



TAGSAM blowby test Contamination Knowledge Report (draft)

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Summary

On January 19, 2017 a test firing of a flight spare TAGSAM pyro valve and N₂ bottle was carried out to collect and characterize particles and volatiles entrained in the gas for contamination knowledge. Optical imaging of a Teflon filter used to collect particulate blowby debris showed that it was penetrated by a number of large (hundreds of micrometers) impactors. Two large metal grains (1 mm) were also recovered. Numerous 1 – 50 micrometer particles are embedded into the filter surface but they comprise a small fraction of the particulate mass. The largest metal fragment and a sub-sampling of the small particles on the Teflon filter are composed of stainless steel (~99% by number). The N₂ gas collected in the blowby test was measured for abundances of 100 trace molecular species. With the exception of a few compounds attributed to pre-cleaning of the gas plumbing, no volatile contaminants were above ~ppm detection limits.

The greatest sample science concern from these results is the unexpectedly large mass of stainless steel entrained in the N₂ gas. These observations suggest that macroscopic fragments of stainless steel may be directly injected at high speed into the collected sample. Although stainless steel is easily distinguished from asteroidal materials, the accuracy of bulk chemical measurements of regolith could be adversely impacted by the presence of stainless steel fragments. A positive finding is that the particulate contamination is almost exclusively composed of a single material that is a major component of the TAGSAM. Moreover the absence of any detectable volatile molecular contamination attributable to the pyro valve firing is a welcome surprise.

Recommendation

It will be important to determine the minor and trace element abundances of the stainless steel collected to allow for accurate corrections to future bulk chemical measurements. Although we did not identify any obvious pyro chemical products, carbonaceous particles may have been difficult to distinguish on the Teflon filter substrate. The science team requests a description of the type of pyro used in the TAGSAM to validate these findings.

Introduction

Firing of pyrotechnic valves to initiate N₂ gas flow during sample collection is a potential contamination risk. This is due to the possibility of that combustion products from the discharged pyrotechnics and other particulate debris will be directly injected into the sample and TAGSAM interior. Discharged pyro valves may produce an array of organic compounds of potential scientific importance in asteroidal materials. Organic and inorganic particles generated and mobilized by the pyro valve firing and high pressure nitrogen flow also pose a potential science risk. Since the blowby debris and pyrotechnic combustion products may be intimately mixed with the sample at microscopic levels, it is important to determine the composition of this material for contamination knowledge. Due to the unique design and construction of the TAGSAM and lack of useful literature data on pyro valve blowby, the needed contamination knowledge could only be obtained by a test firing under carefully controlled conditions.

TAGSAM blowby test setup

The TAGSAM blowby test apparatus consisted of a flight spare N₂ bottle and pyrovalve fed to stainless steel tubing and a 6L evacuated gas collection bottle. A Teflon filter was placed in line to collect particulate debris. A Teflon filter was used here because Millipore filters could not survive the high pressure N₂ gas flow. All components were precision cleaned at LM at the individual component level using a detailed multi-step process and were validated to be clean to a level of 50A/2. The main cleaning solvent used was IPA. The gas collection bottles were pre-cleaned at JSC using well-established procedures that result in sub-ppm blank levels for target volatiles. The gas bottles were evacuated, baked, purged, and evacuated. As a final step, a tracer gas was introduced to improve quantification of later gas measurements. For this test, gas samples included the following:

- N₂/He from the source K-bottle
- N₂ taken through the flight loading system
- N₂ taken through the flight loading system and qual bottle heated for 24 hours prior to transfer
- N₂ captured during the blowby test

CK analysis methods

Gas collection bottles were delivered directly to the JSC Toxicology and Environmental Chemistry group for analysis. Volatile organic compound measurements were carried out by gas chromatography (GC) and GC mass spectrometry (GCMS). Additionally, samples were analyzed for volatile organic compounds using a GC-flame ionizer detector for quantifying high levels of certain compounds such as isopropanol.

The Teflon filter was first visually inspected by optical microscopy in a class 1000 clean room at JSC. A section of the Teflon filter 860 × 580 microns in size containing particulate debris was removed by hand using a scalpel and placed with tweezers on double-sided C tape attached to a ½ inch aluminum (Al) SEM pin stub. This was then coated with a layer of ~3 nm of sputtered

platinum (Pt) to prevent surface charging. Before beginning detailed particle analysis, a large-area image mosaic (individual images acquired at 180×) was acquired, covering the entire filter surface using Low Angle Backscatter Electron (LBE) imaging. Individual particles were then characterized using light element EDX at 15 keV with spectra acquisition times ranging from 100 – 200 s.

The largest metal fragment recovered was mounted on double sided C tape adhered to a ½ inch aluminum (Al) SEM stub. An image mosaic (85×) was acquired, covered the entire metal chip, using Low Angle Backscatter Electron (LBE) imaging. Particles and surface textures were characterized using light element EDX spectroscopy. Spectra were acquired for 200 s. at 15 keV, with the exception of two large area spectra that were acquired for 340 s. at 5 and 15 keV.

