Organic Contamination Baseline Study

In NASA JSC Astromaterials Curation Laboratories

Summary Report

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2012 Organic Contamination Baseline Study

In preparation for OSIRIS-REx and other future sample return missions concerned with analyzing organics, we conducted an Organic Contamination Baseline Study for JSC Curation Laboratories in FY12:

- Compiled a history of JSC Curation collections involving organic laboratory testing from Apollo program to present (over 40 years):
  - Apollo Program and the Lunar Receiving Laboratory
  - Lunar interim curation laboratory and the construction of B31N
  - Xylan contamination in Lunar lab and lessons learned
  - ALH84001 and the Organic Contamination Review Group – Bada committee
  - Genesis Mission and Prospects of Mars Sample Return (1990s)
  - Organic Contamination Results in Gloveboxes from 1998 to 2001 and the Dixon Report
  - Genesis Testing – a Decade of Detailed Organic Testing in an ISO Class 4 Cleanroom
- For FY12 testing, organic baseline study focused only on molecular organic contamination in JSC curation gloveboxes: presumably future collections (i.e. Lunar, Mars, asteroid missions) would use isolation containment systems over only cleanrooms for primary sample storage. This decision was made due to limit historical data on curation gloveboxes, limited IR&D funds and Genesis routinely monitors organics in their ISO class 4 cleanrooms.

2012 Organic Contamination Glovebox Testing

Advanced curation glovebox (ACG) and an Apollo 11 Lunar processing glovebox (LPG) were chosen for molecular organic contamination testing . The test plan was to clean each glovebox with curatorial technical support procedure (TSP) 23: Ultra-Pure Water (UPW) ONLY cleaning. Afterwards, the following tests would be done:

- Liquid particle counts on UPW rinse water from cleaning
- SEM particle identification from UPW rinse filters from cleaning
- TD-GC-MS analysis by Vertical Silicon Wafer Exposure
- TD-GC-MS analysis by Surface Silicon Wafer Exposure
- TD-GC-MS analysis by Absorbent Tube Exposure
- NVR/FT-IR Analysis by Methylene Chloride Surface Exposure (ACG ONLY)
- GC-MS analysis by Methylene Chloride Surface Exposure (ACG ONLY)

Three measurement constraints:

1) Test the difference between a working glovebox (LPG) after being cleaned compared to a cleaned glovebox (ACG) without samples, tools, and supplies.
2) Test current cleaning procedures and the difference of cleaning a glovebox in-situ in the laboratory versus relocating a glovebox to preclean for cleaning.
3) The methylene chloride surface exposure was only done in the ACG due to the remote possibility of contaminating lunar samples.

Lunar Processing Glovebox (LPG)

Possible Known Organic Material Sources:

- Teflon – bags, jars, and fittings
- Nylon – tool bags
- Viton – gaskets
- Polycarbonate – window
- Neoprene – gloves
- Silicone – heat sealer

Note: Lunar sample processing/handling during testing and use of the heat sealer on Teflon bags.

LPG located inside the ISO Class 6 cleanroom environment

Advanced Curation Glovebox (ACG)

Possible Known Organic Material Sources:

- Viton – gaskets
- Hypalon – gloves

Note: Testing with minimal disturbance. No sample processing or tool use during testing.

