

9 Appendices and Supporting Files

9.1 Appendix 1: Charter

Mars 2020 Contamination Study Panel

Introduction

The proposed Mars 2020 rover is a strategic mission sponsored by NASA's Planetary Science Division, through the Mars Exploration Program (MEP), all of which are part of the Science Mission Directorate (SMD). This mission is designed to advance the scientific priorities detailed in the National Research Council's Planetary Science Decadal Survey, entitled "Vision and Voyages for Planetary Science in the Decade 2013-2022." The baseline design of the Mars 2020 rover is largely based upon the Mars Science Laboratory architecture that successfully carried the Curiosity rover to the martian surface. Additional mission information can be found at <http://mars.jpl.nasa.gov/mars2020/>.

The Mars 2020 Science Definition Team report (http://mepag.nasa.gov/reports/MEP/Mars_2020_SDT_Report_Final.pdf) recommended that, among other *in-situ* science and technology objectives, the mission should acquire scientifically selected samples and place them into a cache that could potentially be returned to Earth by a future mission. These samples, should NASA choose to return them, would provide opportunities for performing a variety of Earth-based experiments including ones related to the search for signs of life.

In order to meet the requirement that the cache be returnable, the MEP and the Project must define hardware requirements and mission characteristics that would affect the quality of the samples and future measurement results. One such attribute is the ability to reduce terrestrial organic contamination to a point where its presence would not interfere with sensitive investigations of martian organic geochemistry—or with our ability to distinguish terrestrial from martian organic molecules. It is anticipated that these requirements will place constraints on spacecraft cleanliness (particularly organic cleanliness) and sampling/caching system capabilities, including potentially introducing a requirement for blanks, witness plates, and check material.

In order to further define these requirements, the MEP is convening a Contamination Study Panel. The summary statement of purpose of the Mars 2020 Contamination Study Panel is as follows:

Evaluate draft Mars 2020 mission sample contamination requirements. Assess implementation approaches with respect to returned sample science objectives to support the investigation of martian organic geochemistry in the returned samples and differentiation of indigenous molecules from terrestrial contamination.

Assumptions

1. Assume that one central purpose for returning samples to Earth is to make scientifically defensible, measurement-based interpretations of Mars-sourced organic molecules in the samples. This requires either avoiding or recognizing and distinguishing potential Earth-sourced organic contaminants.
2. For the purpose of this study, assume that Earth-sourced organic molecules are the only source of organic contamination on returned Mars samples that would interfere with our objectives. Contamination by Mars-sourced organics, for example from a previously collected sample, is not in the scope of this study.
3. Assume that eventual life-detection/biohazard protocols will be defined by a later panel and are not in the scope of this study.

4. The type and quantity of organic contaminants that may affect the samples during their time in a Sample Receiving Facility prior to analysis are assumed to be small relative to the contaminants delivered to the samples by the Mars 2020 mission—and, thus, can be ignored for the purpose of this study.

Statement of Task

1. Decide which is the most relevant use of terms such as “organic,” “reduced carbon,” and “hydrocarbon” when considering organic contamination and consider how these terms may relate to fragments of or whole terrestrial microbes. Define and systematize their use. The panel’s determination regarding usage may supersede the usage of the terms in this charter.
2. Mars 2020 will not be perfectly clean, and it will unavoidably deliver some Earth-sourced organic contaminants to the samples it collects and stores. Propose one or both of two kinds of limits for Earth-sourced organic contamination on the potential returned martian samples at the point in time when they are first analyzed for organic molecules: either a) total organic contamination or b) total unrecognized organic contamination (i.e., contamination above measured blank levels).
 - a. Based on current knowledge and capabilities, construct a list of measurements anticipated to be made on the returned samples in support of scientific objectives related to martian organic geochemistry, including the presence of past or present life. Generate a list of representative instruments capable of these measurements and their performance characteristics, including detection limits.
 - b. Determine the types and quantities of Earth-sourced organic contaminants of greatest concern, if they were on the samples, with regard to their possible adverse impact on the scientific objectives of potential future returned sample science. At minimum, specify a total organic carbon constraint.
 - c. Assess possible implementation approaches for recognizing and distinguishing Mars-sourced organic molecules in the samples from Earth-sourced organic molecular contamination. Approaches should include, but not be limited to:
 - i. Establishing a system of positive and/or negative control standards, in order to document the state of contamination at specific times/places. Consider separately control standards that would need to go to Mars on the Mars 2020 sampling rover vs. those that wouldn’t.
 - ii. Designing a set of blanks, witness plates, and other kinds of control samples that are taken before the rover is launched from Earth, then preserved for analysis when the Mars samples are potentially returned to Earth in the future.
 - iii. Designing a set of control standards that could be used in association with the organic molecule measurements within the Sample Receiving Facility.
3. Evaluate draft Mars 2020 mission sample organic contamination requirements and draft verification methodologies (to be provided by the Mars 2020 project).
 - a. Propose modifications to the draft Mars 2020 requirements and verification methodologies as needed.

Methods

The panel will have approximately 10 members, plus involvement of Program/Project/discipline support personnel. It is anticipated that the panel members would have expertise and knowledge spanning astrobiology, organic chemistry/geochemistry including theory and state-of-the-art lab practices, and contamination control and measurement.

The panel will meet by teleconference once or twice per week between March 1 and July 1, with 1-2 face-to-face meetings. The Mars Program Office at JPL will provide logistical support.

Deliverables

Draft findings/conclusions (PPT format) will be due May 8, and a final report (text format) July 1. The report should not contain any material that is proprietary or ITAR sensitive. Additional supporting documents may be prepared as needed.

The Study Group will produce a draft set of findings for review by the National Research Council Space Study Board (NRC SSB)-convened Meeting of Experts (MoE), also including participation from the European Science Foundation. The report will be made available to the NRC SSB by a date to be named later. The chair of the Study Group, or other community-appointed Study Group member, will present the findings of the report at an NRC SSB-convened MoE.

Michael Meyer, Lead Scientist, NASA Mars Exploration Program

Lisa May, Lead Program Executive, NASA Mars Exploration Program

9.2 Appendix 2: OCP Roster

9.2.1 Primary team

<i>Name</i>	<i>Professional Affiliation</i>	<i>Interest/Experience</i>
<i>Chair</i>		
Summons, Roger	MIT	organic geochemistry, exobiology
Sessions, Alex	Caltech	organic geochemistry, stable isotopes of organic molecules, instrument development
<i>Technical Members</i>		
Allwood, Abby	JPL/Caltech	astrobiology, ancient microbial biosignatures, fieldwork to laboratory
Barton, Hazel	Univ of Akron	geomicrobiology, ancient ecosystems in caves, organic geochemistry, PP; PHX and MSL
Blakkolb, Brian	JPL/Caltech	Contamination Control Engineer for Mars 2020
Canham, John	ATK	contamination control, measurement, and effects; analytical chemistry; verification and validation; PP; surface science, analytical methods development; SAM (MSL); MOMA (ExoMars)
Clark, Benton	SSI	geochemistry, sampling strategies for contamination issues, PP; Viking and MER, OSIRIS-REX sampling system
Dworkin, Jason	GSFC	origins of life; CC for OSIRIS-REX; organics in meteorites
Lin, Ying	JPL/Caltech	chemical engineering, organic chemistry, in-situ organic molecule detection, PP, contamination control; ExoMars
Mathies, Richard	UC Berkeley	physical chemistry, laser spectroscopy, biomolecular tracers, contextual experiments for contamination
Steele, Andrew	Carnegie Inst., Wash	microbiology, meteorites, organic geochemistry; SAM (MSL), PP, 2020SDT
<i>Facilitation</i>		
Beaty, Dave	JPL/Caltech	Chief Cat-Herder; Mars Chief Scientist at JPL
Milkovich, Sarah	JPL/Caltech	Documentarian and Assistant Cat-Herder; Mars 2020 science systems engineer

9.2.2 Ex officio

<i>Name</i>	<i>Professional Affiliation</i>	<i>Interest/Experience</i>
May, Lisa	NASA HQ	Mars Lead PE; MSR Program Exec
Meyer, Michael	NASA HQ	Mars Lead Scientist; MSR Prog. Scientist
Pugel, Betsy	NASA HQ	NASA HQ Planetary Protection
Ken Farley	Caltech/JPL	Proj. Scientist, Mars 2020
Matt Wallace	JPL/Caltech	Deputy PM, Mars 2020
Conley, Cassie	NASA HQ	NASA PPO

9.2.3 Expert Reviewers

<i>Name</i>	<i>Professional Affiliation</i>	<i>Interest/Experience</i>
Sephton, Mark	Imperial College, London	Organics in meteorites
Sherwood Lollar, Barbara	University of Toronto	President, Geochemical Society
Mahaffy, Paul	NASA GSFC	PI, MSL SAM Instrument
Calaway, Mike	JSC--Curation	JSC curation
Des Marais, Dave	NASA Ames	Led astrobiology roadmap
Farmer, Jack	Arizona State Univ.	recognizing past life in rocks
Oehler, Dorothy	JSC--Research	organics in Earth's geology

9.3 Appendix 3: Glossary of Definitions of Terms

Organic carbon – for the purposes of this report, any carbonaceous substance that is not inorganic. Typical definitions include the presence of covalent C-C and/or C-H bonds, average oxidation state < 4 , yielding CO_2 upon combustion, and others. All of these definitions comprise (different) subsets of the broader definition that we adopt here. Examples include formic acid, ethanol, glucose, hydrocarbons including methane, lipids, amino acids, purines, pyrimidines, urea, chlorofluorocarbons, Teflon, dimethylsilicone, etc. The term organic carbon does not imply formation by a biological process.

Inorganic carbon – the boundary between “organic” and “inorganic” carbon is ambiguous, and no single definition is broadly accepted. Here we use ‘inorganic’ to refer primarily to materials comprised of oxygen and carbon. Examples include gaseous CO and CO_2 , dissolved CO_3^{2-} and HCO_3^- , and carbonate minerals such as calcite and dolomite. Many definitions of inorganic carbon also include metal and metalloid carbides, cyanides, and elemental carbon, although for clarity we refer here to such materials specifically by name rather than as inorganic carbon.

Elemental carbon – materials that contain only the element carbon, such as graphite, diamond, fullerenes, and graphene.

Macromolecular organic carbon – complex, high molecular weight, organic carbon compounds which are formed by polymerization or cross-linking of smaller subunits. Organic macromolecules include ordered biopolymers such as proteins, DNA, polysaccharides, and lignin; synthetic polymers including polyester, polytetrafluoroethylene (Teflon), and silicone; and irregular geopolymers such as humic acids, asphaltenes, and kerogen.

Organic particulates – macromolecular organic material that can be captured by sieving filters (for example $> 1 \mu\text{m}$ particulates).

Biologically relevant functional groups – atoms other than C or H in an organic molecule that impart functionality to the compound. Examples include: alcohols, carboxylic acids, amines, amides, esters, and phosphate esters. Carbon-carbon double bonds are typically included in this definition.

Amino acid – organic carbon compounds that contain both an amine and carboxylic acid functional group. The linking of amino acids via a peptide bond $[(\text{C}=\text{O})-(\text{NH})]$, allows the formation of peptides and proteins in terrestrial biological systems. Terrestrial organisms use only 22 standard amino acids of specific chirality, although many more such compounds exist. Examples include alanine, cysteine, glycine, etc.

Carbohydrate – organic carbon compounds with the generic formula $(\text{CH}_2\text{O})_n$, containing multiple hydroxyl and carboxyl functions. Individual monomers (a.k.a. monosaccharides, sugars) can be polymerized via acetal and hemiacetal bonds to form polysaccharides (carbohydrate polymers). Examples include glucose, sucrose, cellulose, and starch.