Findings – optical microscopy

The initial visual inspection of the Teflon filter showed right away that large debris fragments were present in the blowby. Optical microscope images show that the main mass of the debris is in large metal fragments, most of which fully penetrated the filter (Figures 1 &2). Higher magnification optical imaging revealed the presence of numerous fine particles, some metallic in appearance and many dark particles of uncertain composition. Scanning electron microscopy of one section of the filter was carried out to verify the compositions of the fine particles. The light triangular pattern in the image below is due to the Teflon filter's support frame below.

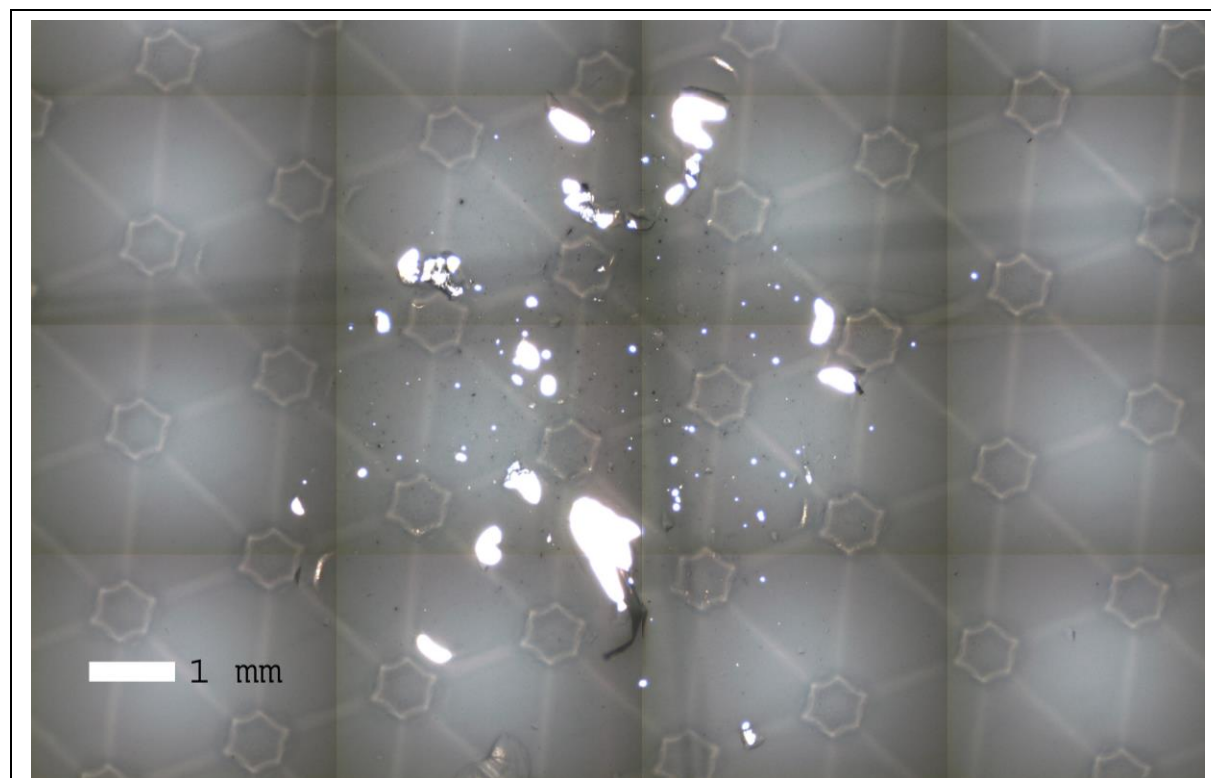


Fig. 1 The image above is a photomosaic of the debris collection filter. Large bright spots are holes that were probably created by large metal (stainless steel) fragments.

