Supercritical CO_2 Cleaning for Planetary Protection and Contamination Control

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Abstract—We have designed and built a prototype Supercritical CO_2 Cleaning (SCC) system at JPL. The key features of the system are: 1) the parts inside a high-pressure vessel can be rotated at high speeds; 2) the same thermodynamic condition is maintained during First-In First-Out flushing to keep solvent power constant; and 3) the boil-off during decompression is induced in a separate vessel downstream. Our goal is to demonstrate SCC's ability to remove trace amounts of microbial and organic contaminants down to parts per billion levels from spacecraft material surfaces for future astrobiology missions. The initial cleaning test results showed that SCC can achieve cleanliness levels of 0.01 $\mu g/cm^2$ or less for hydrophobic contaminants such as dioctyl phthalate and silicone and it is less effective in the removal and inactivation of the hydrophilic bacterial spores as expected. However, with the use of a polar co-solvent, the efficacy may improve dramatically. The same results were obtained using liquid CO_2. This opens up the possibility of using subcritical cleaning conditions, which may prove to be more compatible with certain spacecraft hardware.

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1. INTRODUCTION

Astrobiology mission plans are incorporating instrument technology with very high sensitivity for bio-organic compounds. For example, instruments on the Mars Science Laboratory (MSL) are capable of detecting target organic molecules in Martian samples. The goal is to detect organics at parts per billion levels (nanograms of analyte per gram of soil).

Conventional cleaning methods include sterilization, high temperature baking, vapor degreasing, and wiping. Sterilization methods are intended for killing live microorganisms. Alcohol wiping and liquid sonication reduce the bio-burden on surfaces. Both may leave remnants of dead or live microbes, or other residues, on surfaces, posing risk of cross contamination of extraterrestrial samples. Wiping is ineffective in cleaning parts with complex geometry. Vapor degreasing is not as effective at removing medium or low molecular weight hydrophilic biomolecules of relevance to astrobiology.

To address the new bio-organic cleanliness requirements, we are developing an innovative new cleaning technology that will support the current Planetary Protection requirements and will facilitate future spacecraft contamination control requirements. This will provide additional technology needed to achieve the science goal of detecting very low levels of extraterrestrial materials in samples without significant risk of interference by terrestrial contaminants carried from Earth.

Supercritical CO_2 precision cleaning has been proven to be a viable method in the manufacturing environment for cleaning common oil, grease, and hazardous solvents [1]. We adapt this precision cleaning technology to clean bacteria and organic molecules from small to medium sized parts with complex geometry in order to meet the flight instrument science requirements. The critical point of CO_2 is moderately at $T = 31$ C and $P = 1070$ psi. In a typical application region of $32 < T$ and $1{,}070 < P < 3{,}500$ psi, supercritical CO_2 fluid has high density, high diffusivity and low viscosity, and tremendous solvent properties regarding non-polar molecules. It is able to spread out along a surface because of its negligible surface tension, dissolve the non-polar molecules, and remove them from the surface even if it has an intricate geometry. In this paper, we present the design and development of our prototype SCC system, SCC cleaning procedures, and preliminary cleanliness results of several known contaminants.

2. SCC SYSTEM AND PROCEDURES

We have designed and built a prototype SCC system as shown in Fig. 1. The main components of our prototype system are: a) high-pressure cleaning vessel V_{clean}, b) boil-off vessel V_{boil} located downstream from the cleaning vessel, c) syringe type high-pressure pump subsystem, d) heat exchanger, and e) Back Pressure Regulator (BPR).