Lipid – lipids, in comparison to ‘hydrocarbons,’ are generally inferred to be of biologic origin. They commonly comprise long, hydrophobic hydrocarbon backbones with a polar end group and few functional groups. They can have linear chains (e.g., fatty acids, leaf waxes), branched chains (phytol, methyl-branched fatty acids), cyclic moieties (e.g., alkyl benzenes) or polycyclic moieties (e.g., sterols, lignin).

Hydrocarbon – formally, any molecule containing only the elements H and C. However, usage has expanded to include any hydrophobic molecule originating in rocks or fossil fuels regardless of composition (e.g., “this rock contains $5 \mu\text{g/g}$ extractable hydrocarbons”). For this report, we adopt the latter meaning, and use it in conjunction with ‘lipids’ to distinguish between biotic and abiotic sources.

Chirality – a characteristic stemming from the 3-dimensional nature of organic carbon compounds. When a carbon atom is surrounded by four different moieties, it can exist as either of two non-superimposable mirror images (enantiomers). Enantiomers can rotate plane-polarised light in opposite directions and are so designated as "right-" or "left-handed" based on this property.

Homochirality – a collection of structurally similar molecules that are chiral in the same sense i.e. all left-handed (amino acids in terrestrial life) or all right-handed (sugars in terrestrial life). Homochirality is considered a characteristic of terrestrial biological systems.

Chain-length preference in lipids – the synthesis of lipids requires the addition of carbon atoms to a precursor to increase carbon-chain length. In biological systems, these carbons come from two-C donors (such as acetate) or five-C donors (isoprenoids), forming long-chain carbon skeletons with specific chain lengths. Compounds formed from acetate show strong preferences for even or odd numbers of carbon atoms (e.g. C12, C14, C16, C18, etc in fatty acids, or C27, C29, C31, C33, etc in hydrocarbons).

Pyrolysis products – organic compounds generated when a sample is heated, in the absence of oxygen, to the point of thermal decomposition.

Volatile and semi-volatile organic compounds – molecules with substantial vapor pressure either at room temperature (volatile) or at some elevated temperature (semivolatile). Molecules that thermally decompose before entering the gas phase are termed involatile. There is little agreement on precise temperature cutoffs between these categories, hence we adopt the practical definitions above.

Isotopes – atoms of the same element having a different number of neutrons, and hence mass. They are chemically identical and form the same compounds, phases, etc, but the mass difference causes them to react at subtly different rates. Radioactive versus stable isotopes (^{14}C vs ^{13}C , ^3H vs ^2H) are frequently distinguished, and the relative abundance of certain isotopes (in organic matter, primarily ^2H , ^{13}C , ^{15}N , ^{18}O , and ^{34}S) are frequently used to distinguish between materials of terrestrial versus extraterrestrial origin.

Isotopic fractionation – any chemical, physical or biological process that alters the relative abundance of isotopes in a material. An example is the depletion of ^2H and ^{18}O in water vapor evaporating from a liquid. Many natural processes have characteristic isotopic fractionations, e.g. fixation of CO_2 in the photosynthesis. The loss of radioactive isotopes (e.g., ^{14}C or ^3H) due to decay is not typically regarded as fractionation as it occurs regardless of physical or chemical processes.

CONTAMINATION TERMINOLOGY

Organic contamination – Any substance that significantly interferes with our ability to detect the presence of martian organic compounds or prevents our confidently determining that an organic compound is of martian and not terrestrial origin.

Constant Contamination – background levels, such as in a blank, which are well characterized, constant and can be readily addressed in the evaluation of the compositional analysis. These are often mitigated or controlled by design and selection of materials and processes.

Random or variable contamination – spacecraft are huge systems requiring long periods of building. As a result, there is the potential for contamination to be introduced from entirely unpredicted events (*Black swan* events). Such variable contamination can be identified, limited or controlled by continuous monitoring of processes, systems and witness plates.

Adventitious carbon – when surfaces are cleaned to a high level, the removal of surface oxidation layers, etc. results in the formation of a charged surface. Adventitious carbon comprises the charged carbon molecules within the atmosphere that are attracted to and bind to cleaned surfaces, therefore the chemistry of this carbon reflects the conditions of the environment in which it forms.

Contamination control – limiting the introduction of contaminants through processes and design.

Contamination knowledge – the use of witness plates, controls and process monitoring to quantitatively and qualitatively characterize and understand the types of contamination such that interpretation of acquired data is possible and the science objectives can be met.

Contaminants of concern – the organic molecules identified by our scientific understanding of the environment, bioburden and process design that provide the best indication of contamination that could interfere with the anticipated sample analyses and defined scientific objectives.

Surface contact transfer – the transfer of contaminants from a sampling surface to the sample. While the efficiency of this transfer is variable (depending on the types and nature of the contaminants and sample matrix), in a worst-case scenario it is assumed to be 100%.

Blank – a measurement designed to establish the amount of analyte due to sources other than the sample. Blanks can have many different contributing components, which may or may not be distinguished, e.g. sample handling and storage blank, processing blank, reagent and solvent blank, instrument blank, etc. Can also be referred to as a **negative control standard**.

Background – signals detected by the instrument that are due to sources other than the targeted analyte, for example fluorescence or adsorption of sample matrix in optical techniques, contaminants present in the vacuum system of mass spectrometers, etc. The term is often, though not always, used to denote signals that interfere with or degrade measurement capabilities.

Witness plate – provides a background measurement alongside sample measurement to document where, when and what contaminants are introduced during the mission. Witness plates are generally comprised of more than one type of material, each having different adherence properties (such as sapphire and silicone wafers), and can include clean plates, organic check material, or stored materials.

Pristine – in the context of sample collection, pristine can be considered as the level to which background contamination can be removed to within the cost and technical limitations of the time.

Noise floor – the lowest, reasonably achievable limit of contamination.

ANALYTICAL TERMINOLOGY

Analyte - the element, isotope, compound, substance, etc. of interest in an analysis.

Sample matrix – the sample material that surrounds and contains the analytes of interest, e.g. sediment, rock, water, etc. The sample matrix affects the manner in which sample is prepared and introduced into a measurement technique (i.e. liquid vs solid-phase extraction), as well as potentially affecting the analytical measurement itself.

Detection limit – is by convention defined as the quantity of a material yielding a detected signal at some specified level above the blank or noise in the measurement (signal/noise ratio). This may be regarded as the minimum level at which there is sufficient certainty in the measurement to state that the analyte is unambiguously detected; and as the maximum level to state that the analyte is not there. Different signal/noise ratios are adopted for different applications, but typically vary between 3 and 20.

Sensitivity – the amount of analyte required to provide a unit of measurable signal, i.e. picomoles/mV. This term is often confounded with detection limit.

Resolution – the ability to separate or distinguish adjacent signals or compounds. The term has various meanings in different analytical techniques, i.e. in chromatography refers to the ability to separate distinct molecular structures, whereas in spectroscopy refers to the ability to distinguish different wavelengths.

Quantitative analysis – an analysis carried out to measure the amount (or concentration) of analyte in a sample. This is typically achieved by comparing the instrument response from the sample to a calibration curve generated from authentic laboratory standards, although other approaches are possible. Note that the term does not imply that a measurement is free from error or uncertainty.

Qualitative analysis – an analysis carried out to determine the identity, structure, functionality, or other properties of the analyte. Because generating calibrating curves for quantitative analysis typically requires knowing what analytes are targeted, qualitative analysis typically precedes quantitative analysis in the study of unknown materials. Estimates of relative abundance from (typically uncalibrated) qualitative analysis are sometimes called ‘semi-quantitative,’ although this term is ambiguous.

ANALYTICAL TECHNIQUES

Chromatography – a family of techniques, that relies on different rates of migration of analytes in a fluid phase travelling in a solid or liquid phase, for physically separating analytes in a mixture. The separation relies on differing physical and/or chemical properties of the analyte, such as vapor pressure, solubility, hydrophobicity, ionic strength, size, shape etc. Techniques for organic separations are often distinguished based on the mobile phase used for the separation, i.e. gas chromatography (analytes in a gas phase) vs liquid chromatography (analytes in a liquid phase).

Capillary electrophoresis – a family of analytical separation methods performed in a narrow bore (capillary) where the analytes are separated by migration through an electrolyte solution under the influence of high electric fields.

Magnetic resonance – a family of techniques (generically “NMR”) that detect the absorption and reemission of electromagnetic energy by atoms in a strong magnetic field, due to spin-flipping of nuclei. The technique is non-destructive, and is widely used for structural elucidation of unknown organic compounds.

Mass spectrometry - a family of analytical techniques based upon the ionization of molecules, followed by manipulation, separation, and detection of those ions in magnetic and/or electrical fields. The technique typically yields the mass/charge ratio of each ion, which is useful in determining identity and structure. A variety of different ionization methods (e.g. electron-impact, chemical ionization, photoionization, electrospray, MALDI, secondary-ion impact, etc) and mass analyzer designs (sector-field, quadrupole, ion trap, time-of-flight, FT-ICR, etc) can be combined. Hyphenated techniques with chromatography (e.g., GC-MS and LC-MS) are very common. Techniques using multiple stages of ion manipulation (i.e., MS-MS or

MSⁿ) are sometimes used to increase specificity of analysis, or to help elucidate structure. Mass spectrometry is considered a ‘destructive’ analytical technique.

Optical spectroscopy – a family of analytical techniques that work by observing the interaction of photons (light) with the sample. Techniques can include measuring light reflection or scattering, absorption, fluorescence (absorption and re-emission at a longer wavelength), and Raman scattering (scattering with a minor energy loss arising from stimulation of a vibrational mode). Observations at different wavelengths target different properties of molecules, with x-ray wavelengths targeting atomic (elemental) composition, UV and visible light targeting molecular electronic transitions, and infrared wavelengths targeting molecular rotations and vibrations. Techniques can sometimes provide spatially resolved analysis, as in Raman microscopy. Optical techniques are typically non-destructive.

Mass spectroscopy – a mass/charge versus relative intensity plot used in chemical analysis. Typically, mass spectra are formed using a mass spectrometer when an organic carbon compound is ionized, decomposes according to the laws of chemistry. The fragments are separated according to their mass/charge, counted and viewed as a relative abundance plot. Mass spectra, obtained under identical conditions can be a rapid, reliable and sensitive means of identifying unambiguously identifying organic carbon compounds.

Total carbon/total organic carbon analysis – related techniques for the analysis of bulk materials that aim to determine total levels of (organic) carbon via combustion of analytes to CO₂, with quantitation of the evolved CO₂. Because the analysis is operationally defined (i.e., anything that yields CO₂ at a given temperature), techniques that differ in temperature, time, PO₂, etc can include or exclude different materials. For example, graphite would be detected in a total carbon analysis at 1000°C but not at 500°C.

Laser desorption - the process by which incident laser radiation results in the separation of a molecule from a surface or matrix, allowing sampling of molecules with fewer matrix effects. This process may result in ionization of the molecules.

Secondary ionization mass spectrometry (SIMS) – a family of techniques in which samples are sputtered and ionized by the impact of a beam of primary ions, typically followed by mass spectrometric analysis. They are particularly useful in providing spatially-resolved mass spectrometric analysis (but see also laser desorption). High-energy primary ion beams (typically Cs⁺ or O⁻) typically achieve more aggressive sample sputtering (can be used to ablate surface layers) and yield monoatomic ions suitable for elemental and/or isotopic analysis, whereas low-energy ion beams typically sample only surface layers and yield molecular ions suitable for identification and structural analysis. The former technique is commonly known simply as SIMS (or NanoSIMS, depending on the spatial resolution of the primary ion beam), whereas the latter is often known as TOF-SIMS (although the combination of TOF mass spectrometry with low-energy primary ion beam is not required, it is commonly employed). Note that the acronym SIMS is also commonly used for “selection ion mass spectrometry” which is a different technique.

