Fuel Oxidizer Reaction Products (FORP) Contamination of Service Module (SM) and Release of N-nitrosodimethylamine (NDMA) in a Humid Environment from Crew EVA Suits Contaminated with FORP

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Abstract: The Service Module (SM) is an element of the Russian Segment of the International Space Station (ISS). One of the functions of the SM is to provide attitude control for the ISS using thrusters when the U.S. Control Moment Gyros (CMG's) must be desaturated. Prior to an Extravehicular Activity (EVA) on the Russian Segment, the Docking Compartment (DC1) is depressurized, as it is used as an airlock. When the DC1 is depressurized, the CMG's margin of momentum is insufficient and the SM attitude control thrusters need to fire to desaturate the CMG's. SM roll thruster firings induce contamination onto adjacent surfaces with Fuel Oxidizer Reaction Products (FORP). FORP is composed of both volatile and non-volatile components. One of the components of FORP is the potent carcinogen N-nitrosdimethylamine (NDMA). Since the EVA crewmembers often enter the area surrounding the thrusters for tasks on the aft end of the SM and when translating to other areas of the Russian Segment, the presence of FORP is a concern. This paper will discuss FORP contamination of the SM surfaces, the release of NDMA in a humid environment from crew EVA suits, if they happen to be contaminated with FORP, and the toxicological risk associated with the NDMA release.

Key words: Fuel Oxidizer Reaction Products, FORP, NDMA, EVA

1. Introduction

When the Docking Compartment (DC1) of the International Space Station (ISS) is depressurized for Extravehicular Activities (EVAs), the Service Module (SM) attitude control thrusters need to fire because the U.S. Control Moment Gyros (CMGs') have insufficient margin of momentum to maintain attitude. Thruster firings produce Fuel Oxidizer Reaction Products (FORP). One of the components present in FORP is the potent carcinogen N-nitrosdimethylamine (NDMA). For EVAs on the aft end of the Service Module (SM) of the Russian Segment (RS), there is a concern that when the EVA crewmember translates around the FORP contaminated area they could brush against the FORP and transfer some of it to their suit. When this FORP on the suit is brought back into the humid environment of the ISS cabin, it can release NDMA into the atmosphere. The NDMA represents a toxicological risk to the crew.

Figure 1 shows the discoloration visible around the SM zenith roll thrusters. The image was taken during the ISS Flight 5A Orbiter fly around. The pitch thrusters are closest to the aft end of the SM. The roll thrusters are to the left of the pitch thrusters in the image and are raised above the surface of the SM. The discoloration (brown color) can be clearly seen, below the thrusters, in the zoom image, close to the roll thrusters. Contamination has been observed around both the zenith and nadir roll thrusters. Figure 2 shows the relative position and direction of the SM attitude control thrusters. It can be seen that the roll thrusters' plume centerline is directed 47° away from the surface normal, while the pitch and yaw thrusters' plume centerline is directed 13° away from the surface normal. In addition the pitch and yaw thrusters are recessed, while the roll thrusters are elevated above the surface. So the roll thrusters are more likely to contaminate the SM surfaces.

The image in figure 1 was acquired before shields (GZUs - Gas dynamic protection devices) were installed on the thrusters in Jan 2002. The purpose of the GZUs is to constrain the thruster plume to limit contamination of the surrounding areas. Figure 3a shows the GZU for the roll thruster prior to flight. It can be seen that it fits over the roll thrusters. The handle on the GZU is used during installation and is not used for translating during EVAs, as it becomes contaminated. The brackets are used to install the GZU on fittings pre-installed on the SM surface. Figures 3b and 3c shows images of the roll thruster prior to installation of the GZU.

