figure 1. TIC chromatograms of ExoMars molecular wipe samples A (repeated for ease of comparison), B, C, D, E, F, G, H, the procedural blank, and an extracted unused molecular wipe are presented in Figure 2. Peaks labelled are those which were identifiable, with a high degree of accuracy, by the NIST spectral library.

All solvents, water, acetonitrile, and toluene consistently allowed the detection of the pyrene internal standard, which the data were scaled to. Compounds detected in the water and acetonitrile extracts were highly similar with 2,4-dimethyl pyridine; trifluoromethyl-bis-(trimethylsilyl)methyl ketone; bis-*N*-(trimethylsilyl)ethylamine*; N, N'*-methanetetraylbis(1,1,1-trimethyl)silanamine; 1,2-bis(trimethylsiloxy)ethane; decamethyltetrasiloxane detected in all samples. trifluoromethyl-bis-(trimethylsilyl)methyl ketone; bis-*N*-(trimethylsilyl)ethylamine and 1,2-bis(trimethylsiloxy)ethane were also detected in the water extract of the procedural blank as these are by-products of the BTSTFA derivatization agent used.

Toluene extracts were also very similar across all wipe samples. 2-4-bis(1,1-dimethylethyl)phenol, dibutyl phthalate, *n*-alkanes (between C_{23} and C_{28}), and 4-octyl-*N*-(4-

383 octylphenyl)aniline were detected in all wipes. *N*-pentadecane was also detected in wipes A
384 and F.

385 3.2. **Thermal desorption**

386 Thermal desorption TIC chromatograms for the potential contaminant source materials
387 analyzed (Dacron tape, Chofoil tape, Kapton film, Kapton cable, PTFE, PMI foam) are
388 presented in Figure 3. The internal standard naphthalene-d8 was detected in all samples, with
389 unevaporated pentane, from the internal standard solution, also detected in Dacron tape,
390 Kapton film, Kapton cable, PTFE.

391 Compounds identified from the thermal desorption of the Dacron tape were acetic acid;
392 methyleneheptane; ethylhexanol; acetic acid, ethylhexyl ester; propenoic acid, ethylhexyl
393 ester.

394 Compounds identified from the thermal desorption of the Chofoil tape were acetic acid;
395 butanol; 2-methyl-4-methylene-hexane; heptanone; 2-ethyl-1-hexanol; acetic acid, 2-ethyl
396 hexyl ester; 2-propenoic acid, 2-ethylhexyl ester.

397 Compounds identified from the thermal desorption of the Kapton film were pentane;
398 benzene; 2-methyl-4-methylene-hexane; 2-ethyl-1-hexanol; acetic acid, 2-ethyl hexyl ester.

399 The only compound identified from the thermal desorption of Kapton cable, unrelated to the
400 addition of the internal standard, was toluene.

401 No compounds, other than those related to the addition of the internal standard, were
402 identified from the thermal desorption of PTFE.

Compounds identified from the thermal desorption of PMI foam were butane; propanol, benzene; butenoic acid, methylethyl ester; propenoic acid, 2-methyl ; *N*-tert-butyl formamide; methacrylamide; α-methylstyrene; *N*-tert-butylmethacrylamide; acetophenone.

3.3. **SPME-GC-MS**

SPME-GC-MS TIC chromatograms for the potential contaminant source materials analyzed (Dacron tape, Chofoil tape, Kapton film, Kapton cable, PMI foam, epoxy, PTFE, grease, Delrin) are presented in Figure 4, with labelled peaks being those of most significance to this study and most reliably identified with a high degree of accuracy.

Compounds identified from the SPME headspace sampling of Dacron Tape were xylene; benzaldehyde; phenol; butenoic acid, hexyl ester; 2-ethyl-1-hexanol; benzenemethanol; methyldecane; nonanal; acetic acid, 2 ethylhexyl ester; dimethylundecane; heptadecane; methylnapthalene; dodecane; dimethylnapthalene; unidentified branched alkanes; bibenzyl; propanoic acid, 2-methyl-, 1-1, 3-propanediyl ester; hexadecane.