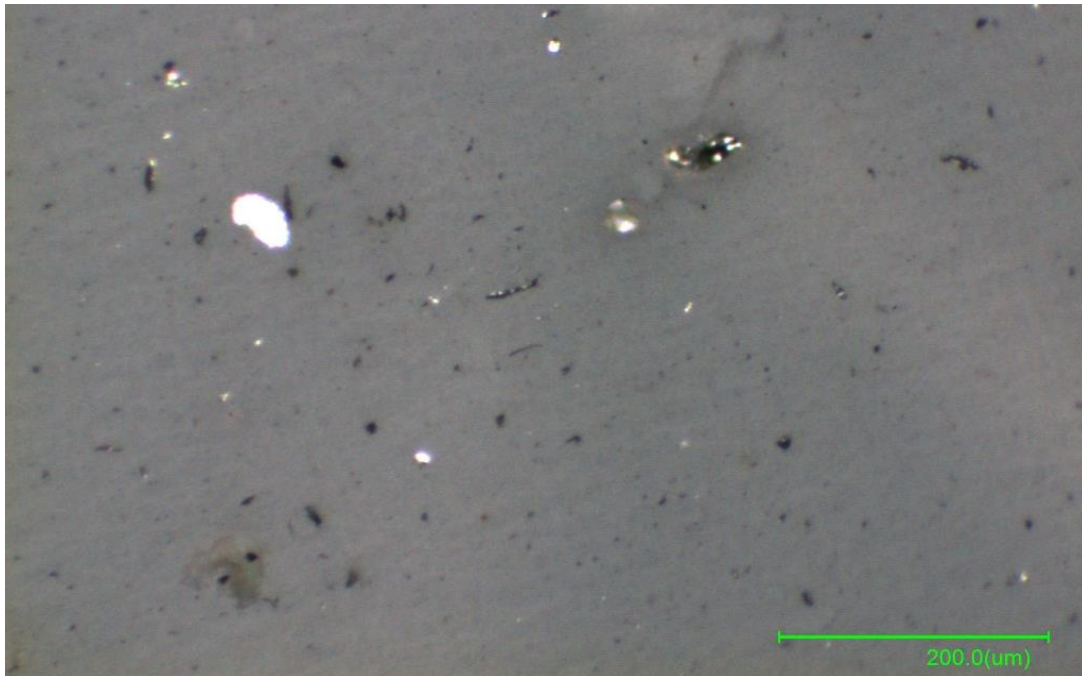


Fig. 2: High magnification image of the debris collection filter showing numerous 1 ~ 30 micrometer size particles embedded into the surface. Several large metal fragments remain embedded in the surface.

Findings – SEM examination of Teflon filter

SEM imaging of the Teflon ($-(F_2C-CF_2)_n-$) filter showed it to be a porous matrix composed of intercrossed fibers interconnected by semi-rounded blebs (Fig. 3-5). Particles present on the surface of the filter, and in some cases partially embedded within, were almost all smaller than 10 μm in their longest dimension.

The vast majority of these particles (>95%) had element abundances dominated by iron (Fe) along with nickel (Ni) and chromium (Cr) – a composition that is consistent with stainless steel (Fig. 4). The remaining particles were rich in carbon (C), silicon (Si), phosphorous (P) and manganese (Mn). The largest particle observed was C-rich and measured $\sim 30 \times 8 \mu\text{m}^2$ (Fig. 5).

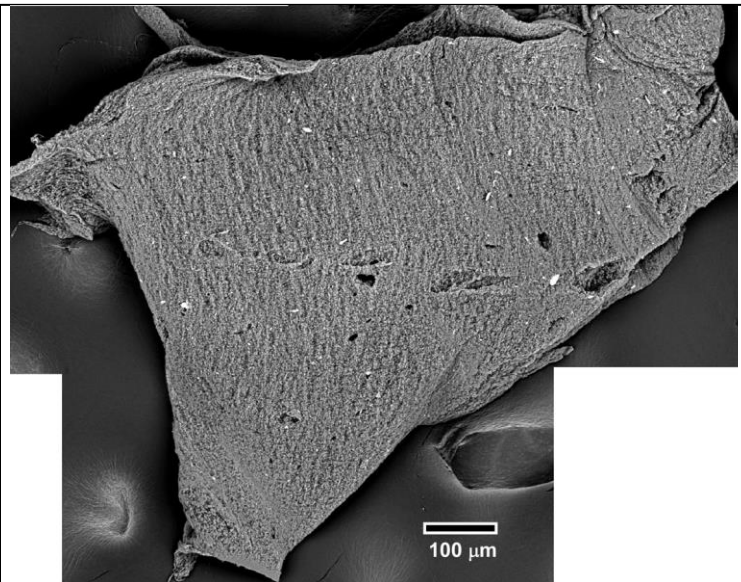


Fig. 3: LAME SEM image of the Pt-coated Teflon filter. The bright spots are particles composed of stainless steel.

