

THE UNIVERSITY OF ALABAMA IN HUNTSVILLE

FINAL REPORT

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*"Atomic Oxygen Task"*

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Submitted by:

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## **1. Introduction:**

This report details work performed by the Center for Applied Optics (CAO) at the University of Alabama in Huntsville (UAH) on the contract entitled "Atomic Oxygen Task" for NASA's Marshall Space Flight Center (contract NAS8-38609, Delivery Order 109, modification number 1).

Atomic oxygen effects on exposed materials remain a critical concern in designing spacecraft to withstand exposure in the Low Earth Orbit (LEO) environment. The basic objective of atomic oxygen research in NASA's Materials & Processes (M&P) Laboratory is to provide the solutions to material problems facing present and future space missions. The objective of this work was to provide the necessary research for the design of specialized experimental test configurations and development of techniques for evaluating in-situ space environmental effects, including the effects of atomic oxygen and electromagnetic radiation on candidate materials. Specific tasks were performed to address materials issues concerning accelerated environmental testing as well as specifically addressing materials issues of particular concern for LDEF analysis and Space Station materials selection.

## **2. General:**

UAH provided personnel with specialized technical expertise needed to accomplish evaluations necessary to make specific recommendations for modifications to existing MSFC atomic oxygen test facilities and test procedures to accommodate ambitious test objectives of monitoring in-situ the effects of atomic oxygen and simulated solar ultraviolet radiation on candidate space materials. UAH performed the necessary experimental investigation and analytical studies to accomplish these activities.

The combined environmental experimentation was accomplished by UAH personnel primarily at NASA/MSFC using the unique facilities of the M&P Laboratory. The materials analysis for comparison to LDEF and other space mission results was performed at UAH. UAH reviewed and evaluated the design, operational status, and experimental utility of existing MSFC atomic oxygen simulation facilities, including the Atomic Oxygen Drift-Tube system, the Advanced Atomic Oxygen Simulation system (5 eV neutral beam), and associated UV radiation source and monitoring equipment. In order to accomplish the objectives of this effort, UAH provided design and technical review of modified facility instrumentation.

## **3. Technical Approach:**

The specific tasks to be associated with this effort were:

Task 1. UAH was to provide analytical studies and evaluation for the development and

utilization by MSFC of in-situ monitoring of both atomic oxygen and simulated solar UV and vacuum UV irradiation effects on candidate space materials.

- Task 2. UAH was to provide evaluation and review of existing atomic oxygen and UV test facilities at MSFC as required for providing a multi-functional capability for combined environmental exposure of materials using existing MSFC systems.
- Task 3. UAH was to review the literature and analyze some available experimental flight data in order to help MSFC determine the most effective experimental procedure for in-situ monitoring of atomic oxygen and UV effects on materials.
- Task 4. UAH was to investigate a few selected materials analytically and experimentally prior to and following exposure in the MSFC experimental facilities to determine the functional utility of the designed in-situ instrumentation and the testing procedure.
- Task 5. UAH was to conduct a detailed investigation and present a summary report on the emitted visible light from an oxygen plasma as a possible method for determining atomic specie density of the plasma. The technique of interest was known as spectral line ratioing.
- Task 6. Using the resources developed above, UAH was to provide a preliminary report concerning the effects on materials exposed in atomic oxygen alone, UV radiation alone, and the combined effects of AO and UV.

Most of the above tasks were to be carried out using the 5 eV, neutral atomic oxygen beam facility being developed at MSFC. However, due to unforeseen delays encountered by MSFC in building the new 5 eV system, it was not operational before the end of this contract. Thus, it was not possible for UAH to carry out any of the work mentioned above that involved the 5 eV system. During the contract it was decided, in conjunction with the MSFC scientists, that the most important task was number 5 - the investigation into the spectral line ratioing method of determining atomic oxygen (AO) fluence. An accurate, non-invasive method of determining AO fluences in the various test chambers at MSFC was needed. Thus, most of the contractual effort was focused onto this task.