Isotope-ratio mass spectrometry (IRMS) – a subcategory of mass spectrometry in which the specific intent is to provide highly precise measurements of isotopic abundance, usually at the expense of losing structural information because analytes must be converted to a common molecular form (i.e., H₂, CO₂, N₂, SO₂, etc). For organic molecules, such techniques generally employ electron-impact ionization with sector-field spectrometers and multiple parallel detectors. The technique is commonly distinguished from SIMS, even though both provide similar types of information.

Isotope-ratio optical spectroscopy (IROS) – a subcategory of optical spectroscopy in which the specific intent is to provide highly precise measurements of isotope abundance. Specific techniques typically employ either very-long pathlength absorption cells (integrated cavity-output spectroscopy, ICOS) or cavity-ringdown spectroscopy (CRDS), and both require that analytes be converted to a common molecular form

(i.e., H₂O, CO₂, N₂, etc). Although the optical detection is nondestructive, conversion to common analyte form is destructive.

X-ray Photoelectron Spectroscopy (XPS) – a technique where a surface is irradiated with soft x-rays, leading to ionization of the surface atoms. The subsequent release of emitted photoelectrons allows a spectrum to be obtained of the distribution and kinetic energy of the surface atoms to be determine, the intensity of specific peaks allows a quantitative analysis of each analyzed atom.

PROCESSING TECHNIQUES

Combustion – heating a material in the presence of molecular oxygen, or a source of oxygen, to generate carbon dioxide.

Destructive sampling – sampling or measurement processes, which result in the destruction of the sample.

Solvent Extraction – use of a liquid phase to selectively dissolve (solubilize) and separate particular compound classes from a complex matrix. Solvents of different polarities can be used to differentially extract different compound classes.

Pyrolysis – heating a material in the absence of oxygen to induce thermal decomposition. Typically, this approach relies on a defined temperature regime. Pyrolysis at temperatures up to ~ 600°C is used to convert a solid macromolecular material to smaller, volatile products that were amenable to separation by gas chromatography and identification by mass spectrometric analysis. The composition of these pyrolysis products is used to infer the nature of the macromolecular precursor. Pyrolysis at temperatures exceeding 1000°C typically converts the precursor to its elements (e.g. C, H₂) or small molecules such as CO.

Thin section – a thin slice of sample prepared either for the evaluation of internal composition or to allow access to a technique requiring a thinner cross section of material.

9.3.1 Glossary of Acronyms

	Adventitious Carbon
AC	
ALHT	Apollo Lunar Hand Tools
ALSRC	Apollo Lunar Sample Return Container
ATLO	Assembly, Test, and Launch Operations
ATP	Adenosine triphosphate, the energy storage molecule of a cell
CAPTEM	Curation and Analysis Planning Team for Extraterrestrial Materials, a committee that is part of the NASA advisory structure
DART/MS	Direct Analysis in Real Time - Mass Spectrometry
DNA	Deoxyribonucleic Acid
DRIFT	Diffuse Reflectance Infrared Fourier Transform spectroscopy
EDL	Entry, Descent, and Landing
EDX or EDAX	Energy-Dispersive spectroscopy
FTIR	Fourier Transform Infrared spectroscopy
GCMS	Gas Chromatography - Mass Spectrometry
GSFC	NASA Goddard Space-Flight Center
IR	Infrared
ISO	International Organization for Standardization
ITAR	International Traffic in Arms Regulations
IUPAC	International Union of Pure and Applied Chemistry
JPL	NASA Jet Propulsion Laboratory
LCMS	Liquid Chromatography - Mass Spectrometry
LM	Lunar Module
LOD	Limit Of Detection
LRL	Lunar Receiving Laboratory
Mars 2020	Mars 2020 Mission
M-Mars 2020	Mars 2020 Science Definition Team
SDT	
MEP	Mars Exploration Program
MEPAG	Mars Exploration Program Analysis Group
MoE	Meeting of Experts, a process used by the U.S. National Research Council
MOMA	Mars Organic Molecule Analyzer (an instrument on ExoMars 2018)
MSL	Mars Science Laboratory
MSR	Mars Sample Return
MSR SSG (II or 2)	Mars Sample Return Science Steering Group II
NASA	National Aeronautics and Space Administration
NRC	National Research Council
NRC SSB	National Research Council Space Study Board
NVR	Non-Volatile Residue
OCM	Organic Check Material
OCP	Organic Contamination study Panel
OCSSG	Organic Contamination Science Steering Group
OSIRIS-REx	Origins Spectral Interpretation Resource Identification Security -- Regolith Explorer
PAH	Polycyclic Aromatic Hydrocarbons
PCR	Polymerase Chain Reaction
PLSS	Primary Life Support System
PP	Planetary Protection

QCM	Quartz Crystal Microbalance
RAD	Radiation Assessment Detector (instrument on MSL)
RGAs	Residual Gas Analyzer
SA/SPAH	Sample Acquisition / Sample Processing And Handling (instrument on MSL)
SAM	Sample Analysis at Mars (an instrument on MSL)
SEM	Scanning Electron Microscopy
SIMS	Secondary Ion Mass Spectrometry
SMD	Science Mission Directorate
S/N	Signal-to-Noise ratio
SRC	Sample Return Capsule
SRF	Sample Receiving Facility
TAGSAM	Touch-And-Go Sample Acquisition Mechanism (instrument on OSIRIS-REx)
TEGA	Thermal and Evolved Gas Analyzer (instrument on Phoenix)
TOC	Total Organic Carbon
TOF-SIMS	Time-of-Flight Secondary Ion Mass Spectrometry
UV	Ultraviolet
WSTF	White Sands Test Facility
WP	Witness Plate
XPS	X-ray Photoelectron Spectroscopy

9.4 Appendix 4: Summary of Instruments and Measurements Available as of 2014 for Investigating Organic Molecules in Rock and Soil Samples

Key to Measurement Goals related to Martian Organic Geochemistry and Planetary Protection

1 Determine whether the samples contain organic compounds

1A Use non-destructive methods to search for the presence of organic compounds

1B Quantify the bulk organic content of the samples

2 Determine the origin of any organic compounds in the samples

2A Determine the molecular composition of organics

2B Determine the isotopic composition of organics

2C Study spatial variations in abundance and characteristics of organic molecules in the sample matrix, relative to mineralogical, chemical, and textural features

2D Investigate the chirality of amino acids

2E Examine long chain hydrocarbons for chain length effects

2F Quantify the degree of contamination by viable or recently deceased terrestrial microbes and their residues

SURVEY ANALYTICAL METHODS TO BE USED in LIGHT YELLOW

TARGETED ANALYTICAL METHODS TO BE USED in LIGHT BLUE

Category 1: Non-Destructive, Sample Surface-Based Technique

Analytical Method	Objectives Addressed	Sample Requirements and Degradation ¹	Performance Characteristics and Detection Limits ¹	Method Notes (Dependencies, Limitations, Assumptions, etc.)	References ²
Deep UV Raman/Fluorescence Spectroscopy	1A, 2C	Non-destructive. No surface preparation required.	Raman: Aromatics <10-4 w/w (<100 ppm) Aliphatics <10-4 w/w (<100 ppm) 50 um/spot at 1 to 10s per spot Fluorescence: Aromatics <10-6 w/w (<ppm) Single cell sensitivity (~2 pg carbon) [6] 50 um/spot at 1s per spot	Performance can be enhanced with longer integration times. Sensitivities depend on organic species and are matrix dependent. Surface roughness can be handled based on optical system with hit against sensitivities or integration times. Quantification is difficult	[1] Beegle, et al., Lunar and Planetary Institute Science Conference Abstracts 45, 2835 [2] Ghosh, et al., Applied Spectroscopy 66 (9): 1013-21 [3] Tuschel, David D, Aleksandr V Mikhonin, Brian E Lomoff, and Sanford A Asher. 2010. "Deep Ultraviolet Resonance Raman Excitation Enables Explosives Detection." Applied Spectroscopy 64 (4), 425-32. [4] Bharita, et al., International Society for Optics and Photonics: 83581A-83581A-9 [5] Johnson, et al., Astrobiology 11 (2): 151-56 [6] Bharita et al., Applied and Environmental Microbiology, 2010, 78(21), p. 7231-7237
Confocal Raman Spectroscopy at up to 360nm micron spatial resolution	1A, 2C	Non-destructive. Benefits from thin section, polished surface prep. Or can be fresh fracture surface with contour following confocal optics.	Lower limit from ~0.1 to 1 wt. % per spot analysis (30s)[1] with absolute detection limit correlated to number of analyzed spots. <50 ppm graphitic carbon [1] Single cell detection sensitivity. [2]	Detection limits strongly dependent on laser wavelength, target species. 532 nm excitation provides non-quantitative detection of hematite, beta-carotene. Raman spectra are subject to organic and mineral background fluorescence, which can be mitigated by time-gating. Careful consideration for laser wavelength and power to avoid sample damage. Quantification is difficult	[1] Wang, et al. Journal of Geophysical Research, 108[E1], 5005 [2] Ref TBD
FT-IR Spectroscopy	1A, 2C	Non-destructive. Benefits from thin section and polished surface prep, but can be used on unprepared surfaces. Ideally KBR pellets are made of samples.	Lower limit ~5 ppm for specific targets 10 um/spot >200 min per spot [1]	Not sensitive to graphitic carbon. Samples are ideally crushed and made into KBR windows [2] Quantification is difficult	[1] Ref TBD [2] General approach for FTIR in literature. [2a] Bhaskar, Nature and Science, 2009,7(5), 45-51 (Dergoon H5 Chondrite) [2b] Matrajt, et al., Astronomy & Astrophysics, 416(3), 2003, 983-990 (Tagish Lake Meteorite) [3] Anderson, et al., Review of Scientific Instruments, 76, 034101 (2005)
IR Reflectance Spectroscopy	1A, 2C	Non-destructive.	Lower limit typically ~0.5-1 wt. % per spot analysis, with absolute detection limit correlated to number of analyzed spots.	Sensitive to only specific organic species. Ideal for rapid mineral context. Quantification is difficult	[1] Not used actively for organics detection

Category 2: Slightly Destructive to Sample Surface

Analytical Method	Objectives Addressed	Sample Requirements and Degradation	Performance Characteristics and Detection Limits	Method Notes (Dependencies, Limitations, Assumptions, etc.)	References
Laser desorption-MS	1A, 2A, 2C	Vacuum exposure, polished thin section or fresh fracture surface, laser beam damage	Semi-quantitative, wide range of sensitivities including sub-fmol.	Specific to PAH or other large conjugated systems. No chromatography, so no distinction of isomers or enantiomers.	
Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS)	1A, 2A, 2B, 2C	Vacuum exposure, polished thin section or fresh fracture surface, ionization damage	Non quantitative, low ppb sensitivity. Very sensitive to surface contamination. Maps organic and inorganic species. For isotopes: ppt sensitivity, 50nm spatial resolution 1 - 5 per mil isotopic resolution dependent on instrument and isotope.	Provides context of isotopes: C, N, S, D/H	
LAL Assay	2F	Wipe, swap, extraction. Sample exposed to water/solvent, wipe/swab debris.		Gram-negative microbes only. Insensitive to gram-positive microbes.	
ATP luminometry	2F	Wipe, swap, extraction. Sample exposed to water/solvent, wipe/swab debris.	Proportional to microbial metabolic activity	Insensitive to spores	
Microbial plating assay	2F	Wipe, swap, extraction. Sample exposed to water/solvent, wipe/swab debris.	~0.01% maximum sensitivity to abundance of microbial flora		