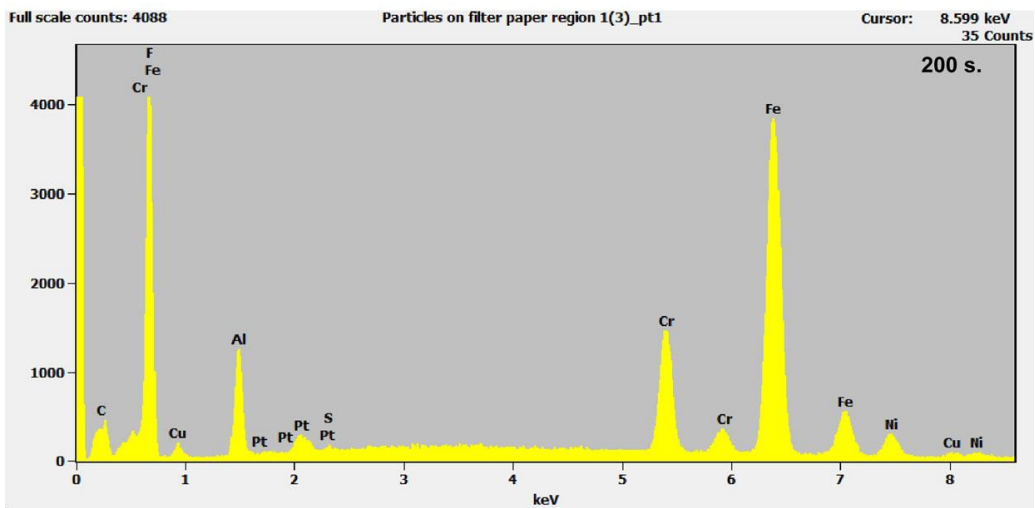
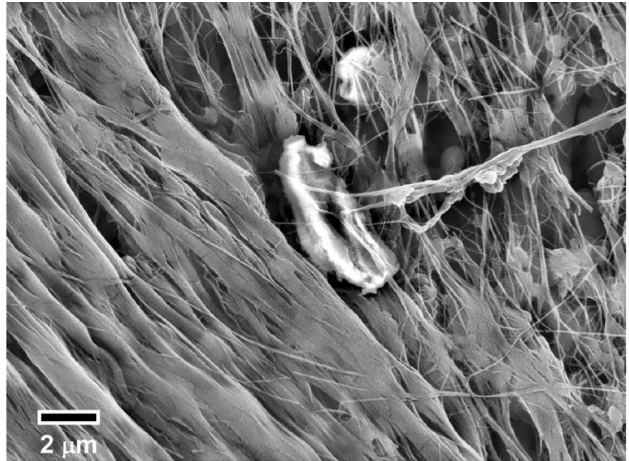


Fig. 4: SEM LAME view of a bright particle (center) on the filter. Bottom: EDX spectrum of the particle indicates it is composed of Fe, Cr & Ni, consistent with SS (note: additional elements are from the filter substrate).

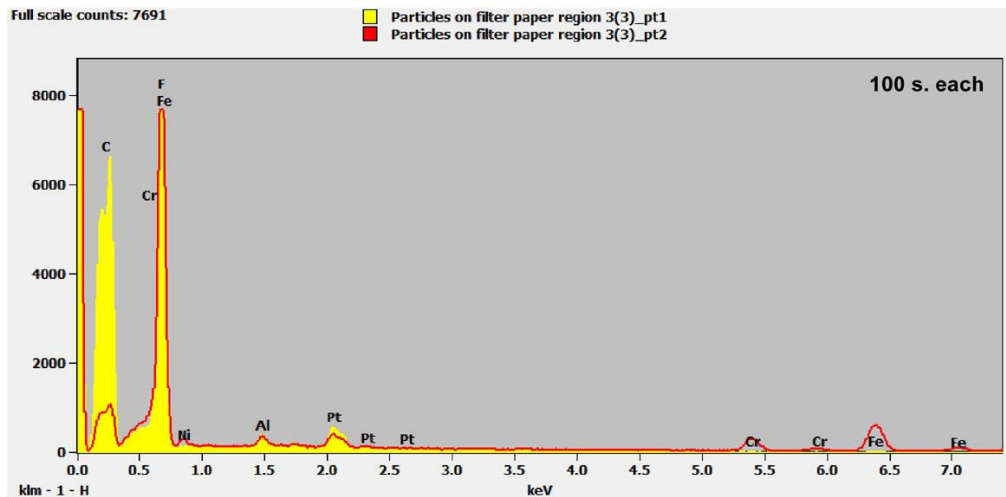
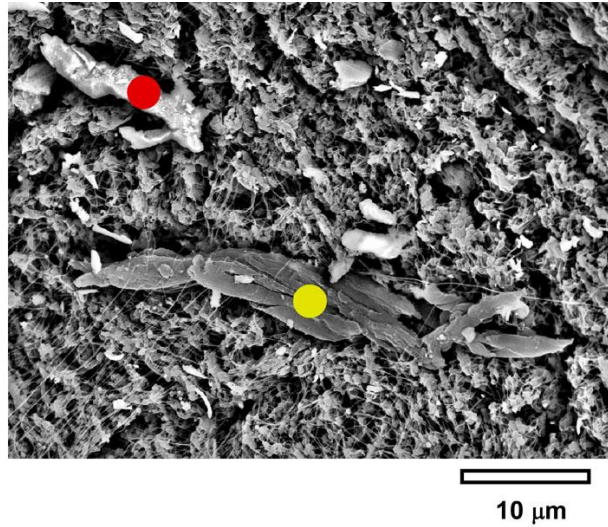


Fig. 5: Top: SEM view of two irregular particles on filter substrate. Bottom: Overlapping EDX spectra showing one particle (indicated by yellow dot in SEM image) is composed of C, while the other (indicated by red dot in SEM image) contains Fe, Cr & Ni (SS). Other elements are from the substrate.