#### **4. Atomic Oxygen Fluence Determination using Atomic Emission Line Ratioing:**

##### **4.1 Background**

Preliminary investigations into the atomic emission line ratioing method of determining atomic oxygen densities & fluences in a reactive plasma were performed by Roger Linton at MSFC. His early tests showed promise. Other common methods, such as Langmuir<sup>1</sup> and

catalytic thermocouple probes and reference samples (e.g. Kapton) require an extra component to be placed into the AO beam, possibly disturbing the fluence conditions at the sample. Another “non-invasive” method, gas-phase titration<sup>2</sup> with NO<sub>2</sub>, can present a hazardous material problem. Lastly, analytical methods of predicting AO fluences from RF power, pressure, oxygen flow rate and/or experimentally-determined correction or calibration factors lack the long-term accuracy required. With this in mind, UAH began a more detailed experimental evaluation of the line ratioing method.

A literature search was performed first. The key paper presenting the line ratioing method, which formed the basis for the approach detailed below, is by Coburn and Chen.<sup>3</sup> The technique was also reported later by Lin, Belser, and Tzeng.<sup>4</sup> Other literature relating to oxygen plasmas in general and other fluence measurement methods were reviewed and are cited as appropriate in this report.

#### 4.2 Experimental Set-Up

It was decided to carry out this initial series of experiments using the March asher belonging to MSFC since it was a fairly well-understood and characterized system. MSFC also supplied an Acton Research Corporation grating spectrometer with a fiber-optic probe. The March chamber (with gas handling attachment and vacuum pump) and the spectrometer were brought to UAH for the first series of tests. The spectrometer was calibrated with a mercury lamp. After getting the system operational and checked-out, the first experiments were carried out on an oxygen plasma with argon as the reference gas. The results (see below) seemed reasonable, but several potential problems were identified. The accuracy of the argon partial pressure readings was questionable when using a thermocouple gage calibrated for air. Also, after a few experiments, the vacuum pump began to fail.

The equipment was then returned to MSFC. The vacuum pump was replaced and a Convectron vacuum gage with digital readout and both oxygen and argon calibration curves was installed on the March chamber. After some tests with the new set-up, it was decided that the needle-point gas flow controllers that were used by the March system were not accurate enough for the very low argon flow rates desired. Thus, two electronic flow controllers (one calibrated for oxygen and one for argon) were brought from UAH and attached to the March chamber. A capacitance pressure gage (independent of gas type) was also brought over from UAH. The combination of the new flow controllers and the pressure gage (all interlinked and with digital readouts) insured precise and accurate control over the oxygen and argon flow rates/partial pressures and the overall chamber pressure. A schematic of this final test set-up is shown in Fig. 1. After some effort to seal leaks in the fairly complex layout and replacement of another faulty vacuum pump, this system was used to perform the final series of line ratioing experiments.