SURVEY ANALYTICAL METHODS TO BE USED in LIGHT YELLOW

TARGETED ANALYTICAL METHODS TO BE USED in LIGHT BLUE

Category 1: Non-Destructive, Sample Surface-Based Technique

Analytical Method	Objectives Addressed	Sample Requirements and Degradation ¹	Performance Characteristics and Detection Limits ¹	Method Notes (Dependencies, Limitations, Assumptions, etc.)	References ²
Deep UV Raman/Fluorescence Spectroscopy	1A, 2C	Non-destructive. No surface preparation required.	Raman: Aromatics <10-4 w/w (<100 ppm) Aliphatics <10-4 w/w (<100 ppm) 50 um/spot at 1 to 10s per spot Fluorescence: Aromatics <10-6 w/w (<ppm) Single cell sensitivity (~2 pg carbon) [6] 50 um/spot at 1s per spot	Performance can be enhanced with longer integration times. Sensitivities depend on organic species and are matrix dependent. Surface roughness can be handled based on optical system with hit against sensitivities or integration times. Quantification is difficult	[1] Beegle, et al., Lunar and Planetary Institute Science Conference Abstracts 45, 2835 [2] Ghosh, et al. Applied Spectroscopy 66 (9): 1013-21 [3] Tuschel, David D, Aleksandr V Mikhonin, Brian E Lomoff, and Sanford A Asher. 2010. "Deep Ultraviolet Resonance Raman Excitation Enables Explosives Detection." Applied Spectroscopy 64 (4), 425-32. [4] Bharita, et al., International Society for Optics and Photonics: 83581A-83581A-9 [5] Johnson, et al. Astrobiology 11 (2): 151-56 [6] Bharita et al., Applied and Environmental Microbiology, 2010, 78(21), p. 7231-7237
Confocal Raman Spectroscopy at up to 360nm micron spatial resolution	1A, 2C	Non-destructive. Benefits from thin section, polished surface prep. Or can be fresh fracture surface with contour following confocal optics.	Lower limit from ~0.1 to 1 wt. % per spot analysis (30s)[1] with absolute detection limit correlated to number of analyzed spots. <50 ppm graphitic carbon [1] Single cell detection sensitivity. [2]	Detection limits strongly dependent on laser wavelength, target species. 532 nm excitation provides non-quantitative detection of hematite, beta-carotene. Raman spectra are subject to organic and mineral background fluorescence, which can be mitigated by time-gating. Careful consideration for laser wavelength and power to avoid sample damage. Quantification is difficult	[1] Wang, et al. Journal of Geophysical Research, 108[E1], 5005 [2] Ref TBD
FT-IR Spectroscopy	1A, 2C	Non-destructive. Benefits from thin section and polished surface prep, but can be used on unprepared surfaces. Ideally KBR pellets are made of samples.	Lower limit ~5 ppm for specific targets 10 um/spot >200 min per spot [1]	Not sensitive to graphitic carbon. Samples are ideally crushed and made into KBR windows [2] Quantification is difficult	[1] Ref TBD [2] General approach for FTIR in literature. [2a] Bhaskar, Nature and Science, 2009,7(5), 45-51 (Dergoon H5 Chondrite) [2b] Matrajt, et al., Astronomy & Astrophysics, 416(3), 2003, 983-990 (Tagish Lake Meteorite) [3] Anderson, et al., Review of Scientific Instruments, 76, 034101 (2005)
IR Reflectance Spectroscopy	1A, 2C	Non-destructive.	Lower limit typically ~0.5-1 wt. % per spot analysis, with absolute detection limit correlated to number of analyzed spots.	Sensitive to only specific organic species. Ideal for rapid mineral context. Quantification is difficult	[1] Not used actively for organics detection

Category 2: Slightly Destructive to Sample Surface

Analytical Method	Objectives Addressed	Sample Requirements and Degradation	Performance Characteristics and Detection Limits	Method Notes (Dependencies, Limitations, Assumptions, etc.)	References
Laser desorption-MS	1A, 2A, 2C	Vacuum exposure, polished thin section or fresh fracture surface, laser beam damage	Semi-quantitative, wide range of sensitivities including sub-fmol.	Specific to PAH or other large conjugated systems. No chromatography, so no distinction of isomers or enantiomers.	
Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS)	1A, 2A, 2B, 2C	Vacuum exposure, polished thin section or fresh fracture surface, ionization damage	Non quantitative, low ppb sensitivity. Very sensitive to surface contamination. Maps organic and inorganic species. For isotopes: ppt sensitivity, 50nm spatial resolution 1 - 5 per mil isotopic resolution dependent on instrument and isotope.	Provides context of isotopes: C, N, S, D/H	
LAL Assay	2F	Wipe, swap, extraction. Sample exposed to water/solvent, wipe/swab debris.		Gram-negative microbes only. Insensitive to gram-positive microbes.	
ATP luminometry	2F	Wipe, swap, extraction. Sample exposed to water/solvent, wipe/swab debris.	Proportional to microbial metabolic activity	Insensitive to spores	
Microbial plating assay	2F	Wipe, swap, extraction. Sample exposed to water/solvent, wipe/swab debris.	~0.01% maximum sensitivity to abundance of microbial flora		

Category 3: Destructive of Whole Sample					
Analytical Method	Objectives Addressed	Sample Requirements and Degradation	Performance Characteristics and Detection Limits	Method Notes (Dependencies, Limitations, Assumptions, etc.)	References
Total inorganic carbon and total organic carbon	1B, weight % abundance of organic carbon	Both non acid and acid digestion used to separate inorganic from organic	~1-10 ppb in 1 ml of gas or about 1E-11 to 1E-12 g of CO ₂ .	Splitting to NPD detectors, nitrogen may be accessible.	
Total inorganic carbon and total organic carbon	1B, weight % abundance of organic carbon	Both non acid and acid digestion used to separate inorganic from organic	~1-10 ppb in 1 ml of gas or about 1E-11 to 1E-12 g of CO ₂ (??)	Probably similar detection limit to above (methanizer w/ flame ionization), depending upon MS capability. Back calculating the sensitivity dependent upon the background, detector noise, ... kind of tough to say in general. Evolved compounds other than CO ₂ can be detected. Nitrogen can be done at the same time. Need nitrogen perhaps even DIH.	
Microfluidic Capillary Electrophoresis	2A, 2D, 2F		1 to 10 ppb following extraction, derivatization	Process blanks?	
GC/MS FAME using cyanopropyl stationary phase	2A, 2E, 2F		Detection down to below ~ 1 ng per compound	Detection limits are potentially lower if GC does not have significant non-specific absorption, or other issues. Lower detection limits possible by radio GC or LC using radiolabeled derivatizing agent.	
GC/MS using high temperature GC column, and ammonia chemical ionization				Probably similar detection limit to above (methanizer w/ flame ionization), depending upon MS capability. Back calculating the sensitivity dependent upon the background, detector noise, ... kind of tough to say in general. Evolved compounds other than CO ₂	
Tunable Laser Spectroscopy	2B	Destructive via pyrolysis. Typical amount of sample required per analysis: x mg			
Pyrolysis-MS, Pyrolysis-GC-MS		Destructive via pyrolysis. Typical amount of sample required per analysis: x mg		Does not indicate compounds present, only their fragments.	
Liquid extraction and derivatization followed by GC-MS	2A, 2D, 2E, 2F	Extraction, destructive	Detection limits are compound-specific, but as low as ~ 1 pmol, more like 100pmol for many hydrocarbons. Nominal mass accuracy in typical system.	Can use library mass spectra to suggest compound class. Qq-QMS can target specific compounds, ultrahigh resolution MS can deduce molecular formulae. Can target chirality (e.g. amino acids, amines, etc). Requires authentic standard for definitive identification.	
LC-MS	2A, 2D, 2E, 2F	Sample crushing followed by destructive solvent extraction, possibly hydrolysis, desalting, and more	Detection limits are compound-specific, but typically ~ 1 fmol 5 ppm to sub ppm mass accuracy possible	Qq-QMS can target specific compounds, ultrahigh resolution MS (e.g. ToF-MS, FT-MS) can deduce molecular formulae. Different ionization modes (ESI, APci, APPI) can target different functionalities. Targets M+1 parent ion. Can target chirality (e.g. amino acids). nano-LC can improve sensitivity 10-100 fold. Can couple mass and optical (fluorescence, absorbance) detections. Requires authentic standard for definitive identification. Cannot use library spectra.	
high resolution MS (infusion or DART)		Sample crushing followed by destructive solvent extraction, possibly hydrolysis. Minimal other workup required	Semi-quantitative, wide range of sensitivities including sub-fmol, sub ppm mass accuracy possible	Ultrahigh resolution MS (e.g. ToF-MS, FT-MS) can deduce molecular formulae. Different ionization modes (ESI, APci, APPI) can target different functionalities. Targets M+1 parent ion. DART required minimal preparation and has ~ 1 mm spot size. No chromatography, so no distinction of isomers or enantiomers.	
liquid ICPMS		destructive; sample oxidized to sulfate	5 nmol dissolved sulfate at 0.15% precision; Paris G., Sessions A. L., Subhas A. V. and Adkins J. F. (2013) MC-ICP-MS measurement of $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ in small amounts of dissolved sulfate. Chemical Geology 345, 1–12.	targets any sulfur in solution as sulfate; can be used for organic compound-class analysis	
combustion EA-IRMS		destructive	25 nmol N, 41 nmol C, both at $\pm 1.0\%$ precision; Polissar P. J., Fulton J. M., Junium C. K., Turich C. C. and Freeman K. H. (2009) Measurement of ^{13}C and ^{15}N Isotopic Composition on Nanomolar Quantities of C and N. Analytical Chemistry 81, 755–763.	relatively low sensitivity but high precision (0.1 permil)	
pyrolysis EA-IRMS		destructive	1 ug organic H or O	precision of 2-4 permil for H, O??	
Tunable Laser Spectroscopy	2B	Destructive via pyrolysis. Typical amount of sample required per analysis: x mg			
GC-combustion-IRMS	2B	Extraction, destructive	130 pmol CH ₄ at 0.1% precision; Merritt D., Hayes J. M. and Marais Des D. J. (1995) Carbon isotopic analysis of atmospheric methane by isotope-ratio-monitoring gas chromatography-mass spectrometry. Journal of Geophysical Research 100, 1317–1326.	Requires excellent separation of compounds and prior identification of structure.	
GC-pyrolysis-IRMS	2B	Extraction, destructive	25 nmol H as heptadecanoic acid at 2.7% precision; Hilkert A., Douthitt C., Schlieter H. and Brand W. A. (1999) Isotope ratio monitoring GC/MS of DIH by high temperature conversion isotope ratio mass spectrometry. Rapid Commun. Mass Spectrom. 13, 1226–1230.	compound must be GC-amenable	
GC-ICPMS	2B	Extraction, destructive	20 pmol S as dimethylsulfide, at 0.3% precision; Amrani A., Sessions A. L. and Adkins J. F. (2009) Compound-Specific $\delta^{34}\text{S}$ Analysis of Volatile Organics by Coupled GC/Multicollector-ICPMS. Analytical Chemistry 81, 9027–9034.	compound must be GC-amenable	
PCR	2F				
FISH – Fluorescence imaging of fluorescently tagged compounds	2F			only useful in very specific conditions for terrestrial contaminants	
ELISA	2F			only useful in very specific conditions for terrestrial contaminants	