Images are being taken at regular intervals from the DC1 window of the SM nadir attitude control thrusters and the Kromka experiment. Figure 4 shows one of these images. Kromka is an experiment to measure how well the GZUs are performing and to test some material samples in space. Kromka is the material tray visible in the middle of the image. It has some small material samples mounted on it. In front of the Kromka are the pitch thrusters with the GZU installed. In front of the pitch thrusters are the roll thrusters with the GZU installed. Figure 5 shows a diagram of the nadir side of the SM. The Kromka experiment is visible near the SM pitch thrusters.

The EVA crewmembers often enter the area surrounding the thrusters for tasks on the aft end of the SM and when translating to other areas of the Russian Segment. This paper will discuss FORP contamination of the SM surfaces, the release of NDMA in a humid environment from crew EVA suits, if they happen to be contaminated with FORP, and the toxicological risk associated with the NDMA release.

2. Laboratory Tests at NASA White Sands Test Facility (WSTF)

Due to the presence of FORP additional EVA constraints needed to be implemented in the areas around the SM thrusters. These constraints included establishing a one meter keep-out zone (KOZ) around the thrusters for 2.5 hours, procedures for inspecting the EVA suits prior to ingress, and procedures for wiping the gloves and suit with towels that are jettisoned to retrograde. Also, once inside the ISS, the gloves are bagged. Since EVAs are generally very time constrained, the ISS Program approved a test program at the NASA White Sands Test Facility (WSTF) to obtain FORP test data that could be used to determine if those EVA constraints could be relaxed.

The program at WSTF included tests to determine the evaporation rate of FORP on the zenith (25° C, hot) and nadir (-40° C, cold) sides of the ISS, the evaporation rate of NDMA within the FORP on the zenith and nadir sides of the ISS, the quantity of NDMA that would be released in a humid pressurized environment from the dried FORP, and the rate at which NDMA re-forms when dried FORP is introduced into a humid environment. Two series of tests were performed.

The first series of tests were performed during CY 2003. Results from these tests included 100 hr evaporation rate data and NDMA formation rate data. Based on these results, the time to remain outside the KOZ was reduced from 2.5 hours to 2 hours. Additional tests were requested to determine if the time to remain out of the KOZ could be further reduced from 2 hours to 1 hour. This was the series of tests performed during CY 2004.

2.1 Preparation of FORP

For each series of tests, a batch of FORP was generated using a permeation technique developed at WSTF (Dee, et.al. 2002). In this technique, separate UDMH and NO2 gas streams are concentrated in a small controlled area. The batch of FORP needed for the tests was prepared over a couple of weeks. For the formation test, a sample of FORP from each batch was evaporated for 5 days at 25° C in a vacuum to generate a sample of dried FORP. Since the FORP was prepared over a long duration, the composition of the two batches of FORP varied. The composition of the FORP batches used in the tests is shown in Table 1. For the CY 2003 FORP, only the composition of the evaporated sample was measured. When comparing the two evaporated samples, it can be seen that the CY 2004 FORP has a higher concentration of Nitrates and Nitrites, 36% vs 48% and 0.08% vs 0.6% respectively. The higher concentration of Nitrates and Nitrites in the CY 2004 likely explain why the CY 2004 has more FORP mass remaining after the 5 day evaporation, 14% vs 10%.

The Nitrite levels of the CY 2004 FORP before evaporation and after evaporation, 20% and 0.6%, indicate that the Nitrite concentration is decreasing. A lower Nitrite level will decrease the NDMA formation rate. This was seen in the results discussed later.

The concentration of dimethylammonium is also higher for the CY 2004 FORP, 13% vs 7.9%. The higher concentration of dimethylammonium and Nitrites indicate that a higher NDMA formation rate would be expected for the CY 2004 FORP.