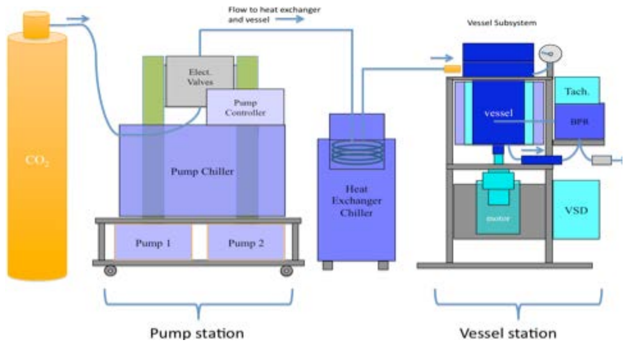

Figure 1 – Schematic SCC system setup with scales in proportion.

Our cleaning procedures follow the steps of soaking, flushing, and decompression. After soaking the parts to be cleaned in V_{clean} for a period, the CO_2 with contaminants are flushed out of V_{clean} using pure CO_2 in a way of First-In-First-Out. The contaminants are trapped in a filter subsystem and used CO_2 is vented out into air via a fume hood.

The main features of our SCC system and procedures are,

(1) The parts to be cleaned are secured in a basket inside V_{clean} as shown in Fig. 2. The basket can be rotated up to a very high speed by a magnetically coupled drive. The fluid flows within the vessel, generated by the centrifugal force, will rub parts' surfaces, enhancing the cleaning effectiveness and shorten the soaking time.

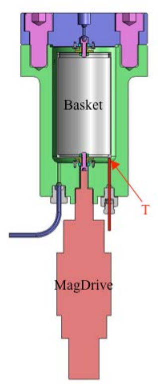

Figure 2 – Expanded view of V_{clean}

(2) During the FIFO flushing, the pump subsystem pushes pure CO_2 into V_{clean} at a constant flow rate while the BPR regulates the pressure in V_{clean} by controlling the needle position in an outlet valve.

(3) The fresh CO_2 gas flows through the heat exchanger at a given temperature before entering V_{clean}. The heat exchanger also pumps temperature regulated fluid to the coils surrounding V_{clean} and V_{boil} to lessen the PID controls loads that use electrical heaters for quick response. A PRT thermometer reads the V_{clean} interior temperature as shown in Fig. 2 that can be controlled precisely at $5 \leq T \leq 40$ C. As a result, T_{clean} remains constant during the FIFO flushing.

(4) Because both T_{clean} and P_{clean} remain unchanged during FIFO flushing, the solvent power remains unchanged, thus minimizing contaminants left behind.

(5) During decompression from liquid CO_2, $T_{boil} \sim T_{sat}(P) > T_{clean}$ prevents bubbles from generated in V_{clean} that could stir up the contaminants sank to the bottom by gravity.

(6) The parts to be cleaned are prepared by first baking at a high temperature to remove any residues from the surface. For hydrophobic contaminations, such as Dioctyl Phthalate (DOP) and Silicone, known concentrations prepared in solutions of dichloromethane and deposited by syringe onto the parts in predetermined amounts. The dichloromethane evaporates leaving the contaminant on the part surface.

(7) After cleaning, parts are prepared for analysis by rinsing the surface with the appropriate amount of dichloromethane there by removing any remaining contaminant from the surface. The rinse is collected and analyzed using Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy. FTIR provides chemical functional group information for quantitative analysis and qualitative identification of materials [2-5]. So the parts cleanliness using SCC method can be verified for the flight instrument science requirements.

3. Results

We prepared aluminum coupons with several known contaminants. For each contaminant, clean coupons are kept as a baseline for analysis. Three clean control coupons were placed in the basket together with three contaminated coupons during the cleaning process for statistical purpose. After the cleaning vessel was sealed and pressurized with pure CO_2 to either supercritical or liquid state, the coupons were soaked for an hour either with or without the basket rotated. Then the cleaning vessel was FIFO-flushed out with pure CO_2 at the same temperature and pressure. It was followed by a decompression process slow enough to make sure that the interior temperature was not too cold due to the Joule-Thomson effect. To prevent bubbles from generated in V_{clean} during decompression that could stir up the contaminants sank to the bottom by gravity, the decompression path never crossed the saturated vapor pressure curve for supercritical CO_2. For decompression from liquid CO_2, the temperature of the boil-off vessel T_{boil} was kept slightly higher than $T_{sat}(P)$ while maintaining $T_{clean} < T_{sat}(P)$. Hence, most of the bubbles formed in the boil-off vessel.