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Total inorganic carbon and total organic carbon	1B, weight % abundance of organic carbon	Both non acid and acid digestion used to separate inorganic from organic	~1-10 ppb in 1 ml of gas or about 1E-11 to 1E-12 g of CO ₂ .	Splitting to NPD detectors, nitrogen may be accessible.	
Total inorganic carbon and total organic carbon	1B, weight % abundance of organic carbon	Both non acid and acid digestion used to separate inorganic from organic	~1-10 ppb in 1 ml of gas or about 1E-11 to 1E-12 g of CO ₂ (?)	Probably similar detection limit to above (methanizer w/ flame ionization), depending upon MS capability. Back calculating the sensitivity dependent upon the background, detector noise, ... kind of tough to say in general. Evolved compounds other than CO ₂ can be detected. Nitrogen can be done at the same time. Need nitrogen perhaps even D/H.	
Microfluidic Capillary Electrophoresis	2A, 2D, 2F		1 to 10 ppb following extraction, derivatization	Process blanks?	
GC/MS FAME using cyanopropyl stationary phase	2A, 2E, 2F		Detection down to below ~ 1 ng per compound	Detection limits are potentially lower if GC does not have significant non-specific absorption, or other issues. Lower detection limits possible by radio GC or LC using radiolabeled derivatizing agent.	
GC/MS using high temperature GC column, and ammonia chemical ionization				Probably similar detection limit to above (methanizer w/ flame ionization), depending upon MS capability. Back calculating the sensitivity dependent upon the background, detector noise, ... kind of tough to say in general. Evolved compounds other than CO ₂ can be detected.	
Tunable Laser Spectroscopy	2B	Destructive via pyrolysis. Typical amount of sample required per analysis: x mg			
Pyrolysis-MS, Pyrolysis-GC-MS		Destructive via pyrolysis. Typical amount of sample required per analysis: x mg		Does not indicate compounds present, only their fragments.	
Liquid extraction and derivatization followed by GC-MS	2A, 2D, 2E, 2F	Extraction, destructive	Detection limits are compound-specific, but as low as ~1 pmol, more like 100pmol for many hydrocarbons. Nominal mass accuracy in typical system.	Can use library mass spectra to suggest compound class. Qq-MS can target specific compounds, ultrahigh resolution MS can deduce molecular formulae. Can target chirality (e.g. amino acids, amines, etc). Requires authentic standard for definitive identification.	
LC-MS	2A, 2D, 2E, 2F	Sample crushing followed by destructive solvent extraction, possibly hydrolysis, desalting, and more	Detection limits are compound-specific, but typically ~1 fmol 5 ppm to sub ppm mass accuracy possible	Qq-MS can target specific compounds, ultrahigh resolution MS (e.g. ToF-MS, FT-MS) can deduce molecular formulae. Different ionization modes (ESI, APci, APPi) can target different functionalities. Targets M+1 parent ion. Can target chirality (e.g. amino acids). nano-LC can improve sensitivity 10-100 fold. Can couple mass and optical (fluorescence, absorbance) detections. Requires authentic standard for definitive identification. Cannot use library spectra.	
high resolution MS (infusion or DART)		Sample crushing followed by destructive solvent extraction, possibly hydrolysis. Minimal other workup required	Semi-quantitative, wide range of sensitivities including sub-fmol, sub ppm mass accuracy possible	Ultrahigh resolution MS (e.g. ToF-MS, FT-MS) can deduce molecular formulae. Different ionization modes (ESI, APci, APPi) can target different functionalities. Targets M+1 parent ion. DART required minimal preparation and has ~1 nm spot size. No chromatography, so no distinction of isomers or enantiomers.	
liquid ICPMS		destructive; sample oxidized to sulfate	5 nmol dissolved sulfate at 0.15‰ precision; Paris G., Sessions A. L., Subhas A. V. and Adkins J. F. (2013) MC-ICP-MS measurement of δ34S and Δ33S in small amounts of dissolved sulfate. Chemical Geology 345, 1–12.	relatively low sensitivity but high precision (0.1 permil)	targets any sulfur in solution as sulfate; can be used for organic compound-class analysis
combustion EA-IRMS		destructive	25 nmol N, 41 nmol C, both at ±1.0‰ precision; Polissar P. J., Fulton J. M., Junium C. K., Turich C. C. and Freeman K. H. (2009) Measurement of 13C and 15N Isotopic Composition on Nanomolar Quantities of C and N. Analytical Chemistry 81, 755–763.	precision of 2-4 permil for H, O??	
pyrolysis EA-IRMS		destructive	1 ug organic H or O		
Tunable Laser Spectroscopy	2B	Destructive via pyrolysis. Typical amount of sample required per analysis: x mg			
GC-combustion-IRMS	2B	Extraction, destructive	130 pmol CH ₄ at 0.1‰ precision; Merritt D., Hayes J. M. and Marais Des D. J. (1995) Carbon isotopic analysis of atmospheric methane by isotope-ratio-monitoring gas chromatography-mass spectrometry. Journal of Geophysical Research 100, 1317–1326.	Requires excellent separation of compounds and prior identification of structure.	
GC-pyrolysis-IRMS	2B	Extraction, destructive	25 nmol H as heptadecanoic acid at 2.7‰ precision; Hilkert A., Douthitt C., Schluter H. and Brand W. A. (1999) Isotope ratio monitoring GC/MS of D/H by high temperature conversion isotope ratio mass spectrometry. Rapid Commun. Mass Spectrom. 13, 1226–1230.	compound must be GC-amenable	
GC-ICPMS	2B	Extraction, destructive	20 pmol S as dimethylsulfide, at 0.3‰ precision; Amrani A., Sessions A. L. and Adkins J. F. (2009) Compound-Specific δ34S Analysis of Volatile Organics by Coupled GC/Multicollector-ICPMS. Analytical Chemistry 81, 9027–9034.	compound must be GC-amenable	
PCR	2F				
FISH – Fluorescence imaging of fluorescently tagged compounds	2F			only useful in very specific conditions for terrestrial contaminants	
ELISA	2F			only useful in very specific conditions for terrestrial contaminants	

9.4.1 Notes Regarding detection limits and capability of surface spectroscopic techniques

Challenges exist in defining the detection limits and capability of surface spectroscopic techniques, as they are strongly dependent on instrument design and sample/measurement specifications.

Factors that affect technique sensitivity due to optical design include:

- 1) *Optical throughput* (laser power, transmission of optics, etc.),
- 2) *Collection efficiency* (f/#, DOF, DOP, etc.),
- 3) *Detector sensitivity*,
 - a. Noise (dark current, shot noise, read noise etc.),
 - b. Performance (dynamic range, gain, QE, etc.),
- 4) *Spectral range* (may require time gating to improve sensitivity based on technique)

Example factors that affect technique sensitivity due to sample/measurement specification:

- 1) *Measurement duration*: In general, increase integration time for spectroscopic techniques with increase S/N and therefore sensitivity of the technique (assuming S/N is not driven by noise sources, other spectral interferences limitations, etc.).
- 2) *Spatial mapping requirements*: Instrument design will be driven by ability to map the core over a given spatial area with a specified resolution. This will drive the optical design and sensitivity. In addition, if the measurement duration is limited, resolution or area can be traded against sensitivity/integration time per spot.
- 3) *Sample working distance*: The optical design can be optimized for any working distance at the expense of sensitivity or instrument size (f/#).
- 4) *Surface Roughness*: Ability for a technique to handle surface roughness will require trades in optical design versus sensitivity or sensitivity to surface only materials (making it less robust to matrix variability).
- 5) *Matrix affects*: Spectroscopic technique sensitivities are strongly dependent on the matrix including:
 - a. Background interferences such as mineral fluorescence and required time gating to increase organic sensitivity in techniques like Raman.
 - b. Variability of depth of penetration based on mineral matrix type will affect ability to localize “organic detection” to surface only or will limit the optical designs to confocal or surface approaches. This will limit surface roughness robustness for the techniques.
- 6) *Species type*: Each spectroscopic technique will have species-specific sensitivities due to molecular interactions (i.e. cross sections for Raman spectroscopy) including technique species-specific interference, which can limit detection sensitivities.

These challenges for defining sensitivity of a survey/spectroscopic non-destructive technique led to an analysis approach that will use a series of instruments that can correlate organics and mineralogy and have complementary sensitivities and specificities.

Future work recommendations would include further constraining the processes and sample expectations to solidify instrumentation requirements including:

- Time for survey measurement, which will be derived by the spatial area and spatial resolution requirements and sensitivity requirement (integration time, DOF, f/#, etc.)
- Making a compilation of potential contaminant species to assess specific detection limits and

interferences.

As a point of procedure, a subset of techniques should be used to analyze identical samples to validate instrument performances and characterize sensitivity and specificity to common species at practical contamination concentrations. This will also help to identify interference levels that inhibit the ability to identify the scientific relevant organics.

Accordingly, and based on instrument capabilities as of the time of writing in 2014 (Table 3 and Appendix 4), the following mass spectrometric survey methods are recognized as being the most specific and sensitive techniques to detect organic contaminants of concern:

- Liquid Chromatography–Mass Spectrometry (LC-MS) in full scan mode can detect a wide range of polar analytes of biological relevance including amino acids and oligopeptides, nucleobases and oligonucleotides, intact polar lipids etc. LC-MS is the preferred means to analyze molecules of any size that are not volatile under normal circumstances. Ionization utilizes the evaporating solvent to assist the addition of either positive or negative charges, most commonly via electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI).
- Gas Chromatography-Mass Spectrometry (GC-MS; also full scan mode) can detect a wide range of molecules that are non-polar and volatile to semi-volatile under moderate temperatures. Typical analytes are aliphatic and aromatic hydrocarbons, low MW lipids, short-chain carboxylic acids and esters, etc.

9.5 Appendix 5: Evaluation of Draft Mars 2020 Mission Organic Contamination Requirements and Methodologies

This appendix contains a set of working concepts for the eventual Mars 2020 Contamination Control Plan, along with feedback on those concepts from the Organic Contamination Panel. This information is intended to constitute input to the development of the actual plan—this appendix is not the plan itself. Section 1.1 below was prepared by the Mars 2020 project team, and Sections 1.2 and 1.3 constitute feedback on this information by the OCP.

It is important to recognize that these early concepts and ideas are incomplete and that the eventual Mars 2020 implementation will undoubtedly be different in some respects. The Contamination Control Plan will need to interface with many other aspects of the project, and critical project information about these other areas will be determined later. Once the actual Contamination Control Plan has been written, it will supersede everything in this appendix. Future readers should therefore recognize that the information in this appendix will shortly become useful only for historical purposes. In the preparation of this report, we have encountered the confusion this situation can create when trying to understand what Viking and Apollo thought about vs. actually did. Similarly, the feedback material in Sections 1.2 and 1.3 will hopefully be valuable as input to writers of the actual contamination control plan, but afterwards, we strongly encourage readers to refer to the actual plan, not this appendix.

9.5.1 Draft Concepts for a Mars 2020 Contamination Control Plan

The Mars 2020 contamination control program would be based heavily on heritage MSL practices so as to leverage the similarities between the two missions. Despite the similarities however, there are a number of differences between MSL and Mars 2020: Some key similarities and differences are listed in Table 9.

MSL constructed a contamination control program intended to enable the in-sample contamination requirements for the SAM instrument. From the science and engineering requirements, requirements are derived for surface cleanliness of the sample transfer chain, the Rover in general, and the remainder of the flight system and launch vehicle interface. The flight system would be separated into ‘contamination zones’ based on an assessment of the efficiency of potential transport of (terrestrial) contaminants to the samples collected. An example of the concept used on MSL is shown in Figure 21. Hardware comprising the solid sample acquisition system could be identified as ‘Zone-1,’ having the highest potential opportunity to contamination solid samples; regions further removed from the sample path are designated as lower risk, therefore allowing a relaxation of hardware cleanliness requirements relative to Zone-1.

A similar requirements derivation process would be applied to the Mars 2020 system, with the proposed encapsulated samples as the driving element of system contamination sensitivity. Focused mitigations would be applied to meet the contamination sensitivity of the other payloads and engineering systems comprising the mission.

As with MSL, Mars 2020 would identify all foreseeable locations or transport paths for contamination to get into the sample, and formulate a valid, verifiable requirement on it based on a credible transport mechanism model. The vectors for potential introduction of terrestrial contaminants into sealed samples are presented pictorially in Figure 21. Also in common with MSL, contamination transport models would play a role in the Mars 2020 mission. That said, it is worth emphasizing that the Mars 2020 sample transfer chain, including the samples and their unique cleanliness constraints, would be dramatically different from the MSL system. While some of the underlying generalized physical models of contamination transport used to conduct MSL analyses (e.g., free molecular flow in the vacuum

regime; convection and diffusion for surface operations) apply to Mars 2020, these must be tailored to the specific science objectives, configurations (with special emphasis of non-heritage elements), environments, and contamination vectors of the Mars 2020 mission.