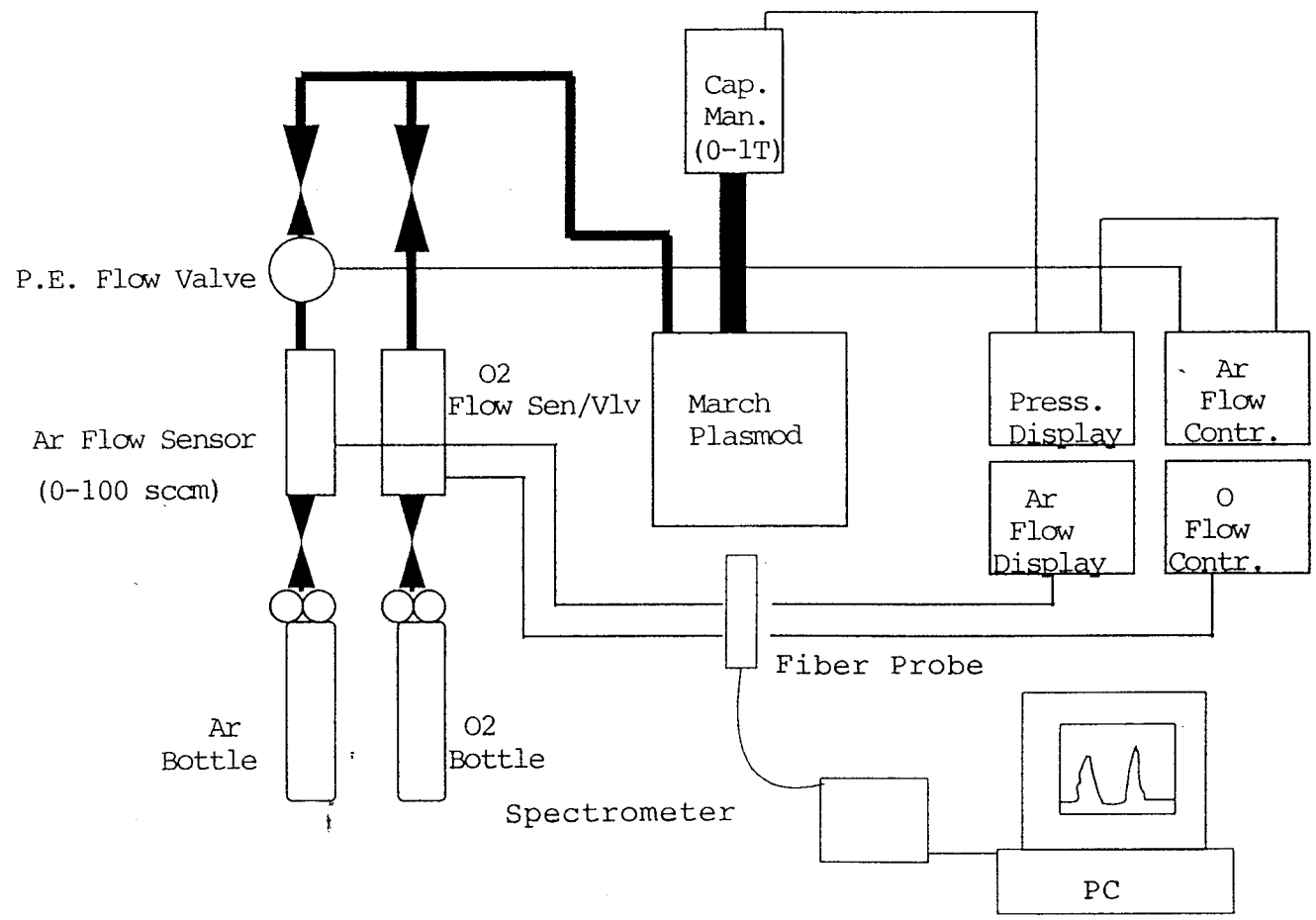


Fig. 1. Spectral line ratioing experimental set-up.

### 4.3 Detailed Method and Results

**This section is a text version of a Mathcad worksheet developed and used to analyze the data taken during experiments on the line ratioing method.**

General optical emission intensity vs. species density relation:

$$I = n\alpha\eta k \quad (1)$$

where I is the measured intensity of the selected emission line,  
n is the density of the corresponding atomic species,  
 $\alpha$  is the transition probability of the observed line,  
 $\eta$  is the excitation efficiency of the discharge for the observed transition (not a constant - dependent on discharge power, gas density, & gas composition),  
and  
k is a constant of proportionality which is a function of the light collection efficiency, the collection time, and the particular detector & data acquisition system used.

Now, for the case of an oxygen plasma, want to measure the density of the atomic oxygen (AO) that is dissociated from the molecular oxygen ( $O_2$ ) that is input. The level of dissociation and the level of subsequent recombination are not easily determined, especially with respect to changes in the discharge parameters (input power, gas temperature, gas pressure, etc.). Thus, would like to use the intensity, I, of an appropriate AO line as a measure of the AO density using the relation above. Solving for n gives

$$n = I/\alpha\eta k. \quad (2)$$

While I is measured and  $\alpha$  is known,  $\eta$  and k are not easily determined analytically. The combined value of these parameters, for a certain set of experimental conditions, can be measured, however, using an inert atomic gas such as argon (Ar). In this case, the density of the argon,  $n_A$ , can be calculated from the argon partial pressure and temperature using the ideal gas law. A measurement of the intensity of an argon atomic transition line,  $I_A$ , with a known probability,  $\alpha_A$ , at a given  $n_A$  now yields a value of

$$\eta k = I_A/(\alpha_A n_A). \quad (3)$$

For an argon emission line very near in energy to the observed AO line and for the same plasma conditions, the excitation efficiencies for the two lines will be almost identical. And, if the same optical system is used to observe both lines, then k will be the same for both species. Thus,  $\eta k$  will be the same for both species and can be determined from measurements made on the argon. This  $\eta k$  value can be determined through addition of a small amount of argon to the oxygen

plasma; this insures that both the discharge parameters and the light measurement system are identical for the two species. Now, any subsequent measurement of the AO line intensity, IO, can be used in equation (2) to calculate the AO density at the observed location in the plasma.