Compounds identified from the SPME headspace sampling of Chofoil tape were heptanone; benzaldehyde; ethylhexanol; undecane; nonanal; acetic acid, ethylhexyl ester; benzoic acid; dodecane; propanoic acid, ethylhexyl ester; isopropenylnapthalene; 1, 1'-biphenyl, 4-methyl; bibenzyl; propanoic acid, 2-methyl-, 1-1, 3-propanediyl ester; unidentified branched alkane.

Compounds identified from the SPME headspace sampling of Kapton film were xylene; benzaldehyde; trimethylbenzene; dimethyloctane; ethylhexanol; nonanal; 2-ethyl-4-methylhexane; unidentified silanes; unidentified branched alkanes; propanoic acid, 2-methyl-, 1-1, 3-propanediyl ester; dibutyl phthalate.

Compounds identified from the SPME headspace sampling of Kapton Cable were xylene, a series C_{10} to C_{17} *n*-alkanes (peaking at dodecene), and a range of unidentified branched alkanes.

Compounds identified from the SPME headspace sampling of PMI foam were heptanol, methacrylamide; trimethylbenzene; phenol; methylstyrene; octanol; nonanol; benzoic acid; *n*-alkanes from C_{13} to C_{16}; dodecamethyl cyclohexasiloxane; and a series of three unidentified branched alkanes.

Compounds identified from the SPME headspace sampling of Kapton tape were propenoic acid, butyl ester; benzaldehyde; various branched alkanes; methylheptanol; octanol; nonanal; benzoic acid; propenoic acid, methylheptyl ester; a series of C_{14} to C_{16} *n*-alkanes; propanoic acid, 2-methyl-, 1-[1,1-dimethylethyl]-2-methyl-1,3-propanediyl ester.

Compounds identified from the SPME headspace sampling of epoxy were xylene; propenoic acid, methylbutyl ester; benzenemethanol; N, N-dimethylbenzenemethanamine; benzoic acid.

Compounds identified from the SPME headspace sampling of PTFE were primarily aliphatic hydrocarbons with *n*-alkanes from C_{10} to C_{18} and branched alkanes. There was also a series of four cyclosiloxanes - decamethyl cyclopentasiloxane; dodecamethyl cyclohexasiloxane; tetradecamethyl cycloheptasiloxane; hexadecamethyl cyclooctasiloxane; octadecamethyl cyclononasiloxane; propanoic acid, 2-methyl-, 1-[1,1-dimethylethyl]-2-methyl-1,3-propanediyl ester; diisoproylnapthalene.

Compounds identified from the SPME headspace sampling of silicon grease were a series of siloxanes: octamethyl cyclotetrasiloxane; decamethyl cyclopentasiloxane; dodecamethyl cyclohexasiloxane; tetradecamethyl cycloheptasiloxane; hexadecamethyl cyclooctasiloxane; octadecamethyl cyclononasiloxane.

Response from SPME headspace sampling of Delrin was very low, with peaks at least an order of magnitude lower than other substances tested. Compounds identified were phenol; decane, undecane, an unidentified branched alkane; a series of five unidentified silicon-bearing compounds; tridecane; tetradecane.

The only compounds detected in the procedural blank were decane, a common airborne contaminant, and unidentified siloxanes, which are likely to be sourced from the PDMS coating of the SPME fibre itself. These compounds are identified in some, but not all, of the actual samples analysed, and so may be a result of the SPME fiber intermittently degrading in the GC-MS inlet with extensive use.

4. Discussion

4.1. **Contaminants detected on current ExoMars Rover**

During sampling, it is unlikely that the molecular wipes used would have captured all the types of contaminants present on the rover surfaces, given the differing solubility of organics in solvents used in sampling and the ability of surface materials to selectively absorb organics after they have been dissolved in solvents (Court et al., 2012). More polar contaminants will likely be less soluble in solvents used for sampling, reducing the amount which will be removed from surfaces (Royle et al., 2019). The selectivity of capture by SPME also has implications for the SPME-GC-MS technique, with the potential for testing SPME sampling on different types of material surfaces being required in the future.

Given the SPME fiber choice in this study, organics present in the toluene extracts from the molecular wipes (Figures 1 and 2) should be of most relevance to those detected from the material tested. Those in the remaining extracts will be more polar and/or higher molecular

mass; therefore, it is not likely to be feasible to detect them by the current SPME-GC-MS method.