Findings – SEM examination of large metal fragment

SEM examination confirmed that the largest recovered metal fragment (~1.4 mm in length) is composed of stainless steel (Fig. 6). The minor element composition (18 chromium (Cr) / 8 nickel (Ni)) is specifically consistent with austenitic stainless steel (SS) – see Table 1. Overall the metal is quite uniform in its composition, but a detailed study revealed some interesting features. Two types of surface textures were identified: (1) ‘*unmelted*’ having a striated appearance that is fine-grained and has an irregular surface porosity; and, (2) ‘*melted*’ displaying a flow-like textures containing sub- μm grains along with abundant cavities (Fig. 7). Both surface textures displayed identical elemental compositions as determined by energy dispersive x-ray (EDX) spectroscopy. When imaged in backscatter mode long irregular features were apparent on the exposed surface of

Element	TAGSAM SS (wt.%)	Austenitic SS (SAE 304 SS)
C	N.D.	Max 0.08
Al	2.0	N.D.
Si	1.4	Max 1.00
Mn*	N.D.	Max 2.00
P	N.D.	Max 0.045
S	0.5	Max 0.030
Ni	7.5	8.00-10.50
Cr	19.3	18.00-20.00
Mo**	N.D.	N.D.

Table 1: Minor element abundances of the large stainless steel (SS) fragment determined by SEM/EDX compared with literature values of austenitic SS. *Mn_{K α} (5.989 keV) overlaps with Cr_{K β} (5.946 keV); Mn_{K β} (6.490 keV) overlaps with Fe_{K α} (6.403 keV). Mn was present in the chip, distributed heterogeneously as MnS. **Mo_{L α} (2.293 keV) overlaps with S_{K α} (2.308 keV).

the shard, appearing brighter than the surrounding surface, and ranged up to ~600 μm in length. These features are consistent with localized surface roughening and abrasion that likely occurred in the same process that created the metal shard. In a number of instances manganese sulfide (MnS) inclusions were found embedded in the surface.

Particles present on the surface of the metal shard generally had elongated, semi-rounded irregular shapes and textures similar to that of ‘melted’ regions, and ranged from sub- μm to tens

of μm in their longest dimension. These particles, identical in major element composition to that of the bulk surface, also contained minor carbon (C). In some cases, particles appeared to have been melded together to form stringers up to several hundred microns in length. A few particles, that appeared to be loosely bound, were C-rich and consistent with biogenic sources and are likely contaminants acquired after the pyrovalve test. This contamination could have been introduced from the container that the metal grain was stored in or possibly acquired as the metal grain was mounted for SEM examination.

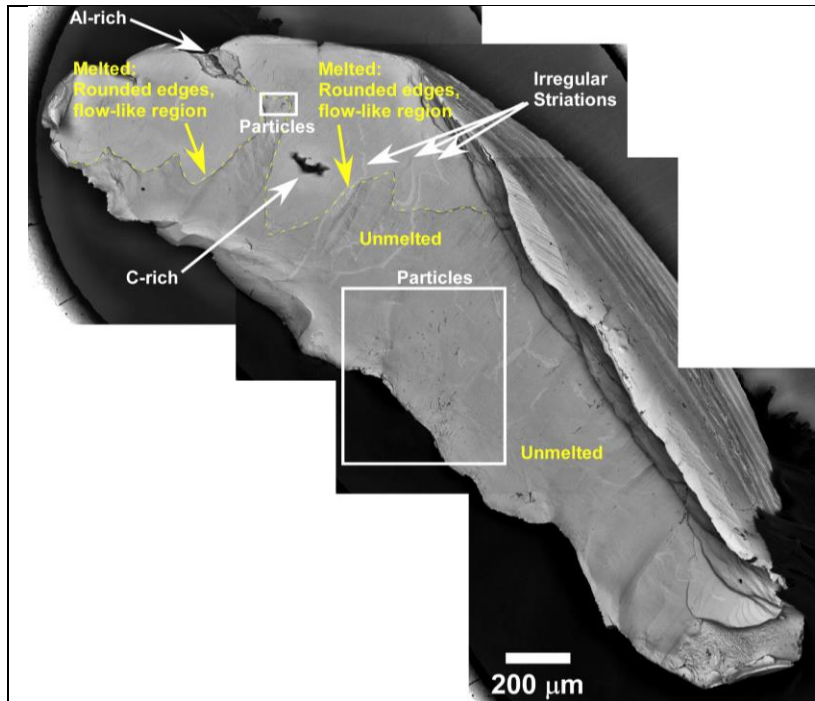


Fig. 6: LBE SEM image of the largest recovered metal fragment. Regions of interest are labeled with some of the ‘melted’ regions outlined by a dashed yellow line.