Synthetic FORP was also prepared for some tests in CY 2003. This was FORP where the neat components of FORP were mixed (dimethylammonium nitrate and Sodium nitrite)

2.2 NDMA Evaporation Rate

The test results in figure 6 show the concentration of NDMA relative to the initial mass of FORP decreases rapidly. The test results are for the nadir (-40° C, cold) case. The red squares are from the CY 2004 tests and the blue squares are from the CY 2003 tests. It can be seen that the CY 2004 FORP starts (time=0) with a higher concentration of NDMA than the CY 2003 FORP. However, by the time it reaches the time = 2 and 4 hr data points, the concentration of NDMA relative to the initial amount of FORP is comparable and the CY 2004 and CY 2003 data points overlap.

The results in figures 7 are for the zenith (25° C, hot) case. It can be seen that the NDMA concentration drops more rapidly for the 25° C than for the -40° C. After 1 hour the concentration has dropped approximately 2 orders of magnitude, compared with the 1 order of magnitude for the -40° C case. It can also be seen that by 1 hour the concentration drop has reached a plateau.

2.2 FORP Evaporation Rate

Figure 8 shows that the FORP volatilizes rapidly to a stable mass that persists over a long period of time. The results show that within 1 hour the FORP has reached a stable mass and that the CY 2004 FORP settles at a higher mass than the CY 2003 FORP. For CY 2004, the FORP remaining after 1 hour is ~36%. The results for CY 2003 showed 12 to 22%. The higher mass remaining is likely due to the higher concentration of nitrites and nitrates present in the FORP.

The results in figures 9 are for the zenith (25° C, hot) case. These results showed that the CY 2004 remaining after 1 hour was 22% and that for CY 2003 it was 10 to 11%.

2.3 FORP Formation Rate

Table 1 shows the Nitrite levels of the CY 2004 FORP before evaporation and after evaporation, 20% and 0.6%, indicate that the Nitrite concentration in the FORP is decreasing. A lower Nitrite level will decrease the NDMA formation rate. This was seen in the results, as no NDMA formation was detected in the CY 2003 when moisture was introduced into the sample of dried FORP. For the CY 2004 sample of dried FORP, the NDMA formation rate was negligible when moisture was introduced. To form NDMA, Nitrite has to be present in the sample. Both the CY 2003 and CY 2004 dried FORP samples were spiked with Nitrite before the formation rate was measured. The Nitrite introduced was 25% of the mass of Nitrate present in the sample.

Table 1 also shows that the concentration of dimethylammonium is higher for the CY 2004 FORP, 13% vs 7.9%. The higher concentration of dimethylammonium indicates that a higher NDMA formation rate would be expected for the CY 2004 FORP.

Figure 10 shows the formation rate of the FORP that was measured. The plot shows the rate for both the CY 2003 (red symbols) and CY 2004 FORP (blue symbols). The solid symbols indicate FORP where nitrite is added, and the open symbols are FORP with no nitrite added. It can be seen that when no nitrite is present the NDMA formation rate is very low. For the CY 2003 FORP, no NDMA formation was detected. For the CY 2004, a low rate was measured.

The results in figure 10 show that for the CY 2003 FORP, the NDMA formation rate is 1800 μg NDMA/g FORP present after 2 hours. The formation rate for the CY 2004 FORP was higher, 18400 μg NDMA/g FORP present after 2 hours. One cause for the higher formation rate is the higher Dimethylammonium concentration in the CY 2004 FORP. The mass of CY 2004 FORP remaining after the 5 days of evaporation was also higher. This might indicate that there were other components present in the FORP that might have resulted in a higher formation rate.

3. Methodology

A methodology was developed to determine the FORP and NDMA remaining on the SM surface after the SM roll thrusters fire prior to an EVA and the subsequent release of NDMA in a humid environment due to inadvertent contact by a crewperson with the Service Module (SM) surface in the vicinity of the SM roll thrusters contaminated with FORP. The calculation determined the FORP and NDMA remaining on the SM surface and subsequent release of NDMA in a humid environment.

To calculate the FORP remaining on the SM surface, the Russian plume model was used. The Russian plume model is more conservative because it has a flatter contaminant distribution with off the plume centerline. The thruster firing times were obtained from the Guidance, Navigation and Control group (GN&C). The value of 45 seconds was used as it was the longest firing time observed during the previous EVAs.