The two major species detected in the toluene extracts (Figures 1 and 2) were dibutyl phthalate and 4-octyl-*N*-(4-octylphenyl)benzenamine, both of which consistently represented the two largest peaks in all 8 of the molecular wipe samples. Dibutyl phthalate is used in rubbers and resins as a plasticizer and can be a common lab contaminant due to leaching from plastic laboratory consumables or from packaging (Gross, 1977; Reid et al., 2007). Dibutyl phthalate and similar esters are noted as common contaminants on spacecraft; however, they are relatively easy to characterize as they have well-recognised sources, so would not be highly problematic in the context of life detection experiments on space missions (Chen et al., 1997).

The aromatic amine 4-octyl-*N*-(4-octylphenyl)benzenamine may be sourced from lubricants used during rover construction, given that it is a common additive to act as an oxidation inhibitor. Aromatic amines such as benzenamine have a major use in polyurethane, which in an astrobiological context has been identified as a potential contaminant due to its extensive use in clean room gloveboxes (Calaway et al., 2014).

C_{23} to C_{28} *n*-alkanes are also detected in the toluene extracts; these are also likely to have an origin in lubricating oils/waxes.

Ketones and amines were detected in the water and acetonitrile extracts (Figures 1 and 2); these are silylated due to the BSTFA derivatization. Due to the GC-MS set up used, it is likely they would escape detection without this derivatization step. Alongside the also detected pyridine, these compounds have many common sources, including plastics, paints, and adhesives.

4.2. **SPME contaminant detection potential**

4.2.1. Organics detected in potential contaminant source materials

As previously described by Royle et al. (2019), the SPME-GC-MS method used in this study is not adept at detecting polar and/or non-volatile compounds, due to the analytical window of the GC-MS instrumentation. Overall, this assertion is supported by the GC-MS results of the materials tested in this study, with detection limited to compound classes that include aromatic and aliphatic hydrocarbons, nitrogen containing compounds, alcohols and carbonyls. These groups of organics detected are discussed in the context of representing contaminants of concern for Mars life detection missions, which were given by Mahaffy et al. (2003), given their association with biology and potential for causing false positive detections (Table 6).

The organics detected from the Kapton film, Delrin, Kapton cable, and PTFE samples are mainly aliphatic hydrocarbons (Figure 4). This, along with the fact that these materials are specially designed to remain stable and have a low potential to outgas organics, may suggest that these were not likely sourced from the materials themselves but rather from contamination already present on the material surfaces.

SPME has been demonstrated to be effective at detecting aromatic hydrocarbons by previous studies (e.g. King et al., 2004). The current study also finds this to be the case, with examples of aromatics detected xylene from Dacron, Kapton film, PMI foam and Epoxy, as well as PAHs such as 1-isopropenylnaphthalene detected in the Chofoil tape. The detection of phenol in the Delrin, Dacron and PMI foam is of interest given the presence of phenol, 2,4-bis(1,1-dimethylethyl) as a contaminant on surfaces of the ExoMars rover. This implies that materials

used in the ExoMars rover's construction have the potential of contaminating with aromatic compounds, and that the SPME technique is effective at detecting this contamination.

Aliphatic hydrocarbons were the most common type of organic molecules detected in this study. These include both normal and branched chain alkanes and alkenes. SPME could, therefore, have been used for monitoring of hydrocarbons on the ExoMars rover's hardware surfaces, given the detection of a range of alkanes in the molecular wipe samples (Figure 1). There is an extensive range of potential contaminant sources for the alkanes found on the rover; common sources of which include vacuum pump oil, lubricants, and atmospheric constituents derived from fossil fuels.

Nitrogen containing compounds are of importance in a planetary protection context owing to their close association with biology. The SPME technique utilized here effectively detects amines and other nitro-aromatic compounds, despite not using the suggested suitable fiber for these compound classes (Table 5). The detection of *N*,*N*-dimethylbenzenemethanamine in the epoxy adhesive by SPME is worthy of note given its structural similarity with 4-octyl-*N*-(4-octylphenyl)benzenamine, which was identified previously as an ExoMars rover contaminant, and so may represent a fragment of the larger molecule, volatilized through heating. Amides were also detected in the form of methacrylamide in the PMI foam, which is used in the production of polymers. This high sensitivity of SPME for detection of nitrogen containing compounds, namely, benzenamines, is supported by Kayali-Sayadi et al. (2003), who noted SPME allows for their rapid detection, free from cross-contaminants and producing clearly distinct spectral signals. SPME may, therefore, have been suitable for use as a method for monitoring of these compounds during the construction of the ExoMars rover.