Substituting equation (3) into equation (2) and labeling the oxygen parameters with an O gives

$$nO = (nA/IA) (\alpha A/\alpha O) IO. \quad (4)$$

The most accurate way to determine nA/IA is to determine the best-fit slope of a line plotting measured argon line intensities versus a small range of argon partial pressures (this actually gives IA/nA). The slope value thus determined is valid only for the experimental conditions present at the time of the IA and nA measurements (i.e. same power, same light collection set-up, etc.). For dynamic measurements with changing plasma conditions, one can measure nA, IA, and IO simultaneously to determine nO.

The following data was obtained in the March asher on 11-29-94 with the most optimized experimental set-up of many attempted, and thus should represent the most accurate determination of the AO density/fluence in this system as measured with the atomic emission line ratioing method. The raw data of argon 750 nm line intensity versus argon partial pressure is shown in Fig. 2, along with the original data taken by R. Linton. The linearity of the data is evident even at the higher partial pressures used by Linton.

Measured argon intensities at  $\lambda A = 750$  nm and partial pressures with 100 W RF power and 800 mTorr oxygen :

i = 1..6

$IA_i = \text{READ}(\text{ARO2I})$	$RPA_i = \text{READ}(\text{ARO2P})$	$PA_i = 0.1333 * RPA_i$
$IA_i = 120$	$RPA_i = 10$	$PA_i = 1.333$
270	30	3.999
430	50	6.665
630	70	9.331
820	90	11.997
1010	110	14.663
(arbitrary units)	(mTorr)	(Pascals).

Gas temperature from  $KT = 0.04$  eV (value provided by R. Linton):

$TA = 464.3$  K =  $191.2^\circ$  C.

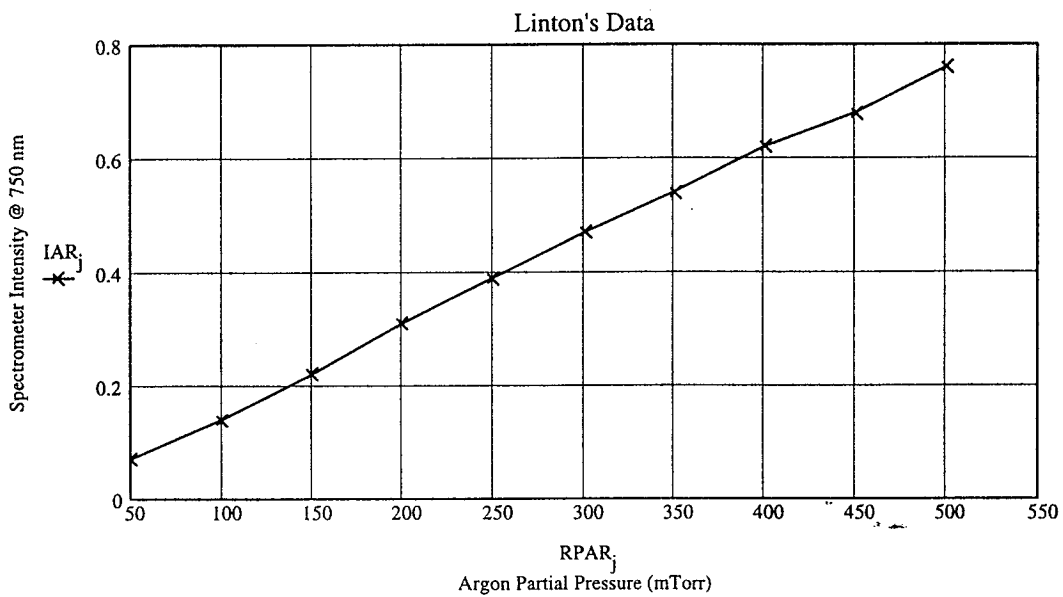
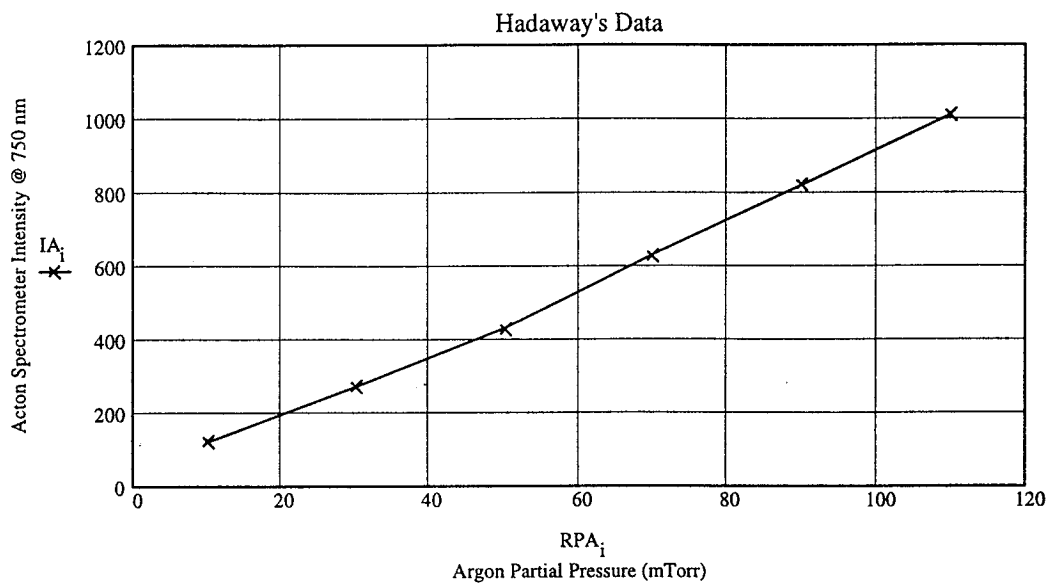