ACG located inside the ISO Class 5 cleanroom environment

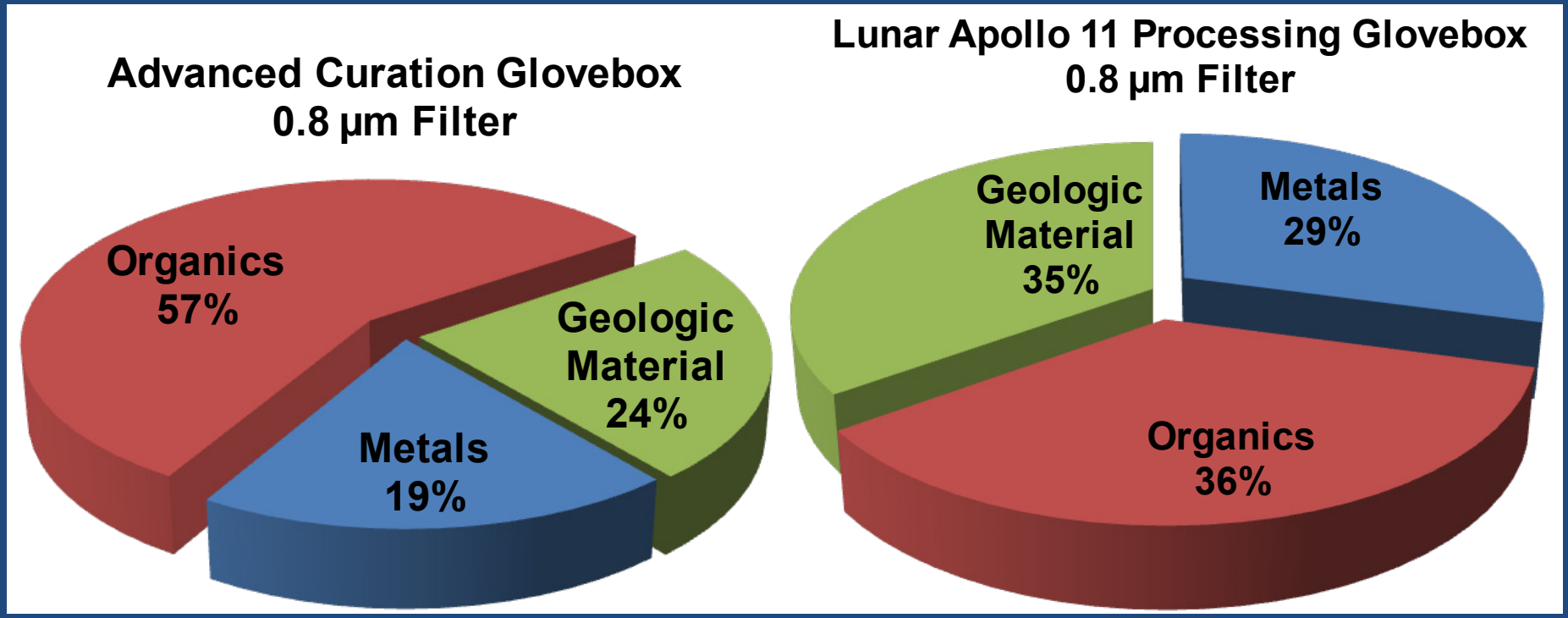
Advanced Curation Glovebox TSP 23 Cleaning							
	UPW Particle Count per 10 ml						
Particle Size (µm)	Genesis Before Control	Rinse 1	Rinse 2	Rinse 3	Final Rinse	Genesis After Control	MIL-STD Level 50
1	27	331.33	104526.33	4412.00	13289.75	45	
3	1	14.00	21167.00	533.33	1806.75	3	
5	1	5.67	6503.33	159.00	707.75	0	5.3
10	1	1.67	492.33	19.00	26.75	0	
25	0	0.33	4.33	0.33	0.50	0	0.34
50	0	0.00	0.00	0.00	0.25	0	
100	0	0.00	0.00	0.00	0.25	0	
150	0	0.00	0.00	0.00	0.25	0	
Note: all counts are averages of measurements.							