Using the laboratory evaporation test data (conservative 36% FORP remaining), the FORP that would remain after 2 hours was calculated. Figure 11 shows a map of the distribution of FORP from the thruster remaining on the SM thruster based on the plume model and laboratory data.

Figure 12 shows that since the GZUs were installed, the closest point on the SM surface that can be touched is ~3.2 in (~8 cm) from the thruster. The diagram is of the zenith side of the SM. The figure on the left shows the roll thrusters with the GZUs installed. The figure on the right shows the distance from the roll thruster to the closest SM surface outside of the GZUs. .

To be conservative it is assumed that all the FORP in a 100 cm^2 area is transferred to the suit. Based on the amount of FORP transferred, the amount of NDMA that would be released from this FORP inside the cabin in the first 2 hours was also calculated, 200 μg NDMA/per g FORP present. The amount of NDMA that would be formed from the dried FORP in the first 2 hours was also calculated based on the more conservative CY 2004 rate, 18400 μg NDMA/g FORP present.

The predicted concentration of NDMA that would be released by an inadvertent swipe into the DC1 and ISS compartments are shown in Tables 2 and 3. It can be seen that the concentration drops off rapidly. Also the closest point is at the GZU itself, which is defined as a "no touch" area by flight rule. This data was given to the Toxicology group for assessment.

4. Toxicological Assessment

The quantity of FORP present and NDMA released into the ISS from an inadvertent swipe by a crewperson of the contaminated area around the SM roll thrusters was calculated and provided to the NASA Toxicology group for an assessment. This data is shown in Tables 2 and 3. The NASA Toxicology Group concluded that for the concentration levels expected in DC1, it is unlikely that NDMA will produce acute toxicity. The NASA Toxicology Group also found that the highest calculated risk from the projected NDMA concentrations in DC1 is less than 4.8×10^{-5}. The NASA Toxicology Group, with the concurrence of the National Research Council Spacecraft Maximum Allowable Concentrations (SMAC) Subcommittee, accepts a cancer risk of 1/10,000 (i.e., 10^{-4}) in deriving SMACs on carcinogenic compounds, such as benzene.

5. Summary

Acute toxicity has not been reported at concentrations below 10 ppm. Therefore, it can be concluded that at concentration below 1 ppm (3 mg/m3), it is very unlikely that NDMA will produce any acute toxicity. The highest projected concentration at DC1 is less than 1 mg/m3.

NASA Toxicology Group, with the Concurrence of the National Research Council SMAC Subcommittee, accepts a cancer risk of 1/10,000 in deriving SMACs on carcinogenic compounds, such as benzene. The highest calculated risk from the projected exposure (-40C, distance 0.03 meter from Thruster) is 4.8 x 10-5.

Based on the results the time to remain outside the 1 meter KOZ could be reduced from 2 hours to 1 hour.

6. References

L.A. Dee, V.D. Davidson, and D.L. Baker, "Laboratory Preparation and Characterization of UDMH/NO2 Reaction Products," Protocol External Contamination Technical Interchange Meeting Fuel/Oxidizer Reaction Products (FORP) Plume Induced Contamination, April 15-26, 2002 (2002)

E.A. Lawton and C.M. Moran, "MMH-nitrate and Plume Deposits from NTO/MMH Engines," APL The 14th JANNAF Plume Technology Meeting, Vol. 1, p. 1-7, SEE N84-22619 13-20 (1984)

V.D. Buchanan and L.A. Dee, "Evaporation rate study and NDMA formation from UDMH/NO2 Reaction Product," White Sands Test Facility (WSTF) Investigative Report, WSTF-IR-0188-001-03 (2003)