Table 1 shows the results of cleaning Dioctyl Phthalate (DOP) off the pre-contaminated coupons. Two sets of coupons, one with 1.2 μg/cm^2 and another with 12.6 μg/cm^2 DOP, were placed inside the basket together with a set of clean control coupons. Two different runs were carried out, one in supercritical CO_2 and one in liquid CO_2. The basket was not rotated in either run. The coupons cleaned with both SCC and liquid CO_2 had the cleanliness levels that meet the current flight-hardware cleaning requirement [4]. The set of clean coupons had same residue as the cleaned ones, indicating a cross contamination in the same solvent. Table 2 shows the results of cleaning silicone off pre-contaminated coupons in the identical runs as done for the DOP contaminants. The same satisfactory cleanliness was obtained.

Table 1. Test results for DOP using both SCC and liquid CO_2.

Sample (Coupons)	Chemical Functional Group	Amount ($\mu g/cm^2$)
Clean - Control	Trace AHC	< .01
Low DOP Positive Control	DOP, AHC	1.2
High DOP Positive Control	DOP, AHC	12.6
Supercritical CO_2		
Light DOP 1	Trace DOP, AHC	~ .02
Light DOP 2	Trace DOP, AHC	~ .02
Light DOP 3	Trace DOP, AHC	~ .02
Heavy DOP	Trace DOP, AHC	~ .02
Heavy DOP	Trace DOP, AHC	~ .02
Heavy DOP	Trace DOP, AHC	~ .02
Liquid CO_2		
Light DOP 1	Trace AHC	< .01
Light DOP 2	Trace AHC	< .01
Light DOP 3	Trace AHC	< .01
Heavy DOP	Trace AHC	< .01
Heavy DOP	Trace AHC	< .01
Heavy DOP	Trace AHC	< .01

We also prepared the coupons contaminated with 1.1 $\mu g/cm^2$ L-Cysteine. As expected, neither SCC nor liquid CO_2 had any effect on cleaning L-Cysteine off the pre-contaminated coupons.

Another set of experiments was conducted to determine if SCC or liquid CO_2 can clean or inactivate spores deposited on aluminum coupons. The coupons were each inoculated with approximately 6.2×10^5 *Bacillus atrophaeus* spores. Preliminary results show SCC and liquid Co_2 are ineffective in the removal of the hydrophilic bacterial spores even the basket with coupons in it was rotated at a very high speed.

4. Conclusion

A new cleaning method using supercritical CO_2 has been developed in a prototype to face the new challenges of continuously improving instrument sensitivity for bio-molecule detection. Supercritical CO_2 was used as both solvent and carrier for removing organic and particulate contaminants. The cleaning test results showed that the supercritical CO_2 cleaning method can achieve a cleanliness of 0.01 $\mu g/cm^2$ or less for hydrophobic contaminants such as dioctyl phthalate (DOP) and silicone [5]. This level of surface cleanliness will meet the current working guideline for hardware that will be in direct contact with the extraterrestrial sample. Since the supercritical and liquid CO_2 were both highly effective at cleaning and removing the DOP and silicone contaminants, it opens up the possibility of using subcritical cleaning conditions, which may prove to be more compatible with certain spacecraft hardware.

None of the first three spore experiments showed any significant reduction in the number of spores remaining on the aluminum coupons.

Once it is proved to be efficient at cleaning spacecraft and instrument surfaces that are incompatible with other solvents, it can be incorporated as an in-situ cleaning or extraction method for future Mars missions since 95% of the Martian atmosphere is CO_2.

As expected, preliminary results show that this technique is less effective in the removal and inactivation of the hydrophilic bacterial spores. Further tests will be performed with the use of a polar co-solvent and the efficacy may improve dramatically.