Esters are common contaminants in laboratories and on hardware surfaces on spacecraft, with the ester dibutyl phthalate detected in the ExoMars molecular wipes samples. The ability of the SPME-GC-MS method to detect dibutyl phthalate, along with esters of carboxylic acids (Figure 4), is therefore significant, as it means the method is amenable to detecting another group of organics that (prior to the launch of Mars Sample Laboratory/Curiosity) were identified as contaminants of concern for landed Mars missions (Mahaffy et al., 2004). SPME also proved suitable for detection of alcohols with normal and branched alcohols being major constituents in the Chofoil, Dacron, and Kapton tape chromatograms.

4.2.2. SPME issues and applicability to ExoMars contamination monitoring

While it has been shown that certain types of organics commonly associated with spacecraft contamination can be detected by SPME, the limits of the detection of these organics have not been tested. Materials were subjected to headspace SPME sampling rather than the sampling of organics directly from analogue spacecraft hardware surfaces as performed by Royle et al. (2019), with the absorbance of analytes onto the fiber potentially being more favorable via the headspace method. On the actual surfaces of spacecraft, the concentrations of organic contaminants would likely be much lower than those given off by materials tested in this study, and it would be ideal to combine the approaches of the previous study (Royle et al., 2019) with that of this one to directly sample spaceflight hardware surfaces using the SPME fibres.

If it had been utilized to directly sample spaceflight hardware surfaces, however, the SPME-GC-MS method would likely have been a promising addition to the suite of methods used for contamination monitoring during the construction of the ExoMars rover. It would have allowed for rapid—approximately 25 minutes from sampling to GC-MS data output—

qualitative assessment of complex mixtures of contaminants present on the rover surfaces; albeit limited to the range of organics discussed previously.

It must be noted that, with an alteration to the method through the use of liquid chromatography-mass spectrometry (LC-MS) or high-performance liquid chromatography (HPLC), SPME-LC-MS or SPME-HPLC could be a viable option for detection of polar and non-volatile compounds (Kataoka et al., 2000) by removing the limitations of GC-MS.

4.3. SPME vs Thermal desorption

4.3.1. Organics detected by thermal desorption

The thermal desorption results for the Kapton film, PTFE, and Kapton cable follow those observed with the SPME method, which can again be explained as the organics detected likely sourced from external contaminants present on the materials rather than from the materials themselves.

It proved difficult to obtain consistent internal standard peaks using the thermal desorption technique; this was likely due to the variable evaporation of standards from the tubes, which meant reliable quantitative analysis of results was not possible. The thermal desorption method also showed more variability between repeats, with reproducibility much better when using the SPME technique, and SPME chromatograms were less impacted by background laboratory contamination.

Overall, on comparison, the thermal desorption and SPME chromatograms of the same materials display close matches for organics detected. There are, however, some notable differences between the two methods in relation to the responses of the same organic molecules. With the Dacron samples, 2-ethyl-1-hexanol is detected by both methods, but gives a much larger response, relative to adjacent peaks, in the SPME chromatogram

583 compared to its thermal desorption counterpart. In the SPME chromatogram for PMI foam,
584 given in Figure 4, α-methylstyrene (prop-1-en-2-ylbenzene) represents the most dominant
585 peak present by far; whereas, in the thermal desorption chromatogram, given in Figure 5., the
586 methylstyrene peak is of comparable size to other major organics present. Variation in
587 relative response between the two techniques may demonstrate a drawback of SPME,
588 showing that, as different organics have a different tendency to both absorb and desorb from
589 the fiber, any attempt at a quantitative method could be more difficult. The varying response
590 of each organic species, in this case α-methylstyrene, suggests a controlling factor to be the
591 affinity of the molecule to the fiber coating, demonstrating how SPME may favorably sample
592 aromatic molecules over others. It is possible that this difference in response may be due to
593 the thermal desorption technique not providing results consistent with the material
594 composition. However, previous work demonstrating the affinity of the SPME technique to
595 aromatic hydrocarbon detection (King et al., 2004; Royle et al., 2019) suggests the former
596 explanation to be more likely.