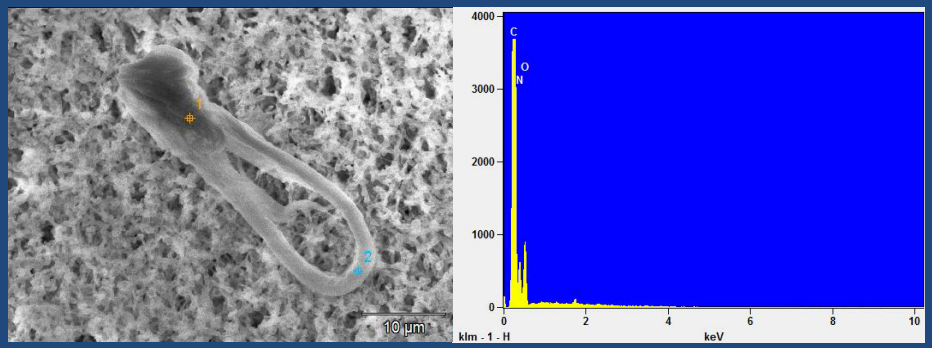
Lunar Glovebox TSP 23 Cleaning							
	UPW Particle Count per 10 ml						
Particle Size (µm)	Genesis Before Control	Lunar UPW Baseline	Rinse 1	Rinse 2	Final Rinse	Genesis After Control	MIL-STD Level 50
1	2	886.40	3622.67	2005.33	1246.60	4	
3	0	54.80	749.67	394.33	128.80	0	
5	0	15.20	340.33	185.67	40.20	0	5.3
10	0	1.60	101.33	47.00	6.20	0	
25	0	0.00	22.00	0.67	0.60	0	0.34
50	0	0.00	19.33	0.00	0.40	0	
100	0	0.00	18.67	0.00	0.40	0	
150	0	0.00	17.00	0.00	0.40	0	
Note: all counts are averages of measurements.							

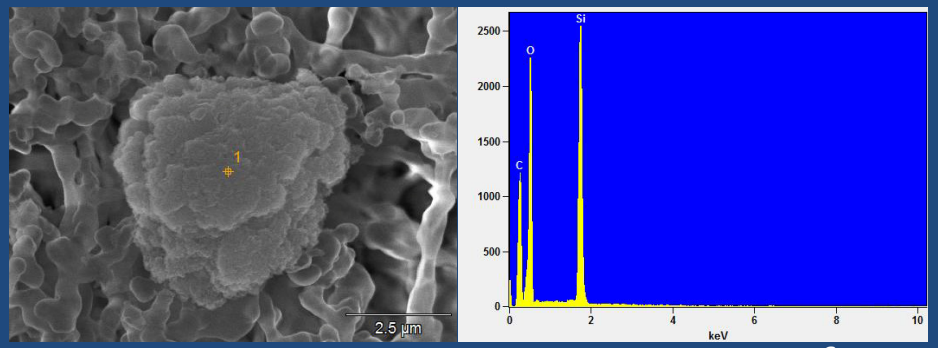
SEM Particle Analysis from Glovebox TSP 23 Cleaning

392 particles were surveyed with over 450 spot analyses

with a low angled backscatter electron (LABe) detector on a JEOL JSM-7600F FE-SEM







TD-GC-MS Analysis Vertical and Surface Silicon Wafer Exposure

Lunar Curation Glovebox			
Hydrocarbons	**Control Wafer (ng/cm²)**	**Vertical Exposure (ng/cm²)**	**Surface Exposure (ng/cm²)**
Low boilers C7-C10	*	*	0.2
Medium boilers >C10-C20	*	1.8	2.5
High boilers >C20	*	0.1	0.2
Sum >= C7	*	1.9	2.9
Identified Compounds			
Diethylformamide	*	*	*
Diethylacetamide	*	*	*
Alkyl amine	*	*	*
2-Butoxyethyl acetate	*	*	*
Octafluoropentanal(m/z:51,69,100,131,151,181,200,231,281)	*	*	*
2-Cyclohexen-1-one, 3,5,5-trimethyl-	*	0.3	0.3
Dibutylformamide	*	0.2	0.2
Cyclo(Me2SiO)6	*	0.2	0.2
2,6-di-tert-Butylquinone	*	*	*
Cyclo(Me2SiO)7	*	*	*
Cyclo(Me2SiO)8	*	*	0.1
Cyclo(Me2SiO)9	*	0.2	0.3
Dibutyl phthalate	*	*	0.1
Cyclo(Me2SiO)10	*	0.1	0.2
Siloxane	*	0.1	0.1
* Recording Limit = < 0.1 ng/cm²			

TD-GC-MS conducted by Air Liquide Electronics Balazs Nanoanalysis , Fremont, CA

Lunar Glovebox TD-GC-MS Results

Identified Chemicals above reporting limit:

- 2-Cyclohexen-1-one, 3,5,5-trimethyl- (Isophorone): solvent used in printing inks, paints, lacquers, adhesives, copolymers, coatings, finishings and pesticides. Also used as a chemical intermediate: ingredient in wood preservatives and floor sealants.