Table 9. Some Similarities and differences between MSL and Mars 2020

Similarities	Differences
<ul style="list-style-type: none"> • Similar process used to produce requirements for allowable in-sample contamination <ul style="list-style-type: none"> – OCSSG in the case of MSL – OCP in the case of Mars 2020 <p>From the start, the Project acknowledgement of the importance of contamination control to the success of achieving mission objectives</p> <ul style="list-style-type: none"> • The system architecture is highly similar for both missions; configuration largely decouples sample cleanliness from rest of the flight system • Modeling tools and methodologies for flight and surface operations used on MSL are applicable to Mars 2020 • System-level contamination control approach emphasizes control and knowledge (characterization) of contaminants • Contamination transport models play a role in verification • Close coordination between CC and PP 	<ul style="list-style-type: none"> • Mars 2020 is able to leverage heritage from a very similar recent mission • Much simpler sampling system • Sampling system is a result of a long technology program with cleanliness a key driving factor • Different PP requirements, associated with sample cache, for both bioburden and organic contamination • Expected minimal use of dilution cleaning • Challenging cleanliness requirements for the Cache; implications for Flight System • May have additional contamination vectors in the form of: <ul style="list-style-type: none"> Additional numbers or different composition of calibration targets Addition of in-situ Resource Utilization payload element which processes gases and would add to the “plume” of contamination around the rover Different thermal paint Potential differences in drill seal material

In addition, there would be a particular focus on fault tolerance to identify points in the design that may present a risk to Science objectives in the event of an anomaly. This process may be informed by ground-based hardware development tests using flight-like hardware and contaminant analogs.

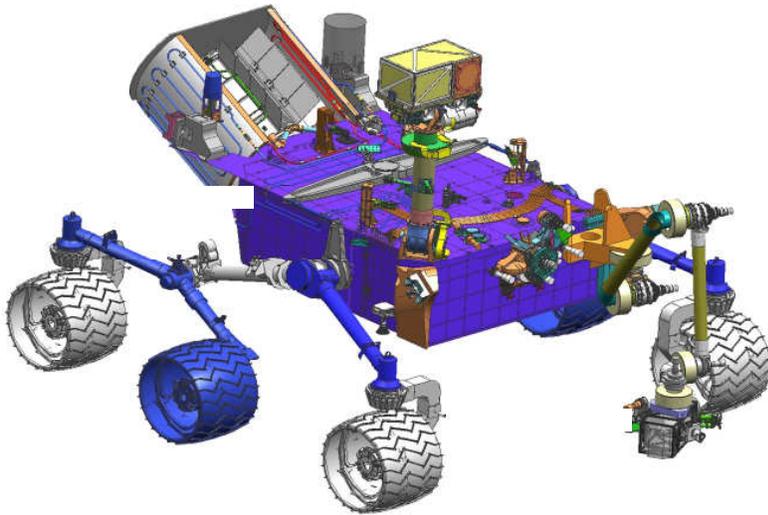


Figure 21: Contamination Zones on MSL

- Zone 1:** Closest proximity to SAM solid and atmospheric inlets. Includes sampling system, arm and everything forward of the Rover suspension rocker.
- Zone 2:** Includes everything on the exterior of the Rover aft of the suspension rocker; extends upward to the descent stage when flight system in cruise configuration.
- Zone 3:** Inside the Rover chassis (WEB)
- Zone 4:** Everything else

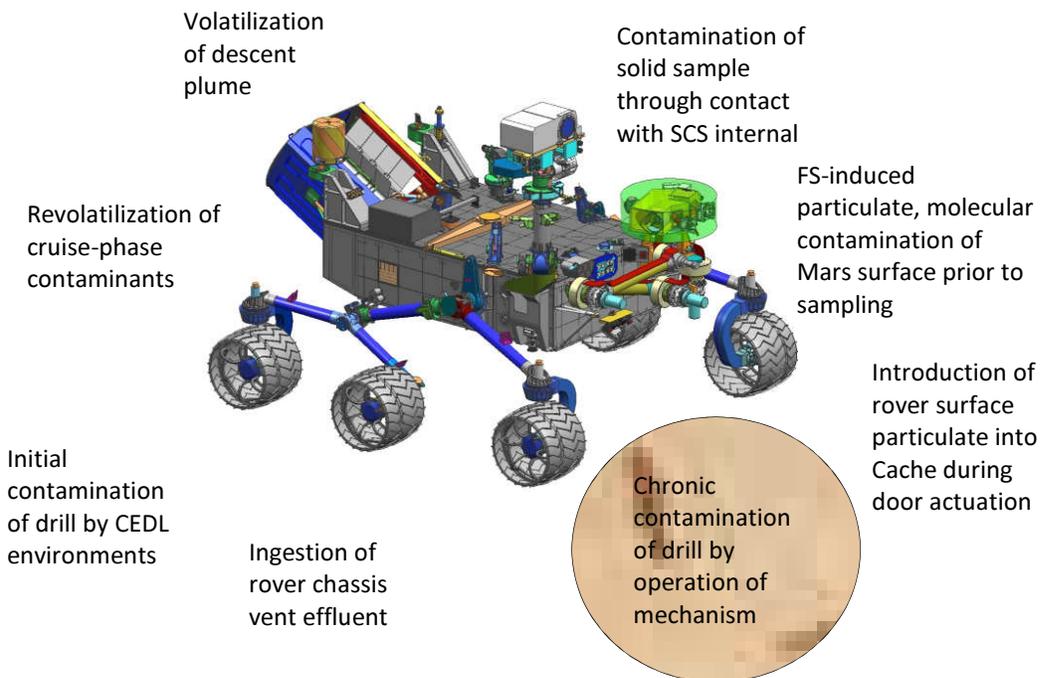


Figure 22. Vectors for potential introduction of terrestrial contaminants into cached samples.

9.5.1.1 Science and Contamination Requirements Linkage

Contamination transport models provide the linkage between the science requirements and the hardware cleanliness requirements. Bounding calculations are used to derive conservative hardware cleanliness requirements—outgassing and surfaces—from the driving Science requirements. A rigorous and systematic program of direct measurements of hardware cleanliness is planned to verify compliance at the

component, sub-system and system levels. The formal hardware delivery process requires documentation of compliance with CC requirements before acceptance of hardware for higher level integration. Measured values for hardware cleanliness subsequently become inputs to the transport models as an element of the verification process showing that the as-flow system enables the science requirements.

9.5.1.2 Design Process

The Mars 2020 project has articulated a system architecting and design process that emphasizes the vital importance of achieving a high degree cleanliness for the samples (Fig. 22). The Mars 2020 system architecture exploits the decoupled nature of the sampling system from the rest of the flight system. Further, there has been placed a special emphasis on controlling or eliminating potential sources of contamination within the hardware elements that make up the sample caching system (SCS). Contamination control is an integral aspect of the SCS design trades currently underway; this is an iterative process wherein allowable in-sample contamination levels and contaminant transport mechanisms inform the design process and function as one of the discriminating criteria amongst competing designs within the trade space.

9.5.1.3 Hardware cleaning

The Mars 2020 project has undertaken an extensive literature search to learn the lessons from Apollo, Viking, Genesis, and other missions (and other industries which require elevated levels of cleanliness) with respect to cleaning flight hardware cleaning methodologies. (Many of relevant references are included elsewhere in this report.) The Project has also been kept informed of institutional technology development efforts in the areas of cleaning and recontamination prevention. The project has taken ownership of some of the more promising activities and would be deciding which to carry forward in further development. At this time, the specific cleaning methods have not been selected. However, whatever process ultimately selected would be validated against the Tier-I, Tier-II contaminants identified elsewhere in the report. A notional process flow for cleaning and acceptance of critical sample contact hardware is shown in Figure 24. To prevent recontamination after cleaning, no polymeric bagging materials would be allowed to come into direct contact with SCS hardware: fired foil or stainless steel containers would be allowed.

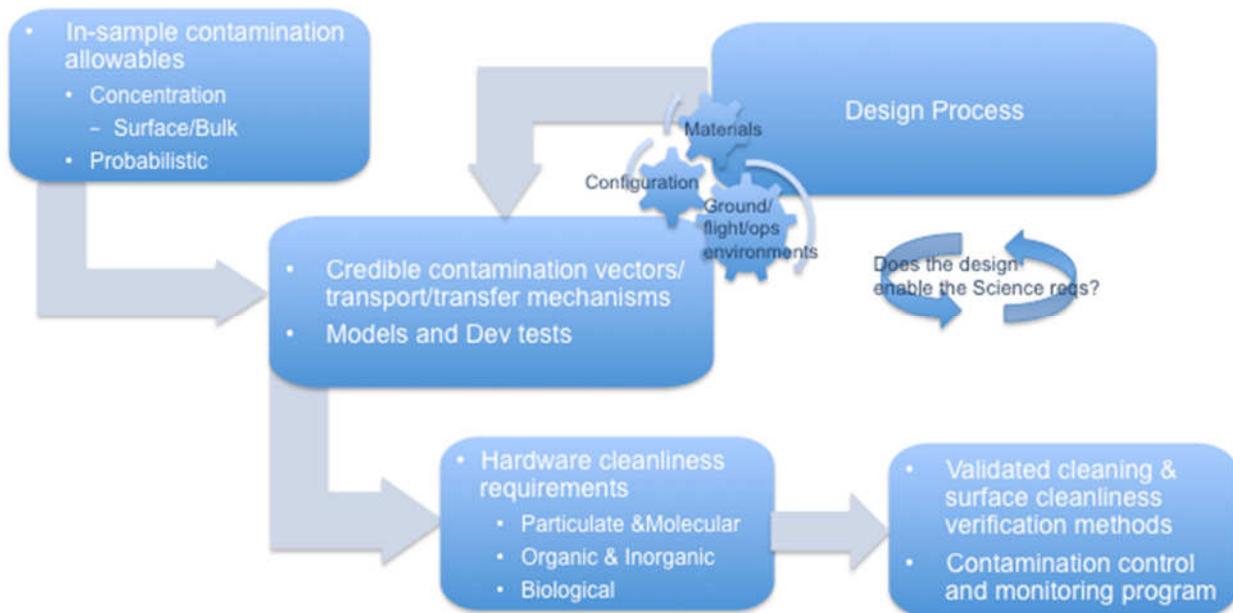


Figure 23. The system architecting and design process emphasizes the vital importance of achieving a high degree cleanliness in samples taken for the Cache.

