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 preperation 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 sensitivites 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 Lemoff, and Sanford A Asher. 2010. "Deep Ultraviolet Resonance Raman Excitation Enables Explosives Detection." Applied Spectroscopy 64 (4): 425–32. [4] Bhartia, et.al., International Society for Optics and Photonics: 83581A–83581A–9. [5] Johnson, et.al., Astrobiology 11 (2): 151–56. [6] Bhartia et, al....Applied and Environmental Microbiology, 2010, 76(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 graphic 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 (Dergoan H5 Chondrite) [2b] Matrajt, et. al., Astronomy & Astrophysics, 416(3), 2003, 983-990 (Tagish Lake Meteorirte) [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 sensitivies 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 detritus.		Gram-negative microbes only. Insensitive to gram-positive microbes.	
ATP luminometry	2F	Wipe, swap, extraction. Sample exposed to water/solvent, wipe/swab detritus.	Proportional to microbial metabolic activity	Insensitive to spores	
Microbial plating assay	2F	Wipe, swap, extraction. Sample exposed to water/solvent, wipe/swab detritus.	~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 preperation 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 sensitivites 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 Lemoff, and Sanford A Asher. 2010. "Deep Ultraviolet Resonance Raman Excitation Enables Explosives Detection." Applied Spectroscopy 64 (4): 425–32. [4] Bhartia, et.al., International Society for Optics and Photonics: 83581A–83581A–9. [5] Johnson, et.al., Astrobiology 11 (2): 151–56. [6] Bhartia et, al....Applied and Environmental Microbiology, 2010, 76(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 graphic 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 (Dergoan H5 Chondrite) [2b] Matrajt, et. al., Astronomy & Astrophysics, 416(3), 2003, 983-990 (Tagish Lake Meteorirte) [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 sensitivies 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 detritus.		Gram-negative microbes only. Insensitive to gram-positive microbes.	
ATP luminometry	2F	Wipe, swap, extraction. Sample exposed to water/solvent, wipe/swab detritus.	Proportional to microbial metabolic activity	Insensitive to spores	
Microbial plating assay	2F	Wipe, swap, extraction. Sample exposed to water/solvent, wipe/swab detritus.	~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 CO2.	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 CO2 (??)	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 CO2 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 CO2	
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. QqQ-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	QqQ-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 (fluorsecence, 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 reqired	Semi-quantitaitve, wide range of sensitivies 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 δ34S and Δ33S 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 ±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.	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 CH4 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 GCMS 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	

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 CO2.	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 CO2 (??)	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 CO2 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 CO2	
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. QqQ-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	QqQ-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 (fluorsecence, 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 reqired	Semi-quantitaitve, wide range of sensitivies 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 δ34S and Δ33S 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 ±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.	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 CH4 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 GCMS 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.