- Dibutylformamide (DBF): additive or reducing agent used in manufacturing of polymers, rubbers, medicines, herbicides, flame retardants in fabrics, solvents, inks, and photo paper.

- Dibutyl phthalate (DBP): plasticizer is found in adhesives, solvents and inks.

- Cyclo(Me2SiO)6
- Cyclo(Me2SiO)8
- Cyclo(Me2SiO)9
- Cyclo(Me2SiO)10
- Siloxane – mainly found in silicone adhesives, etc.

Note: silicones are most likely from heat sealer

TD-GC-MS Analysis Vertical and Surface Silicon Wafer Exposure

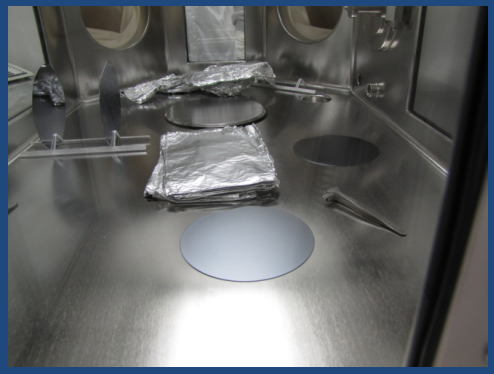
Advanced Curation Glovebox			
Hydrocarbons	**Control Wafer (ng/cm²)**	**Vertical Exposure (ng/cm²)**	**Surface Exposure (ng/cm²)**
Low boilers C7-C10	*	0.4	0.4
Medium boilers >C10-C20	*	7.1	9.6
High boilers >C20	*	1.1	1.8
Sum >= C7	*	8.6	11.8
Identified Compounds			
Dibutylamine	*	*	*
N-Formylpiperidine	*	*	0.1
2-(2-Butoxyethoxy)ethanol	*	0.6	1
Caprolactam	*	0.2	0.6
Tripropylene glycol	*	*	*
Dibutylformamide	*	*	0.1
N,N-Dibutylacetamide	*	*	*
Texanol	*	*	*
Dimethyl phthalate	*	*	*
Diisopropyl adipate	*	*	*
2,6-di-butyl-2,5-cyclohexadiene-1,4-dione	*	*	*
2,6-di(t-butyl)-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one	*	*	*
Cyclo(Me2SiO)7	*	*	*
Diethyl phthalate	*	0.2	0.3
TXIB	*	0.3	0.3
Piperidine, 1,1'-carbonylbis-	*	*	*
Cyclo(Me2SiO)8	*	0.3	0.5
Tri(2-chloroethyl) phosphate	*	0.2	0.2
Benzenesulfonamide, N-butyl- + 3,5-di-tert-Butyl-4-hydroxybenzaldehyde	*	*	*
Benzenesulfonamide, N-butyl-	*	*	*
Isopropyl Myristate	*	*	*
Diisobutyl phthalate	*	0.1	0.1
Cyclo(Me2SiO)9	*	*	0.1
Dibutyl phthalate	*	0.5	0.6
C17-C22 Hydrocarbon	*	*	0.1
* Recording Limit = < 0.1 ng/cm²			

TD-GC-MS conducted by Air Liquide Electronics Balazs Nanoanalysis , Fremont, CA

Advanced Curation Glovebox TD-GC-MS Results

Identified Chemicals above reporting limit:

- N-Formylpiperidine – solvents
- 2-(2-Butoxyethoxy)ethanol – solvents/paints
- Caprolactam – Nylon-6
- Dibutylformamide (DBF) – rubber/polymer additive
- Diethyl phthalate (DEP) – plasticizer
- TXIB – plasticizer
- Tri(2-chloroethyl) phosphate – flame retardant in plastics
- Dibutyl phthalate (DBP) – plasticizer
- Diisobutyl phthalate (DIBP) – plasticizer
- Cyclo(Me2SiO)8 – silicones
- Cyclo(Me2SiO)9 – silicones
- C17-C22 Hydrocarbon