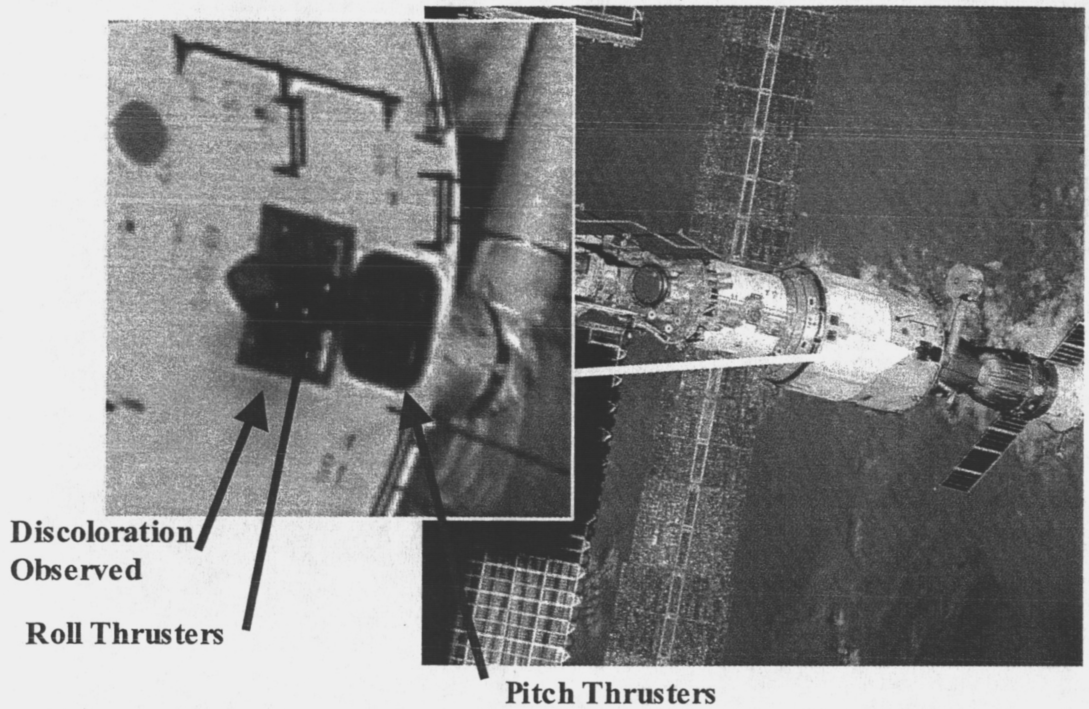

Figure 1. Flight 5A observation of darkening near Service Module (SM) zenith roll thrusters. The inset image shows an enlarged image of the zenith roll and pitch thrusters. The brownish discoloration is visible near the roll thrusters.