597 4.3.2. Evaluation of both methods

598 SPME-GC-MS represents a faster and more straightforward method than conventional
599 thermal desorption, given the relative ease of sample preparation of headspace vials
600 compared to thermal desorption tubes. The SPME method also proved more amenable to
601 producing repeatable, highly consistent results. Thermal desorption, on the other hand,
602 provides a means of quantitative assessment, which SPME currently lacks. The qualitative
603 nature of SPME analysis remains the major drawback for its use because, although qualitative
604 detection is useful, quantification of organic contamination on spacecraft surfaces is also
605 important for monitoring and control. Quantitative SPME analysis has, however, been shown
606 as potentially feasible by studies such as that of Matich et al. (1996), meaning a reliable

607 quantification may be developed through future research. However, Matich et al. (1996)
608 stated that quantification differs depending on the molecular weight of the analytes involved
609 and the time taken for equilibrium to be reached, adding significantly more complexity to any
610 potential solution.

611 In its present form, the SPME-GC-MS method for the monitoring of organic contaminants in
612 a planetary protection context does not represent a universal solution that would be suitable
613 for all monitoring situations. Rather, it may currently be best utilized as a quick and simple
614 diagnostic check of contamination present, in conjunction with complementary and more
615 conventional monitoring techniques (as listed in Table 3). The combination of multiple
616 methods would allow for a rapid, cheap qualitative assessment followed up by a more time
617 consuming and costly quantitation of contaminations present if deemed necessary. The use of
618 GC-MS as a detection and characterisztion technique provides additional benefits for
619 spacecraft that host GC-MS based instruments such as MSL and ExoMars, especially when
620 used in areas corresponding to the rovers GC-MS sample handling chain.

621 ## 5. Conclusions

622 In summary, the present study assessed the applicability of SPME for use in contamination
623 monitoring during spacecraft construction and operation. Analysis of ExoMars molecular
624 wipes identified organic contamination present on surfaces of the rover during its
625 construction, with notable contaminants including 4-octyl-*N*-(4-octylphenyl)benzenamine,
626 dibutyl phthalate, and *n*-alkanes. SPME and conventional thermal desorption were compared,
627 with the ease of sample preparation and rapid, straightforward sampling being the major
628 advantages for SPME, and the potential for quantitative analysis being thermal desorption's
629 main attraction.

Overall, SPME-GC-MS does currently represent a suitable monitoring method for planetary protection; however, it is not amenable to detection of all types of organics, most notably in the astrobiological context: amino acids and large polar molecules (although this could be solved via SPME-HPLC or SPME-LC-MS). Nonetheless, SPME is well suited to the detection of an extensive range of organic molecules, including aromatic and aliphatic hydrocarbons, nitrogen containing compounds, alcohols, and carbonyls. Thus, SPME-GC-MS could have provided a useful addition to the numerous methods used in the contamination monitoring of the ExoMars rover, given its proven ability to detect the types of organic contamination which were identified on the rover surfaces (through more traditional solvent extraction methods). Future space mission administrators would be wise to utilize SPME, given its ability to rapidly assess a relatively wide range of organics and its potential to mitigate against false positive detections.

The potential for future research includes the testing of a larger and more representative inventory of potential contaminant source material and the feasibility of quantitative SPME analysis for contamination monitoring. Additionally, any future study should investigate the use of SPME in combination with HPLC and LC, which would test the absolute limits of SPME's capabilities as a monitoring method for planetary protection and provide a more complete list of organics detectable by the SPME method.

Acknowledgements

We thank Airbus Stevenage Laboratory, in particular Daniel Evans and Zoe Sharp for supporting the analysis of the molecular swabs per ECSS-Q-ST-70-05, and the anonymous reviewers whose detailed and thoughtful suggestions significantly improved the manuscript.

Authorship confirmation/contribution statement

Samuel H. Royle: Methodology, Investigation, Writing-Original draft preparation **Lorcan Cropper:** Investigation **Jonathan S. Watson:** Methodology, Supervision, Writing-Reviewing and Editing **Silvio Sinibaldi:** Conceptualization, Methodology, Writing-Reviewing and Editing, Funding acquisition, Supervision, Project Administration **Michael Entwisle:** Methodology, Investigation **Mark A. Sephton:** Conceptualization, Methodology, Writing-Reviewing and Editing, Funding acquisition, Supervision, Project administration

Author Disclosure Statement

No competing financial interests exist.