TD-GC-MS Analysis Adsorbent Stainless Steel Tube Exposure

Lunar Curation Glovebox		
Hydrocarbons	**Control Blank (ng/L)**	**TD-GC-MS Results (ng/L)**
Low boilers C7-C10	*	1.2
Medium boilers >C10-C20	*	3.8
High boilers >C20	*	*
Sum >= C7	*	5
Identified Organic Compounds		
Cyclo(Me2SiO)3	*	*
Ethylbenzene	*	*
m,p-Xylene	*	*
o-Xylene	*	*
Cyclo(Me2SiO)4	*	0.2
Cyclo(Me2SiO)5	*	*
Methylnaphthalene	*	*
Chlorodecane	*	0.3
C12-C16 Hydrocarbons	*	0.3
* Reporting Limit = < 0.1 ng/L		

Advanced Curation Glovebox		
Hydrocarbons	**Control Blank (ng/L)**	**TD-GC-MS Results (ng/L)**
Low boilers C7-C10	*	0.6
Medium boilers >C10-C20	*	18.8
High boilers >C20	*	0.1
Sum >= C7	*	19.5
Identified Organic Compounds		
Methyl methacrylate	*	*
Cyclo(Me2SiO)3	*	*
Cyclo(Me2SiO)4	*	*
Limonene	*	*
C3 benzene	*	*
C10-C14 Hydrocarbon	*	0.2
C16-C20 hydrocarbon	*	16.8
* Reporting Limit = < 0.1 ng/L		

TD-GC-MS conducted by Air Liquide Electronics Balazs Nanoanalysis , Fremont, CA

TD-GC-MS Analysis Adsorbent Results

- Organics in air results provides a better understanding of the organic cleanliness of the gaseous nitrogen environment and sometimes provides a better Volatile Organic Compound (VOC) load.
- Hydrocarbon load in the LCG is much lower when compared with the ACG. This difference is unknown. However, the hydrocarbon load in the advanced curation glovebox could be indicative of unclean piping infrastructure in B31 compared to nitrogen piping infrastructure in B31N.
- LCG has 0.2 ng/L of Cyclo(Me2SiO)4 ; silicone outgassing
- LCG has 0.3 ng/L of chlorodecane which is a plasticizer indicative of outgassing rubber.
- Cyclo(Me2SiO)4 and chlorodecane: possibly heat sealer with silicone rubber strip.

ISO-AMC air cleanliness class ISO 14644-8

ISO-AMC Class	TVOC Concentration (ng/m^3)
0	10^9
– 1	10^8
– 2	10^7
– 3	10^6
– 4	10^5
– 5	10^4
– 6	1000
– 7	100
– 8	10
– 9	1
– 10	0.1
– 11	0.01
– 12	0.001

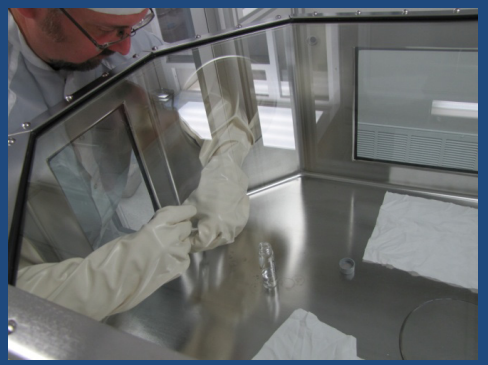
LCG hydrocarbons = 5000 ng/m^3

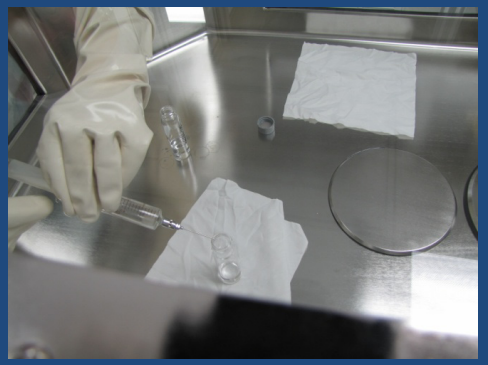
ISO-AMC = – 5 (10^4 ng/m^3)