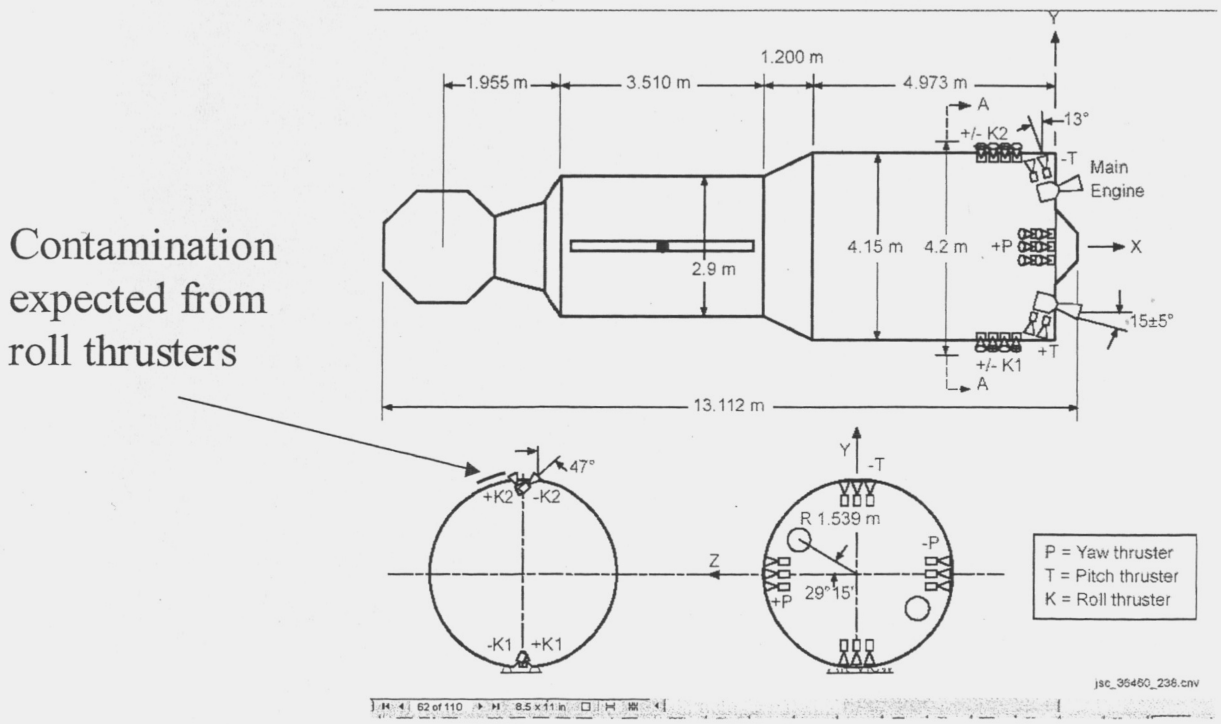

Figure 2. Service Module (SM) attitude control thrusters' position and direction. The pitch and yaw thrusters point away from the vehicle surface (13° from the normal). The roll thrusters point 47° from the normal. Contamination from the roll thrusters is expected on the SM surfaces close to these thrusters.