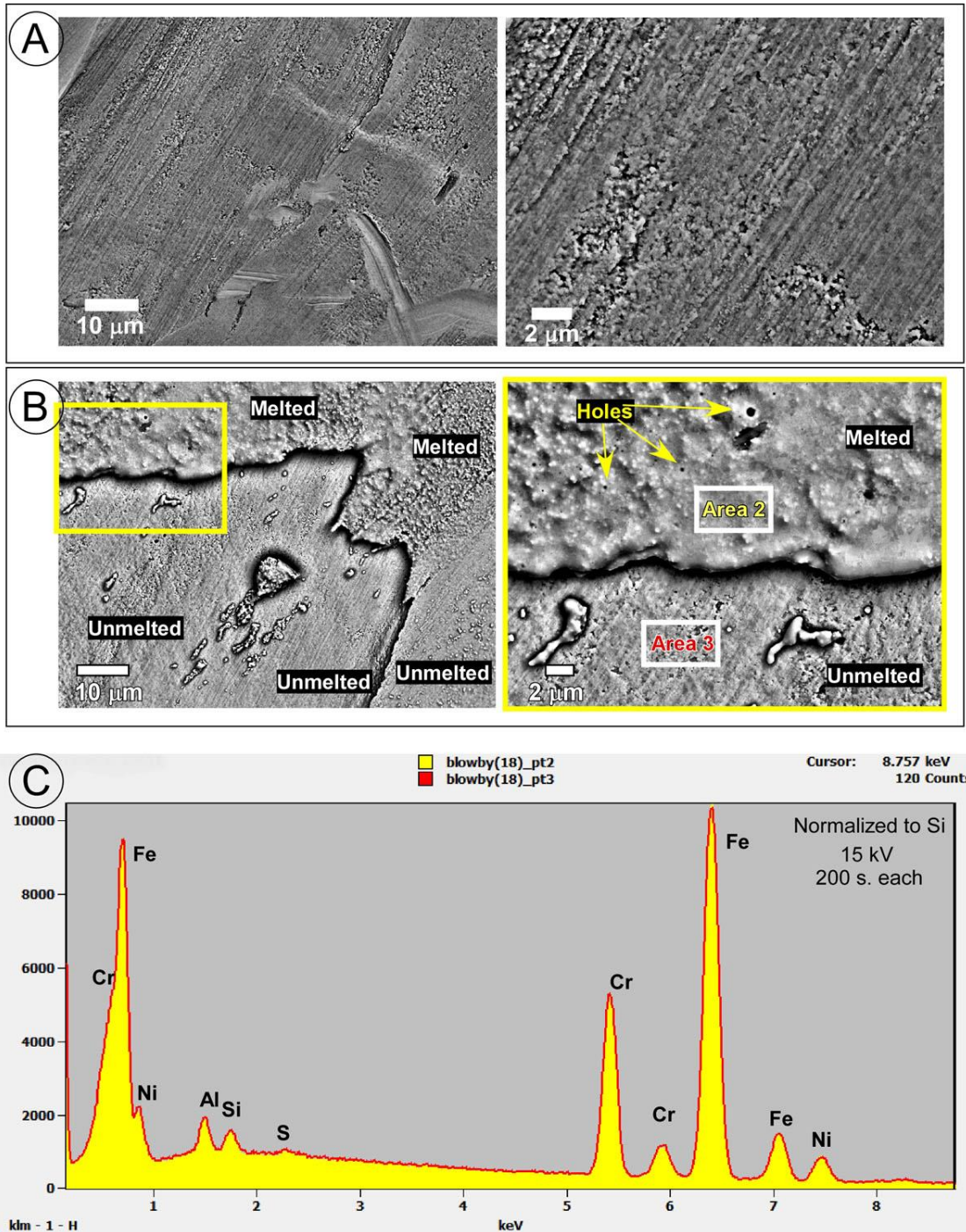


Fig. 7: (A) SEM LABE views of 'unmelted' SS at low (left) and intermediate magnification (right), showing striations and surface roughness. (B) SEM LABE views of 'melted' SS at low (left) and intermediate magnification. The intermediate mag. image on the right corresponds to the yellow boxed area in the low mag. image. The 'melted' region shows a flow-like texture with embedded sub- μm grains (white dots in right view, see Area 2). (C) Large area EDX spectra of 'unmelted' (Area 2; yellow spectrum) and 'melted' (Area 3; red spectrum) are indistinguishable with both containing Fe, Cr, Ni with Al & Si. C was not observed in large area spectra of 'unmelted' and 'melted' regions.

Examination of the metal fragment at a higher level of detail reveals some compositional variations. Surface particles with elongated, semi-rounded and irregular shapes (Fig. 8A) displayed textures similar to that of the ‘melted’ regions. They ranged from submicron to tens of microns in their longest dimension. In some cases, particles appeared to be fused together to form stringers up to several hundred μm in length. In general the major element composition of particles were identical to that of the bulk sample with the addition of minor C (see Fig. 8B).