ACG hydrocarbons = 19500 ng/m^3

ISO-AMC = – 4 (10^5 ng/m^3)

Surface Methylene Chloride Exposure NVR/FT-IR Results





No significant infrared absorption bands

- C-H stretching absorption bands (2958, 2927, and 2856 cm^{-1})
- Carbonyl stretching absorption band (1732 cm^{-1})
- Aromatic ring mode absorption bands (1600 and 1580 cm^{-1})
- C-H bending absorption band (1461 cm^{-1})
- C-H umbrella mode absorption band (1379 cm^{-1})
- C-C-O stretching absorption band (1287 cm cm^{-1})
- O-C-C stretching absorption band (1126 cm^{-1})
- C-H in-plane bending absorption band (742 cm cm^{-1}), which is typical for a dialkyl phthalate (e.g. diheptyl or dioctyl phthalate).

These results show the presence of aromatic hydrocarbons. The carbonyl can be interpreted as indicative of some organometallic complexes. However, the interpretation of the presence of Dialkyl phthalate is a common group of chemical associated with plasticizers mainly in the manufacturing of PVC. This interpretation of the results matches closely with the GC-MS analysis.

NVR/FT-IR conducted by Air Liquide Electronics Balazs Nanoanalysis , Fremont, CA

Surface Methylene Chloride Exposure: GC-MS Results

- 2-Chloro-Ethanol, Phosphate (3:1) or TCEP – $C_9H_{15}O_6P$
  TCEP is commonly used as a reducing agent in biochemistry and in detergents. Also widely used as a flame retardant and manufacturing of PVC vinyl, electronics, adhesives, upholstery, carpeting, rubber, plastics, paints, and varnishes.

- +N-Butylbenzenesulphonamide or NBBS – $C_{10}H_{15}NO_2S$
  NBBS is widely used as a plasticizer in industrial chemicals and drugs. NBBS also has antifungal properties and commonly used on agricultural fields for over 30 years.

- Bis(2-Ethylhexyl) Phthalate (DOP) or DEHP – $C_{24}H_{38}O_4$
  DEHP is a common plasticizer in many plastics manufacturing and most common in the outgassing of PVC type materials. DEHP is widely found in the environment and municipal water supplies in low levels from manufacturing of PVC.

- +1, 2-Benzenedicarboxylic Acid, Dinonyl Ester or DNP – $C_{26}H_{42}O_4$
  DNP is commonly used as an additive to impart flexibility in PVC resins and as an additive in lubricating oils. DNP has also been used in the manufacturing of thermoplastics, rubbers, paints and adhesives.

GC-MS conducted by Air Liquide Electronics Balazs Nanoanalysis , Fremont, CA

SUMMARY

- Hydrocarbons, plasticizers, silicones, and rubbers are found in JSC cleanrooms and gloveboxes.
- It is difficult to trace specific sources given that these additives are used in many different types of manufacturing.
- In some cases, it is unclear if some of these detected organics are from inside the lab or from the background environment (e.g. common plasticizers released into the Houston air and not filtered through the ULPA).
- In some cases, it is unclear if some of these detected organics are from human interaction inside the lab (e.g. soaps, perfumes, nail polish).
- If more of an organic free environment is determined a requirement for future sample return missions, more can be done on choosing better materials as well as modifying current handling and cleaning procedures.
- Final written report (NASA STI) will have detailed information on the history of mitigating organic contamination and recommendation for the future of curation involving organic contamination (pending end of FY13).
- Secured 2nd year FY13 funding to conduct focused organic cleaning studies to reduce organic contamination found by the baseline study, update current procedures, and research industry's state-of-the-art cleaning technologies.