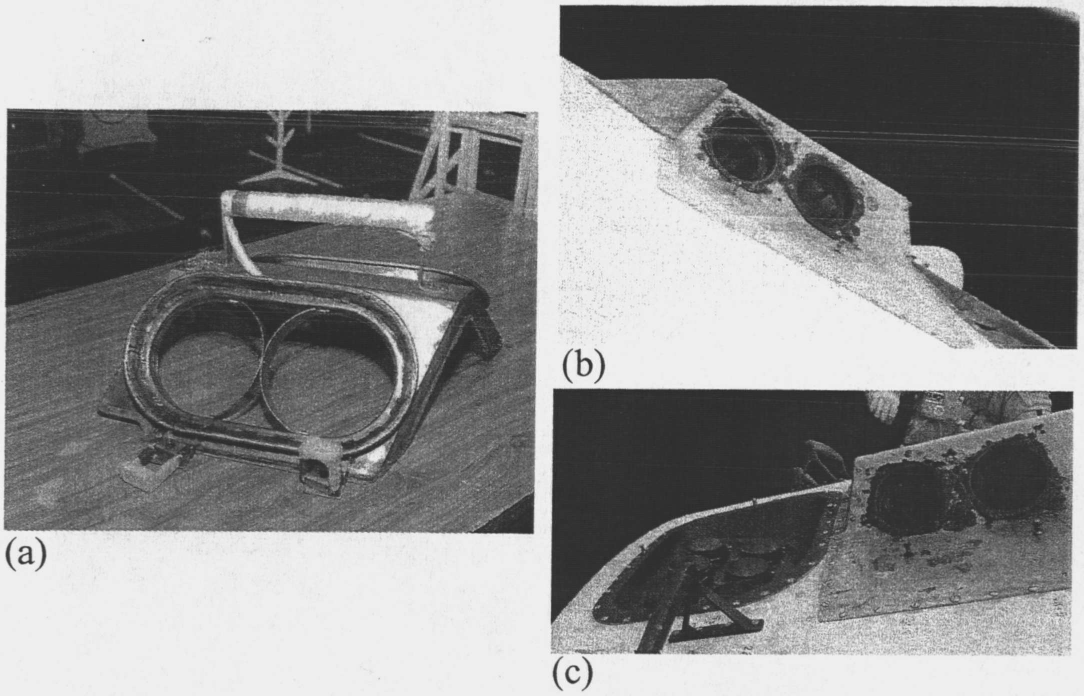

Figure 3. (a) Service Module (SM) Gas Dynamic Protection Unit (GZU) for the SM roll thrusters prior to flight and installation (b) SM roll thrusters prior to installation of the GZU (c) SM roll thrusters on the right side of the picture and pitch thrusters on the left hand side of the picture prior to installation of the GZU.

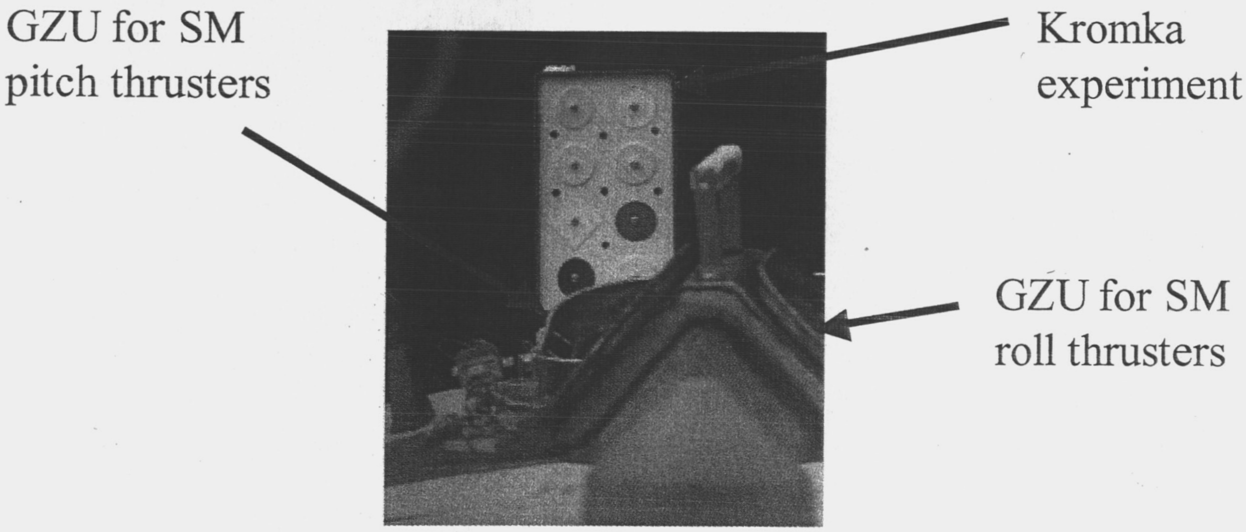

Figure 4. Image taken from Docking Compartment 1 (DC1) window. Kromka is visible in the middle of the image. It is an experiment to determine the effectiveness of the Gas Dynamic Protection Units (GZUs) and to test some materials in space. In front of the Kromka are the pitch thrusters with the GZU installed. In front of the pitch thrusters are the roll thrusters with the GZU installed.