Funding Information

This work was supported by Leverhulme Trust grant RPG-2018-012 and STFC/UK Space Agency grants ST/V002732/1 and STV006134/1.

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Tables and Figure Captions

Table 1 Planetary Protection Mission Categories and Associated Planetary Targets, adapted from Frick et al. (2014)

Mission Category	Mission Type	Planetary Target
I	Flyby, orbiter, Lander	Undifferentiated, metamorphosed asteroids; Io; others TBD
II	Flyby, orbiter, Lander	Venus; Earth's Moon; Comets; non-Category I Asteroids; Jupiter; Jovian Satellites (except Io and Europa); Saturn; Saturnian Satellites (except Titan and Enceladus); Uranus; Uranian Satellites; Neptune; Neptunian Satellites (except Triton); Kuiper-Belt Objects (<1/2 the size of Pluto); others TBD
II*	Flyby, orbiter, Lander	Icy satellites such as: Ganymede (Jupiter); Titan (Saturn); Triton, Pluto and Charon (Neptune); others TBD
III	Flyby, orbiter	Mars; Europa; Enceladus; others TBD
IV a-c (Mars specific)	Lander, probe	IVa: lander systems not investigating extant Martian life or special regions IVb: lander systems investigating extant Martian life IVc: missions investigating Martian special regions, even if they do not include life detection experiments
V (Unrestricted)	Earth-return unrestricted	Venus, Moon; others TBD
V (Restricted)	Earth-return restricted	Mars; Europa; Enceladus; others TBD

812 *Table 2 Condensed list of selected organic detection instruments from the ExoMars Rosalind Franklin rover's Pasteur*
813 *payload, adapted from Vago et al. (2017)*

Instrument	**Scientific reasoning**
Support subsystems	These essential devices are devoted to the acquisition and preparation of samples for detailed studies in the analytical laboratory.
Subsurface drill	Capable of obtaining samples from 0 to 2 m depth, where organic molecules can be well preserved from radiation damage.
Sample preparation and distribution system	Receives a sample from the drill system, produces particulate material preserving the organic and water fractions, and presents it to all analytical laboratory instruments.
Analytical laboratory	To perform a detailed, coordinated analysis of each collected sample. After sample crushing, the initial step is a visual and spectroscopic investigation. Thereafter follows a first search for organic molecules. In case interesting results are found, the instruments are able to perform more in-depth analyses.
VIS + IR imaging spectrometer	Will examine the crushed sample material to characterize structure and composition at grain-size level. These measurements will be used to help point the laser-based instruments (RLS and MOMA).
Raman laser spectrometer (RLS)	To identify mineral phases at grain scale in the crushed sample material, determine their composition, and establish the presence of carbon (inorganic/ organic).
Mars organic molecule analyzer (MOMA)	MOMA is the rover's largest instrument. Its goal is to conduct a broad-range, very-high sensitivity search for organic molecules in the collected sample.

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816 *Table 3 List of methods and their sensitivities suggested for testing contamination levels on the Mars 2020 rover, adapted*
817 *from Summons et al* (2014)