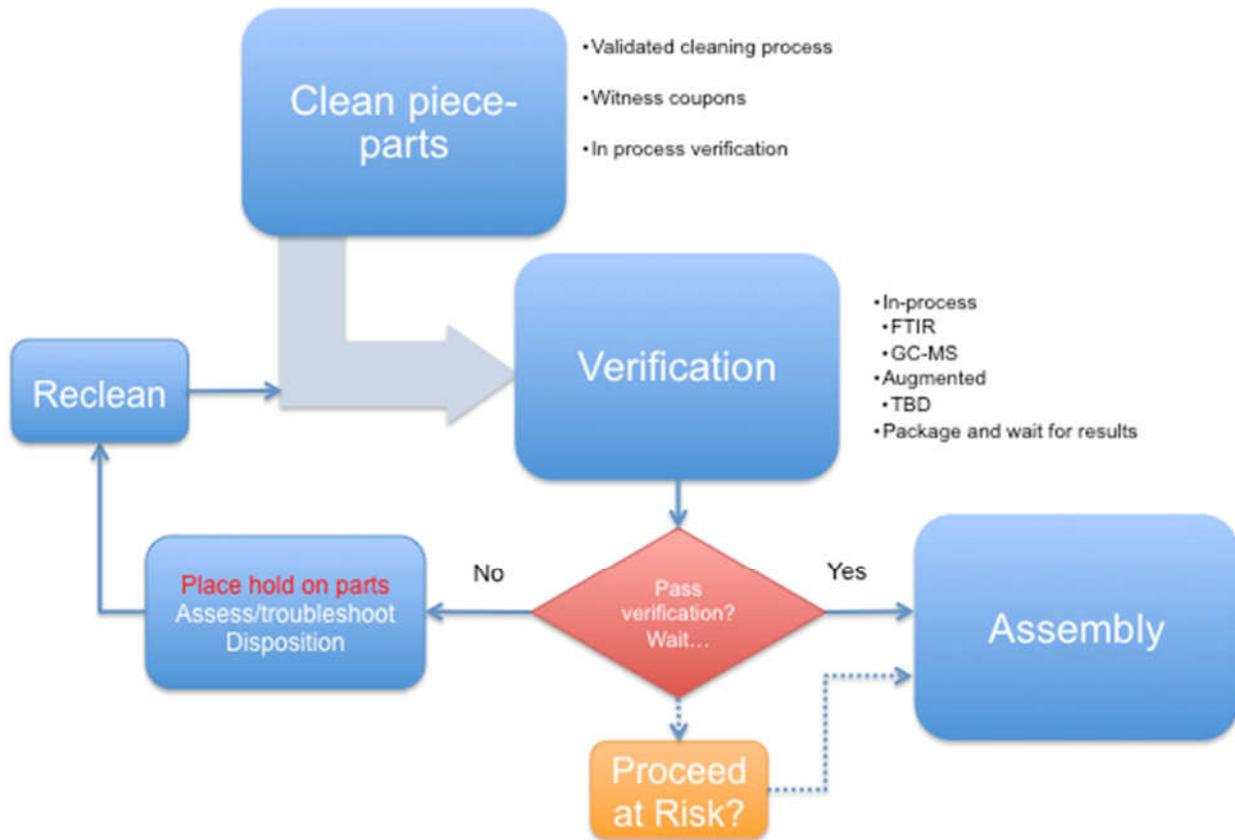


Figure 24. Notional process flow for cleaning and acceptance critical sample contact hardware.

9.5.1.4 Sample System Development

The Mars 2020 project plans to undertake sample system hardware development under Class 1000 (FED-STD-209 Class M4.5; ISO 14644-1 Class 6) protocols. No co-location with other projects would be permitted and the facility would be accessible only by trained personnel. If the venue is to involve the conversion of an existing facility, the facility would first be surveyed to determine whether the native contamination background is acceptable with respect to cleanliness needs of the hardware processing activity or whether a prospective facility can be brought into compliance with project cleanliness requirements. It is anticipated that the development of the sample system would take place off-line in parallel with flight system development (notionally depicted in Fig. 24) so as to maintain a higher level of contamination control until it is integrated late in the system integration flow at the launch site.

It is anticipated that system-level assembly test operations would be conducted in an existing facility operated under Class 10000 (or better) protocols. Real-time monitoring of airborne particulate and similar capability on-line for condensables is planned. The Project is investigating implementation of real-time particle fallout monitoring (<http://www.pmeasuring.com>).

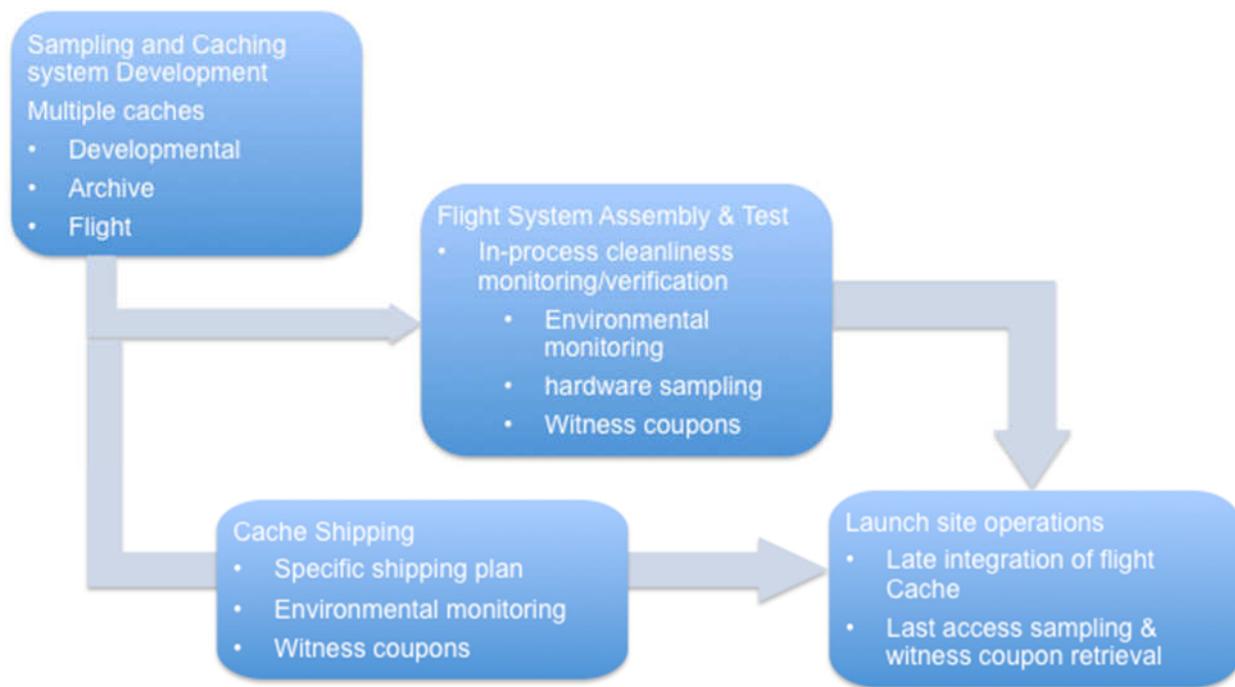


Figure 24. Notional parallel paths for sample system development and flight system development, with late integration into the flight system.

9.5.1.5 Witness plates, Controls & Blanks

The Mars 2020 project recognizes the importance of witness coupons in establishing an adequate data set describing the potential contamination background in returned samples. A comprehensive witness coupon monitoring program would be designed into the hardware processing flows. The design of the monitoring program must be purposeful and provide sufficient contamination knowledge, while at the same time be implementable. Witness plates would follow critical hardware through cleaning process for cleanliness verification. These coupons or analysis results would be archived. Analysis of terrestrial and flight system contaminant sources would be performed and an archive of flight system materials would be collected as a reference for contamination signatures. The Project expects to leverage the lessons and practices of other space sample curation facilities and described elsewhere in this report.

9.5.1.6 Hardware Cleanliness Verification

A suite of measurements have been identified as the set of measurements to be done for cleanliness verification of critical sample system hardware (Table 10); critical being defined as that which contacts sample and or has a credible direct path to samples.

Sampling of surfaces for cleanliness verification is always challenging. So-called analyte recovery efficiency needs to be taken into consideration. Sampling strategy would be determined when requirements are defined, however several novel methods are available for consideration:

- Experiments using solvents show the swab sampling efficiency to be ~70% for adventitious carbon. (The Project is currently performing experiments with slightly acidic solvents that would

dislodge the last monolayer; noting the organic acids reacting with the metal surface forming organic acid salts are the most common, tightly bound form of AC.)

- Witness plates can be measured directly with no solvents via GA-ATR FTIR. The GA-ATR can readily monitor the sampling efficiency of other analytical methods.
- It is possible to abrasively sample surfaces using KBr powder and avoid solvents altogether for DRIFT/FTIR. This method has shown a very high sampling efficiency (90% +)

Table 10 Broad-spectrum assay procedures to detect organic contamination

	Sample Treatment	Extract treatment	Calibration Method	Concern Trigger	Comments
Surface spectroscopic imaging	none	NA	?	>1ng/cm ²	Detects fibers, organic particulates, macromolecular OM
FTIR-Microscope/Raman microprobe	Direct	N/A	Known compounds	TBD	Detects fibers, organic particulates, macromolecular OM
Gas Chromatography-High Resolution Mass spectrometry	IPA/DCM wash	Ionization by electron impact, analyze by scanning MS	External standards	>10 ng/g	Detects polar molecules such as hydrocarbons, chlorinated solvents, plastics, etc
DRIFT (FTIR)	swab/rinse	Deposit on KBr	Known compound classes	TBD	Sampling ϵ can be referenced to direct methods, e.g. GATR
DART-MS	Direct or extract	Optional derivatization	Mass standards	TBD	Broad range of low-volatility materials
Liquid Chromatography-High Resolution Mass spectrometry	IPA/Water wash	ESI and APCI conditions, scan MS and search for masses of targets and unknowns	External standards	>10 ng/g	Detects polar and high-MW molecules Method development

9.5.1.7 Contamination transport analyses

Contamination transport mechanisms differ between the vacuum of space and the Mars surface environment; thus requiring different modeling approaches. Mars 2020 would leverage the analytical tools used to perform the cruise-phase and surface operations phase contamination transport analyses for MSL. Contamination transport models are typically deterministic to a stated level of uncertainty. For Mars 2020, some of the model results may also be expressed probabilistically to be comparable with some prior work done and reported in this manner; for example, Hudson et al. 2010.

9.5.1.7.1 Cruise-EDL Models

Contamination transport analyses would be done to estimate the redistribution of particulate and molecular contamination during the launch, cruise, entry, descent and landing events. Molecular and particulate redistribution calculations use pre-flight measurements prior art, and flight environments as inputs to models. These analyses provide the basis for establishing the datum for the initial hardware surface contamination levels at the beginning of operations on Mars.

9.5.1.7.2 Mars surface models

Unlike the cruise phase where molecular contamination transport is in the free molecular flow regime, on Mars, transport in the martian atmosphere determines relationship between sample contamination requirements and hardware outgassing requirements. Molecular transport an atmosphere, ~6 to 8 torr, is described by fluid equations; molecules move with the wind (ten Kate et al., 2008; Blakkolb et al 2008). Some of the many questions answered by transport models included temporal and spatial variation of ammonia concentration effects: timing of the first sample acquisitions; and contact science.

Analysis of the Descent Stage plume constituents physical and chemical interactions with Mars atmosphere and soil were done for MSL to assess in-sample contamination risk. Also, since the Descent Stage impacts Mars at ~100mph, assume the propellant system ruptures and hydrazine is released. MSL modeled the gas-phase reaction N_2H_4 and Mars $CO_2 \rightarrow$ carbazic acid: $NH_2NHCOOH$. Solid “ash” and sublimation gasses are carried by wind. Transport model calculations including chemistry with martian soil and atmosphere include the effects of N_2H_4 reactions with the surface minerals and with the CO_2 in the atmosphere. Gas phase reaction rate of N_2H_4 and CO_2 were measured in the laboratory at JPL as model inputs. The 3-D simulation included estimates of mixing in turbulent boundary layer. The modeling tools developed for are generalizable such that analyses done for Mars 2020 would be specific to the requirements and conditions of the mission.

Redistribution of particulate debris by winds on Mars during surface operations has also been identified as a potential contamination vector to the sample hardware. The Project has near term plans to undertake bounding analyses to understand the magnitude of redistribution by the saltation mechanism and by physical erosion of surface system materials (so called “sputtering.”) Depending on the outcome of these early studies, more detailed calculations and tests may be undertaken.

9.5.1.8 Conclusion

The Mars 2020 project is in the early phase of its development. As such, details of many aspects of the contamination control implementation are still TBD at this time. However, a significant benefit accrues to Mars 2020 due to the similarity with the recent, largely successful, MSL mission. While the project readily acknowledges the additional challenges presented by the sample hardware, many of the tools and processes used for MSL may be applied as-is or leveraged to form the basis of the Mars 2020 implementation. Contamination control engineering is fully engaged with the hardware design and systems engineering teams and Project management appears fully committed to enabling a successful contamination control program. We strongly encourage, however, that project be proactive in undertaking the necessary development efforts that would be needed to bring new cleaning and cleanliness verification methods on-line with the necessary validation.