5. Acknowledgments

The research described in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration. We acknowledge David Jackson from Cool Clean Technologies Inc for his knowledgeable suggestions in constructing the SCC cleaning apparatus.

Table 2. Test results for silicone using both SCC and liquid CO_2.

Sample (Coupons)	Chemical Functional Group	Amount ($\mu g/cm^2$)
Clean - Control	Trace AHC	< .01
Silicone (low) Positive Control	Silicone, Trace AHC	0.8
Supercritical CO_2		
Silicone (low) 1	Trace Silicone, Trace AHC	< .01
Silicone (low) 2	Trace Silicone, Trace AHC	< .01
Silicone (low) 3	Trace Silicone, Trace AHC	< .01
Liquid CO_2		
Silicone (low) 1	Trace Silicone, Trace AHC	< .01
Silicone (low) 2	Trace Silicone, Trace AHC	< .01
Silicone (low) 3	Trace Silicone, Trace AHC	< .01

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[1] Supercritical Carbon-dioxide Cleaning Technology Review, http://www.pprc.org/pubs/techreviews/CO2/co2intro.html

[2] M. S. Anderson et al "Analysis of Semi-Volatile Residues Using Diffuse Reflectance Infrared Fourier Transform Spectroscopy" in Optical System Contamination: Effects, Measurements, and Control VII; July 2002, edited by Phillip T. C. Chen and O. Manuel Lee; Proceedings of the SPIE, Vol. 4774, pp. 251-261, (2002).

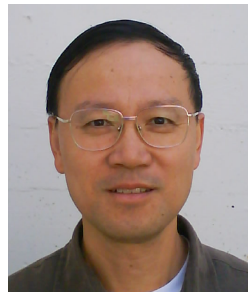
[3] The solvent blanks are less than 10% the amount in the sample and this is subtracted from the reported sample amount. High blanks (greater than 10% of the sample) are noted in the report. A typical solvent rinse has a detection limit of ~0.005 μg/cm^2 of removed residue from a 100cm^2 sample. Note this limit is well below the adventitious carbon level (ref. 5). Lower limits are possible using modified methods.

[4] The analysis conforms to the Institute of Environmental Science and Technology (IEST), Contamination Control Division Document IEST 1246D "Product Cleanliness Levels and Contamination Control Program". The contamination limits are generally set by Contamination Control Engineering. At typical limit is "Level A" (IEST-STD-CC1246D) and this is 1 microgram per square centimeter (μg/cm^2) and this corresponds to an average film thickness of 100 angstroms (assuming a density of 1.0). In many cases more stringent limits apply.

[5] Very clean surfaces, ≤0.02 μg/cm^2, with mono-molecular layers or less are more complex to describe when cleaning or analyzing. Carbon/hydrocarbon based substances are known to rapidly (within ~1 hour) accumulate on most, if not all, freshly exposed surfaces. H. Piao and N. S. McIntyre, "Adventitious carbon growth on aluminum and gold–aluminum alloy surfaces", *Surface and Interface Analysis*, 2002; 33: 591–594.

BIOGRAPHY

Dr. Ying Lin is currently a Planetary Instrument Development Manager at JPL Planetary Science Instrument Development Office. She manages JPL's planetary science instrument research work funded by NASA. She is also a senior member technical staff at JPL's biotechnology and planetary protection group. She has extensive research experiences in biotechnology and instrument development. She is the PI and Co-I of several proposals funded by JPL and NASA on planetary protection and biosensor development tasks. She has been the technical lead of planetary protection technology development for NASA Mars Technology Program since 2004.



Dr. Fang Zhong is a Research Technologist at Jet Propulsion Laboratory in the Applied Low Temperature Physics group. He has over twenty six years of experience in cryogenics, especially high precision measurements in condense matter physics below liquid helium temperature. He has extensive research experience in the critical phenomena near liquid-vapor critical point with 19 publications covering the experimental measurements, computer simulation, and theoretical analysis in the field. He has supported various research and space flight projects at JPL, such as Low Temperature Physics Facility for International Space Station and the measurements of physical properties of cryogenic icy compositions for icy satellites.

