ORGANIC CONTAMINATION BASELINE STUDY ON NASA JSC ASTROMATERIAL CURATION GLOVEBOXES.
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Introduction: Future planned sample return missions to carbon-rich asteroids and Mars in the next two decades will require strict handling and curation protocols as well as new procedures for reducing organic contamination. After the Apollo program, astromaterial collections have mainly been concerned with inorganic contamination [1-4]. However, future isolation containment systems for astromaterials, possibly nitrogen enriched gloveboxes, must be able to reduce organic and inorganic cross-contamination. In 2012, a baseline study was orchestrated to establish the current state of organic cleanliness in gloveboxes used by NASA JSC astromaterials curation labs that could be used as a benchmark for future mission designs [5].

Organic Testing: Two nitrogen enriched gloveboxes were chosen for organic testing: Lunar Curation Glovebox (LCG), Apollo 11 processing cabinet #307-41 in an ISO class 6 cleanroom and the Advanced Curation Glovebox (ACG) in an ISO class 5 cleanroom. The LCG was manufactured with 316L stainless steel, glass and polycarbonate (Lexan) windows, viton gaskets, and neoprene gloves. LCG also contained teflon bags, fittings, jars, nylon tool bags, and a silicone strip on the heat sealer for sealing sample bags. The ACG was manufactured with 304 stainless steel (electropolished), glass viewing windows, viton gasket seals, and four hypalon gloves.

Several tests were performed inside the gloveboxes to assess organic cleanliness:

- TD-GC-MS analysis by vertical silicon wafer exposure (24-hrs vertical)
- TD-GC-MS analysis by surface silicon wafer exposure (23.75 hrs vertical + 15 min. surface)
- TD-GC-MS analysis by adsorbent tube exposure (6 hrs, 100mL/min. flow rate)
- NVR/FT-IR analysis by methylene chloride surface exposure (ACG only)
- GC-MS analysis by methylene chloride surface exposure (ACG only)

Prior to testing, the LCG and ACG were cleaned with heated ultra-pure water (UPW) by JSC curation procedure TSP 23. The ACG was tested empty with little disturbance of main chamber and the LCG was tested during nominal Lunar material processing operations, which included heat sealing Teflon sample bags.

Results: Table 1 and 2 provide thermal desorption gas chromatography mass spectrometry (TD-GC-MS) results from silicon wafer exposure and do not include the identified organic compounds below the reporting limit (< 0.1 ng/cm^2).

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
Compounds			
2-Cyclohexen-1-one, 3,5,5-trimethyl-	*	0.3	0.3
Dibutylformamide	*	0.2	0.2
Cyclo(Me2SiO)6	*	0.2	0.2
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			

Table 1: LCG TD-GC-MS 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
Compounds			
N-Formylpiperidine	*	*	0.1
2-(2-Butoxyethoxy)ethanol	*	0.6	1
Caprolactam	*	0.2	0.6
Dibutylformamide	*	*	0.1
Diethyl phthalate	*	0.2	0.3
TXIB	*	0.3	0.3
Cyclo(Me2SiO)8	*	0.3	0.5
Tri(2-chloroethyl) phosphate	*	0.2	0.2
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			

Table 2: ACG TD-GC-MS silicon wafer exposure

LCG results include: 2-cyclohexen-1-one, 3,5,5-trimethyl- (Isophorone), a solvent; dibutylformamide (DBF), an additive or reducing agent used in manufacturing of polymers, rubbers, and solvents; and dibutyl phthalate (DBP), a plasticizer. The cyclo(Me2SiO)x and siloxane are mainly found in silicone adhesives, however, the most likely source is silicone rubber outgassing from heat sealing.

ACG results include: N-formylpiperidine, a solvent; 2-(2-butoxyethoxy)ethanol, a solvent; caprolactam, nylon-6; dibutylformamide (DBF), rubber/polymer additive; diethyl phthalate (DEP), a plasticizer; TXIB, a plasticizer; tri(2-chloroethyl) phosphate, flame retardant in plastics; dibutyl phthalate (DBP), a plasticizer; diisobutyl phthalate (DIBP), a plasticizer; and cyclo(Me2SiO)8 and 9, silicones.

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
Compounds		
Cyclo(Me2SiO)4	*	0.2
Chlorodecane	*	0.3
C12-C16 Hydrocarbons	*	0.3
* Reporting Limit = < 0.1 ng/L		

Table 3: LCG TD-GC-MS adsorbent tube exposure

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
Compounds		
C10-C14 Hydrocarbon	*	0.2
C16-C20 hydrocarbon	*	16.8
* Reporting Limit = < 0.1 ng/L		

Table 4: ACG TD-GC-MS adsorbent tube exposure

Table 3 and 4 provide the TD-GC-MS results from adsorbent tube exposure. This test offers a better understanding of the volatile organic compounds inside the gloveboxes and the relative purity of the class C nitrogen gas. Based on the hydrocarbon load, the gloveboxes can be classified as ISO-AMC air cleanliness: LGC = - 5 and ACG = - 4.

ACG nonvolatile residue Fourier transform infrared (NVR/FT-IR) spectroscopy surface test results show absorption bands: C-H stretching at 2958, 2927, and 2856 cm^{-1}, aromatic hydrocarbons; carbonyl stretching at 1732 cm^{-1}, possible organometallic complexes; aromatic ring mode at 1600 and 1580 cm^{-1}; C-H bending at 1461 cm^{-1}; C-H umbrella mode at 1379 cm^{-1}; C-C-O stretching at 1287 cm^{-1}; O-C-C stretching at 1126 cm^{-1}; and C-H in-plane bending at 742 cm^{-1}, possibly dialkyl phthalate, a plasticizer.

ACG GC-MS surface test results show 2-chloro-ethanol, phosphate (3:1) (TCEP), common reducing agent; +N-butylbenzenesulphonamide (NBBS), plasticizer; bis(2-ethylhexyl) phthalate (DEHP), plasticizer; and +1, 2-benzenedicarboxylic acid, dinonyl ester (DNP), additive in rubbers, paints and adhesives.

Discussion: All test results indicate that LCG is organically cleaner than the ACG. This is probably a result of an early Lunar degreasing procedure conducted on LCG that used pressurized Freon 113 and 2% nitric acid wash while ACG was never degreased. The hydrocarbons, plasticizers and silicones are commonly found in cleanrooms from offgassing and particle shedding of plastics and adhesives used in the facility. The solvents found are common in inks, paints, lacquers, adhesives, copolymers, coatings, finishings, pesticides, wood preservatives and floor sealants as well as some personal hygiene products.

Summary: Future robotic and human spaceflight missions to the Moon, Mars, asteroids and comets can use these data as a benchmark for developing new organic cleanliness protocols and procedures for isolation containment systems and cleaning technology to preserve the scientific integrity of all future samples.

Reference: [1] Allen C.C. et al. (2011) *Chemie der Erde Geochem.* 71(1), 1-20; [2] Allton J.H. (1998) *LPS XXIX*, 1857; [3] Allton J.H. et al. (2012) *LPS LXXIV*, 2439; [4] Righter K. et al. (2008), *Meteoritics & Planet. Sci.*, 43, A189; [5] Calaway M.J. et al. (2013) *LPS XLIV*, 1241.

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