9.5.2 Feedback on the Mars 2020 Conceptual Contamination Control Plan

As requested by its charter, the OCP reviewed the Mars 2020 Project’s concepts for a contamination control plan (Section 9.5.1 of this report), and has prepared the following feedback.

9.5.2.1 Mars 2020 Sample Return and Heritage from MSL

In Section 9.5.1 it is stated that the Mars 2020 contamination control program is expected to be based heavily on heritage MSL practices. However, MSL was strictly specified as **not a life detection mission**, from the perspective of both science and planetary protection. This mission definition minimized the level and extent that contamination control and planetary protection needed to be accounted for on the mission. Mars 2020, by the addition of the sampling system and sealable sample tubes and the potential for a future restricted Earth return, would be an entirely different mission with different Level 1 mission requirements. As discussed in this report, the Mars 2020 mission should carry requirements that prevent the contamination (biological, organic and particulate) from having an adverse impact on the scientific and planetary protection evaluation of the potential returned samples. MSL had no such requirements, therefore it was possible to accept additional risk of contamination of the samples as a matter of operation. (If a sample is too contaminated, take more samples until a sufficiently clean sample can be acquired to provide useful data.)

- Mars 2020 has a much simpler sampling system, which should help it to be able to meet the much stricter requirements relating to potential sample return.
- Unlike MSL, Mars 2020 is unlikely to make extensive use of dilution cleaning (see also Section 2.1.3 of this report). Looking for known proven methods for cleaning and protecting surfaces from contamination, particularly those that do not have geometric restrictions to their efficacy is the only reasonable course of action. Some cleaning processes, such as ozone cleaning, carbon dioxide snow cleaning, and laser cleaning, have issues with mated surfaces and deep holes. As a result their applicability to real hardware is limited. Known proven methods for removing volatile organic materials, organic particles and biota should be accepted and tested to assure that there is capability to achieve the required levels on all of the hardware as it is developed and assuring that the protection schemes are adequate to assure the contamination levels on delivery to Mars.
- The Mars 2020 samples would need to be considerably cleaner than were the samples collected prior to dilution cleaning on MSL

9.5.2.2 Contamination Control Best Practices

In the conceptual contamination control plan (Section 9.5.1), reference was made to carrying out cleaning, assembly and testing operations of the sensitive hardware in class 1000 or class 10,000 and class 100,000 cleanroom environments, and extensive studies showing long term accumulation of molecular contamination and evaluating real-time particle fall out monitors. OCP endorses these studies. In addition, however, when Mars 2020 writes its contamination control plan, we encourage close attention to strategies to protecting the hardware to decrease the rate of recontamination. Additionally, OCP advises measuring and monitoring the microbial, organic and particle source strength variation in the proposed facilities and their adjacent areas prior to committing to them. This can avoid uncontrolled or poorly controlled environmental conditions and random contamination events, such as diesel forklifts idling next to the air inlets and activities such as spraying lubricant on ground support equipment, trucks idling in truck locks, etc.

9.5.2.3 Contamination Control Plan

Separate processing areas for the sample acquisition hardware and the sample caching hardware should be utilized, using the best available facilities, such as an ISO-5 clean bench in an ISO-7 Cleanroom utilizing hydrocarbon assimilation filters, and following best practices for keeping hardware covered at all times that work is not actively being carried out on it. This would include the use of combustion-cleaned aluminum foil and/or stainless steel containers to decrease the exposure of the hardware to the environment. Periodic reviews of the contamination control practices and facilities could prove invaluable.

9.5.2.4 Combustion Cleaning

The use of combustion cleaning to clean the hardware and storage materials to minimize the molecular organic contamination, the particulate organic contamination and the biological contamination is highly recommended. This is standard practice in terrestrial laboratories doing research on trace microbial species and trace organic chemistry. A starting point for Mars 2020 to consider is the placement of the hardware on clean aluminum foil in an air atmosphere furnace and heating to 550°C and dwelling at this temperature for two hours followed by a slow cool down over 12-16 hours to approximately 50-100°C, in the furnace. At that time the hardware should be wrapped with the foil to minimize recontamination by airborne contaminants. The cost impact of potential redesign of hardware to allow combustion cleaning is very likely less than the cost of development and/or verification of another process and the risk of failure of the other method.

It is well known that decreasing the conductance of the path for contamination provides a good method of prevention of contamination. Simple clean metal foil coverings of hardware decreases the transfer rate of all contaminants to surfaces. The highly constrainable paths reduce the transfer rates by orders of magnitude at the simplest level of approximation. The actual levels of contamination transport are actually constrained significantly more than predicted and the simple approximation level due to the highly complicated and poorly understood interactions of materials on exceedingly clean surfaces.

Finding #31: Baking all sampling hardware in air at >500°C and for >8 hours, followed by rapid isolation from contact with air, potentially provides a means to achieve orders-of-magnitude lower levels of organic contamination. We suggest that the Mars 2020 project substantively investigate this possibility while evaluating sample hardware design options.

9.5.2.5 Blank Standards

As emphasized in Section 5.3 of this report, blank standards that can be field sampled on Mars and included as part of the sample collection are critical to the ability to obtain meaningful information from the samples. These are at least as valuable as the samples, because contamination processes can be random and variable, and the only way of distinguishing sample from contaminant is by use of blank standards. These materials should have similar physical properties and be readily analyzed for trace organics. Mars 2020 needs further discussion on the design of these blank standards. However, a factor to consider is that they should have a carefully chosen permeability to allow penetration of organic contamination into the interior of the blank in a manner that is sufficiently similar to the natural samples. Consideration should also be given to whether these blanks should be drilled and handled in different orientation to determine whether or not there are gravitationally induced effects on the sampling. As has been pointed out elsewhere (e.g. Mustard et al. 2013), without appropriate blank standards the samples would almost certainly not be worth returning in a scientific sense.

9.5.2.6 Witness Plates

OCP would like to emphasize the points made in Section 5.2 of this report regarding the importance of witness plates. Witness plate sets should include multiple identical plates to allow the quick contamination control measurements as well as measurement of the more time consuming contamination knowledge measurements to identify the compositions of the contamination. Work needs to begin soon on evaluating the requirements of the archiving facility not only for the returned samples but for assuring the ability to maintain the witness plates and materials samples required for the sample return mission, which may also include bioburden samples either processed or preserved (see discussion in Section 5.4 of this report). These archiving processes need to be verified and validated prior to collecting materials to be archived. The archive facility needs to be properly budgeted.

9.5.2.7 Additional Planning to Improve Contamination Knowledge

OCP strongly encourages more planning for acquiring contamination knowledge, which we consider extremely high priority (see Findings #3, #5 of this report). This includes how and what is sampled, how and what is measured, who is going to do the measurements, quality control, verification and validation of methods and procedures, etc. This information may potentially be exceptionally important to future investigators, and it is essential that it be collected properly during the project's development phase.

9.5.2.8 Contamination Verification Plan

The contamination verification as provided above is in line with the suggestions and the philosophies of the OCP. It is expected that this would continue to be developed further and that the processes and methods would be verified and validated following the further identification of the total landed system's requirements are identified and that the effort is funded. The proposed scheme for quantifying the organic contaminants seems to be a good starting point.

9.5.2.9 Total Organic Carbon

The project would need to propose a way of measuring Total Organic Carbon. The traditional method for determining total organic carbon in geological samples is by pyrolysis, although as discussed in this report, detection limits of current analytic systems are nowhere near good enough for this application (the pathway to creating such an instrument in the future is clear, so OCP has not worried about this). There are alternate means for measuring the concentration of trace organic molecules on metal surfaces. An additional problem is that analysis of metal surfaces by pyrolysis can result in false signals from metal carbide that is part of the alloy. The Mars 2020 project would need to choose one or more methods (there are TOC analyzers that would reach the necessary detection sensitivity, and ones that would not be interfered with by the metal carbides, but these may be separate instruments). There was a preference within OCP to measuring TOC directly on witness coupons rather than measuring from swab samples and that witness coupons be made preferably from spacecraft or sampling system materials. Multiple material types were also advised as the adsorption of organics on surfaces is material dependent.

Due to the significance of the contamination and planetary protection requirements and the extremely low expectable levels of contaminants in the sample caching systems as well as the additional specific measurements required, verification and validation of the sampling and measurement techniques is called for. Development of the measurement and monitoring techniques well in advance of the actual measurements on the hardware is called for. This in effect buys down the risk of the planned contamination control and planetary protection requirements by allowing verification and validation of the planned cleaning and recontamination protection, reducing mission risk.

9.5.2.10 Relationship to Planetary Protection

Based upon the differences between MSL and the Mars 2020 rover mission, particularly with respect to the expected Planetary Protection driven requirements, it is absolutely necessary that the PP requirements and their impacts on the Contamination Control requirements and implementation be entirely understood across the entire mission, and that potential impacts on systems be explained to the individual system and subsystem leads. It would be a great concern if any of the subsystem leads have inadequate understanding of the rationale behind the planetary protection and contamination requirements. An attitude of "here's my hardware, clean it and get it to meet your PP and CC requirements" would almost certainly lead to difficulties. It is crucial that the subsystem leads accept and be held accountable to designing and delivering hardware meeting these requirements, and that they understand the principles of how to meet the requirements. Organic contamination control is central to the objectives of Mars 2020, and it needs to be embraced by the entire science and engineering teams.

9.5.2.11 Selection and Characterization of sampling system materials

The fundamental physics and chemistry of the materials matters in considering the effects of organic contamination. Many of the contamination issues boil down to a materials issue—some materials are better than others with respect to how they chemisorb, physisorb, or desorb organics. Appropriate material selection accounting for potential Contamination and Planetary Protection issues and limitations

should be included as part of the hardware design from the beginning, which would enable the attainment of the requirements.

It is imperative that sample container materials are characterized in a way that allows for accurate understanding of the interactions between them and the martian environment. Without this, defining a verifiable requirement for organic cleanliness may be challenging. During the review process for this report, concerns were raised about the behavior of the sample container in the martian environment, such as the effects of temperature cycling & seal lifetime, winds, radiation, humidity, insertion of heated Martian rock post-coring. Early testing would be beneficial. A factor that specifically should be considered is the corrosion or other deleterious effects by martian soil (e.g. perchlorates, acid sulfates and other reactive components).

9.5.2.12 Final Cleaning of Hardware

Consider final cleaning of hardware that touches samples with ultrapure water. This would reduce organic residues from solvents. Detailed optical inspection before and after traditional cleaning of stainless steel hardware can show the addition of film-like material (presumably organic from organic solvent) and particles. Ultrapure water has been used for prior sample return missions at other NASA Centers. For example, UPW was used in ISO Class 4 to clean Genesis hardware for flight.

Other techniques such as the utilization of cleaning techniques and technologies that are well known for their ability to remove diverse materials from surfaces, including combustion cleaning, sub-critical water cleaning, supercritical fluid extraction, etc. which are well developed in other industries.

9.5.2.13 Modification of sampling system surfaces

Surface modification for some Mars 2020 surfaces may be appropriate. OCP discussed at length the possibility of adding of a thin surface coating to the sample-contact surfaces to decrease surface energy, as a strategy to decrease the accumulation of adventitious carbon. From the point of view of the samples, this would be equivalent to adding a known contaminant to gain the benefit of reducing the unknown contaminants (“the devil you know is better than the devil you don’t know”). Although the members of this committee had mixed opinions on the consequences of this strategy to the possible eventual sample-based investigations, we agreed as a group that the reasons to oppose it are at least as strong as the reasons to support it, so as a group we agreed to recommend against this approach.