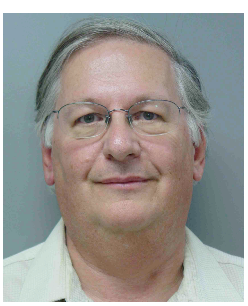
David C. Aveline is a Research Technologist in the Quantum Sciences and Technology Group at Caltech's Jet Propulsion Laboratory. In 2002, he received a Bachelor of Science in Applied and Engineering Physics from Cornell University in Ithaca, NY. He later received his Master's degree from the University of Southern California, where he is completing his Ph.D. in the field of Atomic, Molecular and Optical Physics. His research has included laser cooling and trapping of neutral atoms, Bose-Einstein condensation, and cold atom interferometry. In recent years, he has also worked with JPL's Optical Communications and Biotechnology and Planetary Protection Groups. He has extensive experience designing and building laboratory instruments with technical expertise in the areas of optics, electronics, vacuum and cryogenic systems, and biotechnology. David Aveline is a member of the American Physical Society (APS) and Optical Society of America (OSA).

Mark S. Anderson is a senior chemist at the Jet Propulsion Laboratory in the Analytical Chemistry Laboratory and Materials Development group. He has over twenty five years of experience in providing chemical analysis and consultation for various research and space flight projects. Mark is a highly cited expert in Vibrational Spectroscopy and Scanning Probe Microscopy. Mark was a Co-Investigator and member of the science team on the Mars Environmental Compatibility Assessment Experiment project that developed the flight atomic force microscope on the Phoenix 07 mission to Mars. Mark's work with the

Galileo project led to the discovery of both peroxide and sulfuric acid on Europa with the resulting publications in the journal Science.

Shirley Y. Chung is currently providing contamination control engineering support to the Advanced Mirror Development Project at the Jet Propulsion Laboratory. She supported the contamination control effort to the Mars Science Laboratory project, focusing on Sample Acquisition / Sample Processing and Handling (SA/SPaH). Shirley also have extensive planetary protection implementation experience in various Mars flight projects including Mars PathFinder, MSP'98 Lander and Payloads, Mars Microprobe DS2, Mars'01, Mars Exploration Rover, and Mars Reconnaissance Orbiter. In addition to flight project work, she was involved in various R&D tasks such as using vapor hydrogen peroxide (VHP) as an alternative method to "sterilize" spacecraft hardware, materials compatibility study with VHP, biological cleaning efficiency studies, and organics cleaning study for the Mars Science Laboratory project.

Jerami Mennella is a chemist at the Jet Propulsion Laboratory in the Analytical Chemistry Laboratory and Materials Development group. He performs chemical and imaging analysis for various research and space flight projects. He has worked extensively supporting molecular and particulate contamination investigations on projects such as Dawn, Wise, OCO, Aquarius, M3 and MSL. Jerami has also developed techniques for 3D surface characterization utilizing conoscopic holography, digital microscopy and x-ray imaging. He has provided critical surface metrics for projects such as Dawn, MSL and the Hypervelocity Impact Facility at Cal Tech.



Wayne Schubert is a research scientist in the Biotechnology and Planetary Protection Group at the Jet Propulsion Laboratory. He is currently investigating new and traditional sterilization technologies useful for spacecraft applications, including dry heat microbial reduction and electron beam irradiation. Wayne oversees a task dedicated to archiving microbes relevant to space missions. He has participated in two radiation biology experiments flown aboard the space shuttle and conducted radiation biology experiments using the nematode *C. elegans* at the high energy particle accelerators of Lawrence Berkeley National Laboratory and Brookhaven National Laboratory. He holds BS and MS degrees from California State University, Northridge.