Fig. 2. Raw data for argon emission intensity vs. partial pressure.



Gas constants:

$$N = 6.02 \text{ atoms/mole (w/o } 10^{23} \text{ for now)}$$

$$R = 8.314 \text{ J/mol-K.}$$

Calculated density of argon along with measured argon line intensities:

$nA_i = (N*PA_i)/(R*TA)$	$nA_i =$	$IA_i =$
	0.002	120
	0.006	270
	0.010	430
	0.015	630
	0.019	820
	0.023	1010
	(* $10^{23}$ atoms/ $m^3$ )	(arbitrary units)

Determination of  $IA/nA$  slope:

$$a = \text{slope}(nA, IA) = 4.346 * 10^4$$

Line transition probabilities from CRC<sup>5</sup> (1/s):

$$\alpha A = 0.902 * 10^8 \quad \text{Trans. prob. for 2 lines at 750.4 nm \& 751.5 nm.}$$

$$\alpha O = 1.020 * 10^8 \quad \text{Trans. prob. for all 3 O lines at 777 nm.}$$

Density of atomic oxygen from equation (4):

$$IO = 2240 \quad \text{AO 777 nm intensity w/ 800 mTorr of oxygen.}$$

$$DO = 1 * 10^{23} * 1/a * \alpha A / \alpha O * IO = \mathbf{4.558 * 10^{21} \text{ (atoms/m}^3\text{)}}.$$

Calculate average AO velocity<sup>6</sup> from plasma  $KT$ , 0.04 eV, and oxygen atom mass:

$$KT = 6.408 * 10^{-21} \text{ (J)} \quad MO = 2.6559 * 10^{-26} \text{ (kg)}$$

$$VO = (2.546 * KT / MO)^{1/2} = 783.763 \text{ (m/s).}$$

Finally, calculate atomic oxygen fluence from density & average velocity<sup>7</sup>:

$$FO = DO * (VO/4) * 10^{-4} = \mathbf{8.931 * 10^{19} \text{ (atoms/cm}^2\text{-s)}}.$$

We can also attempt to calculate the AO fluence from the  $O_2$  partial pressure and the ideal gas law. Will assume 10% of  $O_2$  molecules dissociate into two O atoms (from Bell & Kwong<sup>8</sup>).

This method gives:

$FO = 6.5 \times 10^{19}$  (atoms/cm<sup>2</sup>-s) which is pretty close to the value above.