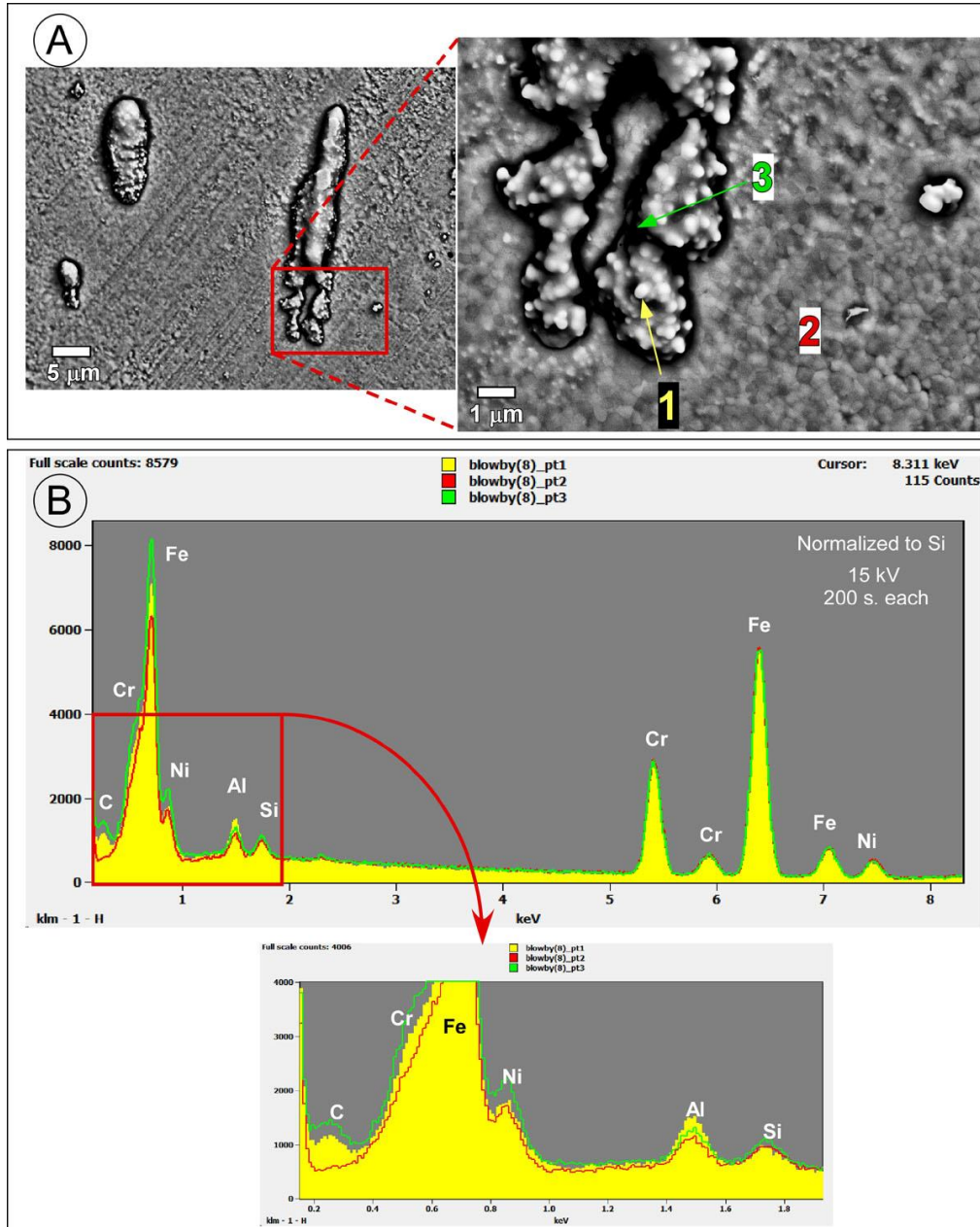


Fig. 8: (A) SEM images of particles on the SS chip surface. Left: Low magnification view of a particle group. Right: Higher magnification view of the region in the red box shown at left. (B) Overlapping color-coordinated spectra (1-3) of regions shown in (A), right view. Both spectra 1&3 shown the presence of C (see bottom spectrum for enlarged view of low atomic number region) while the background (spectrum 2) showed no detectable C.

Findings – gas analysis

The following pages are GC and GC-MS analysis reports provided by the JSC Toxicology and Environmental Chemistry group, as received. The main finding is that all four gas samples are extremely clean. Species measured above background include acetone and isopropanol. Their presence can be attributed to use as cleaning agents in preparation of the TAGSAM blowby test apparatus. The data table is found in a separate pdf.



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Air Quality Lead

SUBJECT: Analytical Results of 4 OSIRIS-REx TAGSAM Gas Samples

INTRODUCTION

At the request of the NASA JSC Astromaterials Research Office, the Toxicology and Environmental Chemistry Laboratory (TEC) analyzed 4 air samples collected by Lockheed Martin (LM) personnel in November 2016 and January 2017 at the OSIRIS-REx (Origins-Spectral Interpretation-Resource Identification-Security-Regolith Explorer) Assembly, Test and Launch Operations (ATLO) facility in Littleton, Colorado. Samples were collected from the flight unit of the Touch-and-Go Sample Acquisition Mechanism (TAGSAM) of the OSIRIS-REx spacecraft. These samples are the fifth and final set of samples received from the processing of the vehicle. The grab samples were collected in verified-clean (proofed), evacuated, passivated stainless steel canisters. Three of the 4 samples were collected in 500mL size canisters and one (#AQI 70014) was collected in a 6L size canister, all supplied by the TEC Laboratory. The samples were received into the TEC-Air Quality Laboratory on January 25, 2017. Sample log information is provided in the table below:

Sample Tracking #	Canister	TAGSAM Sample Description	Sample Date	Date Received	Date Analyses Completed
AQ170015	21191	Flight unit: sample taken through flight loading system	11/14/16	1/25/17	1/30/17
AQ170016	22379	Flight unit: sample taken through flight loading system & Qual Bottle heated for 24 hrs prior to transfer	11/22/16	1/25/17	1/30/17
AQ170014	16193	Flight unit: sample taken through pyrovalve during firing	1/18/17	1/25/17	1/30/17
AQ170017	23687	Flight unit: GN2/GHe from source K-bottle	1/19/17	1/25/17	1/30/17

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METHODS

Analyses were accomplished using both gas chromatography (GC) and gas chromatography/ mass spectrometry (GC/MS). The samples were analyzed for volatile organic compounds (VOCs) by GC/MS according to WI-TEC-210, "Measurement of Volatile Organic Compounds in Air by Gas Chromatography/Mass Spectrometry Using Grab Sample Containers." Additionally, the samples were analyzed for VOCs using the GC method according to WI-TOX-004, "GC Analysis of Volatile Organic Compounds, Carbon Monoxide, Methane, Carbon Dioxide and Hydrogen in Air Samples." This GC flame ionization detector (FID) method is used for reporting high levels of methanol, ethanol, isopropanol, 2-butanone and acetone if the concentration is above 0.15 parts per million (ppm). Additional compounds may be quantified using this method if their levels are sufficiently high.

RESULTS

The analytical results for the 4 gas samples are reported in Table 1. Table 2 provides the results of duplicate analyses on sample AQI 70014. Concentrations of identified compounds are reported as mg/M³ at 14.7 psia and 25⁰C. Quantitative measurements of listed Target Compounds (TO-15) were calculated using a weighted quadratic regression model from the multi-point standardization as described in EPA method TO-15 and WI-TEC-210 for GC/MS measurements. One compound, hexamethylcyclotrisiloxane (HMCTS) in the Special Interest Compounds (SICs) group, was quantified using an average response factor from an internal study performed by TEC-Air Quality. However, the results for HMCTS are estimates due to the variations observed in the response factors at different concentrations. The quantitative measurements of the remaining compounds in the SIC group were based upon estimates of "B" response factors available in the literature ("Compilation of Mass Spectral Data" by A. Cornu and R. Massot). There were no non-target compounds found in the 4 samples having peak areas greater than 10% of the fluorobenzene standard peak. Compound concentrations listed as "< the laboratory reporting limit" indicate that these compounds were analyzed for, but not detected in the sample. The laboratory reporting limit for most compounds was 0.025 mg/M³.

QUALITY REVIEW

Review of the gas sample measurement data was performed as described in WI-TOX-021 "Flight Sample Quality Assurance Review."

The raw data were reviewed from the instrument data systems and printouts for response integration, compound identification and operating parameters.

The GC/MS instrument used to generate report data was determined to be stable and calibrated during measurements of the samples. The instrument stability was demonstrated to meet specifications by daily bromofluorobenzene tune verification and daily calibration verification by analysis of a mid-range standard. The reported concentrations were quantified using 3 different methods: 1) multiple-point calibrations for the Target compounds, 2) a response factor generated from an internal study for one compound in the SIC group, and 3) "B" response factors obtained from the reference previously mentioned.

The GC-FID (high VOCs) instrument was also demonstrated to be linear over a wide range

of concentrations and stable as shown by daily calibration verifications using standard mixtures. The reported concentrations were quantified using a minimum of 4-point calibration curves.

As part of the routine preparation, surrogate compounds (3) were added to the sample canisters prior to delivery to the ATLO processing facility. Laboratory surrogate control canisters were set up at the same time. Upon sample analysis, the recoveries of the surrogate compounds provide useful quality assurance information regarding the entire sampling and analysis process. The recoveries for all 3 compounds for the TAGSAM samples were extremely low, ranging from 0 — 7.8%, whereas, the laboratory control recoveries were excellent (97 — 103%). However, as confirmed by the OSIRIS-REx representative, the 6L container was purged prior to sample acquisition, resulting in the loss of the surrogate compounds. It is presumed that the same or similar sample acquisition process occurred for the other samples. For this reason, a surrogate recovery table is not provided in this report.

Upon receipt of the samples into the laboratory, the pressures were initially measured and also measured during subsequent steps of the sample processing to ensure sample integrity. Instrument calibration and check standard data for each instrument were reviewed along with the results from all sample analyses. All procedures and hardware were monitored for any errors or anomalies and no unusual trends impacting data quality were observed.

A handwritten signature in black ink, appearing to read "Xela T. Walker", is written over a horizontal line.

Internal Quality Reviewer