	Method	Sensitivity	Sampling/Form*	Comments
Vibrational Spectroscopy	DRIFT spectroscopy	<1 ng/cm^2 (from 100 cm^2)	Witness plate or solvent extract**	Provides broad range of chemical functional groups and/or identification. Applied to numerous spacecraft mission, detects common airborne contaminants (AC) and spacecraft molecular contamination. Large spacecraft database.
	FTIR-Grazing angle attenuated total reflection (GATR)	Sub-monolayer 0.5 ng/cm^2	Witness plate or solvent extract	Provides chemical functional groups and identification, detects common AC. Rapid
	FTIR-Microscopy	Sub-nanogram particles	Specialized witness plate	Requires specialized witness plates or particle sampling. Rapid.
	Raman-Microprobe	Sub-nanogram particles	Specialized witness plate	Requires specialized witness plates or particle sampling. Rapid.
Mass Spectrometry (MS)	GC-MS	<0.1 ng/cm^2 (from 100 cm^2)	Witness plate or solvent extract	Identification of components in a complex mixture. Non-volatile components not detected, detects common AC
	Pyrolysis GC-MS	<0.1 ng/cm^2 (from 100 cm^2)	Witness plate or solvent extract	Detects non-volatile components, can run in series with GC-MS.
	Direct Analysis in Real Time (DART)-MS	<0.001 ng/cm^2 (from 100 cm^2)	Witness plate or solvent extract	Identification of components in a complex mixture, molecular weight >1000 amu requires pyrolysis, detects common AC, very sensitive, rapid
	Liquid Chromatography (LC)-MS	<0.1 ng/cm^2 (from 100 cm^2)	Witness plate or solvent extract	Identification of components in a complex mixture, somewhat complex procedures and method development, particularly well-suited for some biological analyses.
	Laser-assisted Desorption (LD)-MS	<1 ng/cm^2	Witness plate or solvent extract	Identification of components in a complex mixture, suited for high molecular weight bio-analytes, complex procedures and method development, expensive instrumentation.
	Secondary-Ion MS (SIMS)	Sub-monolayer	Witness plate	Quantitation difficult, limited molecular identification for organics, very sensitive, detects common AC, complex, expensive instrumentation
Other	X-ray Photoelectron Spectroscopy (XPS)/Auger	Sub-monolayer	Witness plate	Sensitive, elemental information, limited molecular identification, detects common AC, complex, expensive instrumentation
	Total Organic Carbon (TOC) Instruments (pyrolysis and electrochemical)	~3 ng/cm^2	Witness plate	No chemical information, no identification, does not quantify incombustible components

818 **It should be noted that all methods require specialized hardware sampling and/or witness plates*
819 ***Solvent extracts may use a surface rinse or specialized solvent swabs of hardware surfaces*
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821 *Table 4. Potential contaminant source materials and testing performed on each*

Material Category	Commercial Name	Chemical Nature	SPME	Thermal Desorption
Adhesives	Loctite 3430 A&B	2-Part Epoxy adhesive	X	
Adhesive tapes, films and foils	Parker Chomerics Chofoil Tape/ CCJ-18-201-0100	Aluminised foil with conductive adhesive	X	X
	Dr Tuba Dacron adhesive tape	Dacron with adhesive	X	X
	5MIL Kapton tape x Y966	Polyimide/ Y966 acrylic adhesive	X	
Foams	Rohacell 110IG-F	PMI foam	X	X
Reinforced Plastics	Delrin	Polyacetal resin	X	
Lubricants	Molykote High-Vacuum silicone grease	Silicone oil with inorganic thickener	X	
Thermoplastic and plastic films	Filotex Kapton cable	Electrical cable with Kapton, PTFE, Cu, Ag	X	X
	DuPont 200HN Kapton film	Polyimide	X	X
	Teflon	PTFE	X	X

822 *Table 5. Supelco Recommended SPME Fiber Coatings and Thicknesses for Analysis of Different Analyte Types. Taken from*
823 *https://www.sigmaaldrich.com/technical-documents/articles/analytical/selecting-spme-fibers.html*

Analyte type	Recommended coating and thickness
Gases and low molecular weight compounds (MW 30-225)	75 µm/85 µm Carboxen/polydimethylsiloxane
Volatiles (MW 60-275)	100 µm polydimethylsiloxane
Volatiles, amines and nitro-aromatic compounds (MW 50-300)	65 µm polydimethylsiloxane/divinylbenzene
Polar semi-volatiles (MW 80-300)	85 µm polyacrylate
Non-polar high molecular weight compounds (MW 125-600)	7 µm polydimethylsiloxane
Non-polar semi-volatiles (MW 80-500)	30 µm polydimethylsiloxane
Alcohols and polar compounds (MW 40-275)	60 µm Carbowax (PEG)
Flavour compounds: volatiles and semi-volatiles, C3-C20 (MW 40-275)	50/30 µm divinylbenzene/Carboxen on polydimethylsiloxane on a StableFlex fiber
Trace compound analysis (MW 40-275)	50/30 µm divinylbenzene/Carboxen on polydimethylsiloxane on a 2 cm StableFlex fiber
Amines and polar compounds (HPLC use only)	60 µm polydimethylsiloxane/divinylbenzene