Lastly, we can calculate the AO fluence by measuring the mass loss from a Kapton sample exposed to the same plasma conditions as above. Using a value of  $3 \times 10^{-27}$  cc/atom for Re along with a density,  $\rho$ , of 1.4 g/cc for Kapton (from Jason Vaughn) and measuring 9.7 mg mass loss ( $\Delta m$ ) on a 3/4" diameter sample in 50 minutes ( $\Delta T$ ) gives:

$FO = \Delta m / (\Delta T * Re * \rho * A) = 2.7 \times 10^{20}$  (atoms/cm<sup>2</sup>-s) which is a little higher than the others.

The difference in the last value is likely due to an under-estimation of Re within the hot plasma.

#### 4.4 Summary and Conclusions

The following is a summary table of relevant March & Tegal asher AO fluences as determined by several sources/methods. The second entry is from data taken while the March system was at UAH and turned out to be fairly accurate despite the less-than-desirable pressure gage and flow controllers used. R. Linton's value from the original experiments using the Tegal system is also shown, along with the fluence re-calculated using the above method and assumptions - the two are in good agreement. The last entry is from a series of experiments performed on the MSFC Tegal asher in 1990 using an updated catalytic thermocouple probe. As noted, however, these experiments were performed at a much lower RF power level. Except for the Kapton-loss measurement and the lower-power measurement by Carruth, the various fluence values are quite consistent.

<u>Investigator</u>	<u>Asher</u>	<u>Meas. AO Fluence</u> <u>(atoms/cm<sup>2</sup>-s)</u>	<u>Comments</u>
Hadaway	March	$8.9 \times 10^{19}$	2nd try, 100W.
Hadaway	March	$6.5 \times 10^{19}$	1st try, 100W.
Hadaway	March	$6.5 \times 10^{19}$	From O2 part. press.
Hadaway	March	$2.7 \times 10^{20}$	From Kapton loss.
Linton	Tegal	$5.0 \times 10^{19}$	Using ratio.
Hadaway	Tegal	$6.5 \times 10^{19}$	Using Roger's data.
Carruth <sup>9</sup>	Tegal	$3.1 \times 10^{18}$	60 W, elect. probe.

In conclusion, the spectral line ratioing method was found to produce accurate values for the AO fluence in an RF plasma chamber. The accuracy of the method depends on the precision of the vacuum gaging and gas flow equipment used. However, most of the AO systems at MSFC have precision equipment built in. A common grating spectrometer with a fiber optic input and a linear detector array like the Acton unit used here provides adequate spectral measurement accuracy. For certain chambers, auxiliary light collection optics may be required in order to

measure emissions at the appropriate locations. And lastly, line ratio measurements must be made in areas of a chamber where light emission is occurring. The only other non-invasive measurement method, NO<sub>2</sub> titration, is not advisable for routine use do to the toxicity of the gas. The line ratio method should provide a simple, quick way to measure AO fluences in the systems in use at MSFC. It would be prudent, however, to use a second method periodically to confirm the line ratio results. Future work should include use of the line ratioing method on other AO systems at MSFC.

## **5. Conclusions:**

Although most of this effort concentrated on the spectral line ratioing method of determining AO fluence levels, some ideas on the issue of in-situ monitoring of AO as well as UV irradiation effects on materials were developed. Based on UAH's experience with the project, an approach similar in concept to the Optical Properties Monitor (developed by AZ Technology of Huntsville, AL for MSFC) is recommended. The OPM uses a combination of simple instruments to monitor both the LEO environment and the changes induced on material samples exposed to that environment. The OPM was designed to operate in space and will fly on the Russian MIR space station. However, the instrumentation could certainly be configured to work with ground-based, LEO-simulation chambers. The various radiation, contamination, and AO monitors designed for OPM (or the line ratioing method for AO) could be installed in a chamber and/or linked to the chamber through fiber optics to monitor the environment. Then, the reflectometer, VUV spectrometer, and total integrated scatter instrument (for measuring surface roughness) used in OPM could be attached to the chamber (all are designed to operate in a vacuum) and the sample(s) rotated or translated periodically under the instruments for evaluation. Thus, all environmental and sample monitoring would be done inside the chamber under vacuum. Such an approach would benefit from the extensive work already performed and instrumentation problems overcome by the OPM development team. Lastly, data gathered from a ground-based system with an OPM-like monitoring attachment could be directly compared to data collected in LEO by the OPM.

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