824 *Table 6 Summary of the organic moieties detected by the various analytical approaches in this study grouped by the*
825 *'molecular classes of concern for Mars and other astrobiological missions' of Mahaffy et al., (2003)*

Molecular class of concern	**Detected by the methods tested**		
	Molecular wipe extracts	**Thermal Desorption**	**SPME**
C, H aromatics		Benzene Methylated benzenes α-Methyl styrene	Methylated benzenes α-Methyl styrene Methylated napthalenes Bibenzyl 1-Isopropenylnapthalene Diisopropylnapthalene 1,1'-Biphenyl-4-methyl
Non-aromatic hydrocarbons	n-Alkanes	n-Alkenes branched alkanes	n-Alkanes Branched alkanes
Nitrogen containing compounds	4-Octyl-N-(4-octylphenyl)aniline Sialylated amines	2-Propenenitrile, 2-methyl Formamide, N-(1,1-dimethylethyl) Methylacrylamide N-t-butylmethacrylamide	Benzamide Benzenemethamine, N,N-dimethyl
Alcohols	Phenol,2,4-bis(1,1-dimethylethyl)	n-alcohols branched alcohols	Phenol Phenol,2,4-bis(1,1-dimethylethyl) n-Alcohols Branched alcohols Benzenemethanol
Carbonyls	Sialylated ketones	Acetophenone Non-aromatic ketones	Benzaldehyde Non-aromatic ketones
Carboxylic acids and their salts	Dibutyl phthalate	Carboxylic acids Carboxylic acid esters	Carboxylic acid esters Benzoic acid Dibutyl phthalate
S, N, O heterocyclic aromatics	Pyridine, 2,4-dimethyl	N.D.	N.D.
Sulfonic, phosphonic acids		N.D.	N.D.
Lipids and derivatives		n-Alkenes Branched alkanes Carboxylic acids Carboxylic acid esters	n-Alkanes Branched alkanes Carboxylic acid esters Benzoic acid Dibutyl phthalate
Sugars and derivatives		N.D.	N.D.
Proteins		N.D.	N.D.
Amino acids		N.D.	N.D.
Nucleic acids, nucleotides		N.D.	N.D.

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Figure 1 Total ion current (TIC) chromatograms for the water, acetonitrile and toluene extracts of representative ExoMars molecular wipe sample A. Key: a = 2,4-dimethyl pyridine; b = trifluoromethyl-bis-(trimethylsilyl)methyl ketone; c = bis-*N*-(trimethylsilyl)ethylamine; d = *N, N'*-methanetetraylbis(1,1,1-trimethyl)silanamine; e = 1,2-bis(trimethylsiloxy)ethane; f = decamethyltetrasiloxane; g = 2-4-bis(1,1-dimethylethyl)phenol, h = dibutyl phthalate, i = 4-octyl-*N*-(4-octylphenyl)aniline; numbers represent carbon number of n-alkanes. Scaled to the pyrene internal standard peak in the toluene fraction.

Figure 2 Total ion current (TIC) chromatograms for the water, acetonitrile and toluene extracts of ExoMars molecular wipe samples A, B, C, D, E, F, G, H, the procedural blank and the responses from an extracted unused molecular wipe. Key: a = 2,4-dimethyl pyridine; b = trifluoromethyl-bis-(trimethylsilyl)methyl ketone; c = bis-*N*-(trimethylsilyl)ethylamine; d = *N, N'*-methanetetraylbis(1,1,1-trimethyl)silanamine; e = 1,2-bis(trimethylsiloxy)ethane; f = decamethyltetrasiloxane; g = 2-4-bis(1,1-dimethylethyl)phenol, h = dibutyl phthalate, i = 4-octyl-*N*-(4-octylphenyl)aniline; numbers represent carbon number of *n*-alkanes. Scaled to the pyrene internal standard peak in the toluene fraction.

Figure 3 Selected total ion current (TIC) chromatograms for six potential contaminant source materials analysed by thermal desorption and for the procedural blank. Generic compound classes are labelled, see results text for detailed description of identified

848 compounds. IS label stands for the naphthalene-d8 internal standard. Insert shows 10x
849 vertical exaggeration of foam data to better present low intensity compounds detected.

850 **Figure 4** Selected total ion current (TIC) chromatograms for potential contaminant source
851 materials analysed by SPME and for the procedural blank.