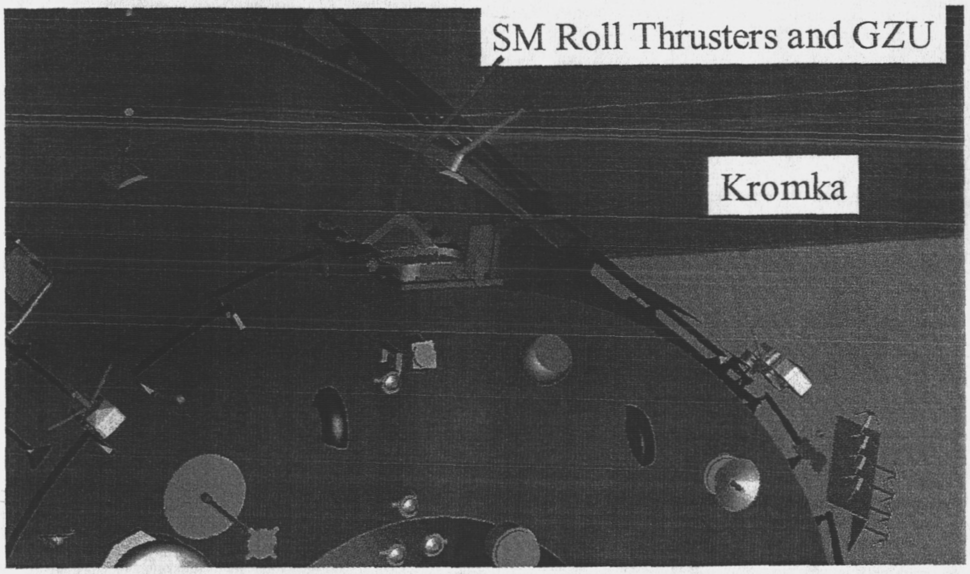

Figure 5. Nadir side of Service Module (SM). The Kromka experiment is visible near the SM pitch thrusters.

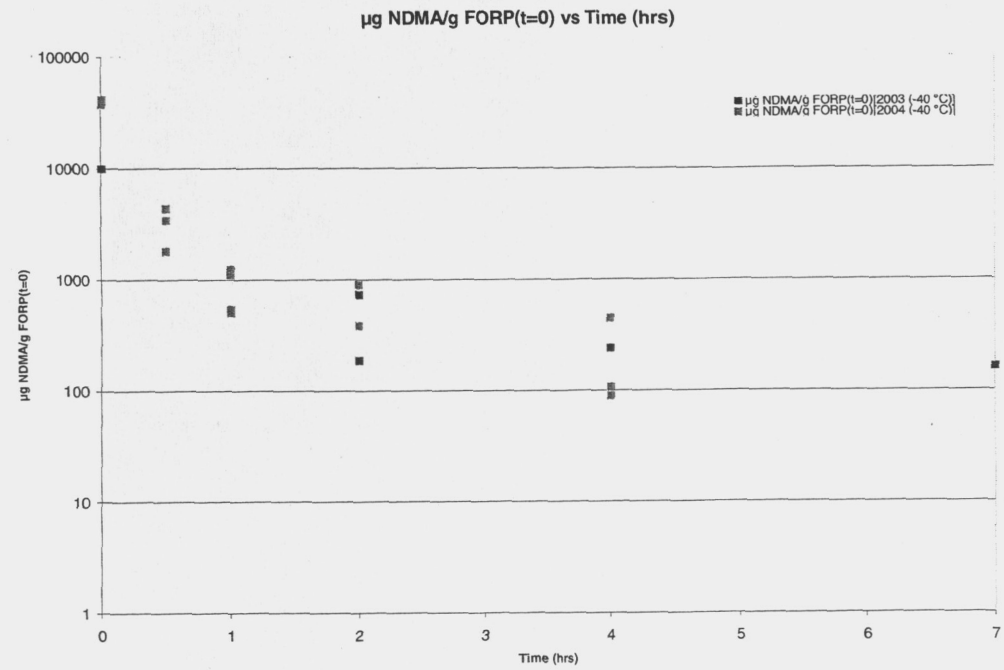

Figure 6. Concentration of NDMA relative to the initial mass of FORP (μg NDMA/g FORP) for the -40° C case (nadir, cold case) decreases rapidly with time. Within 1 hour the concentration level has reached a plateau.

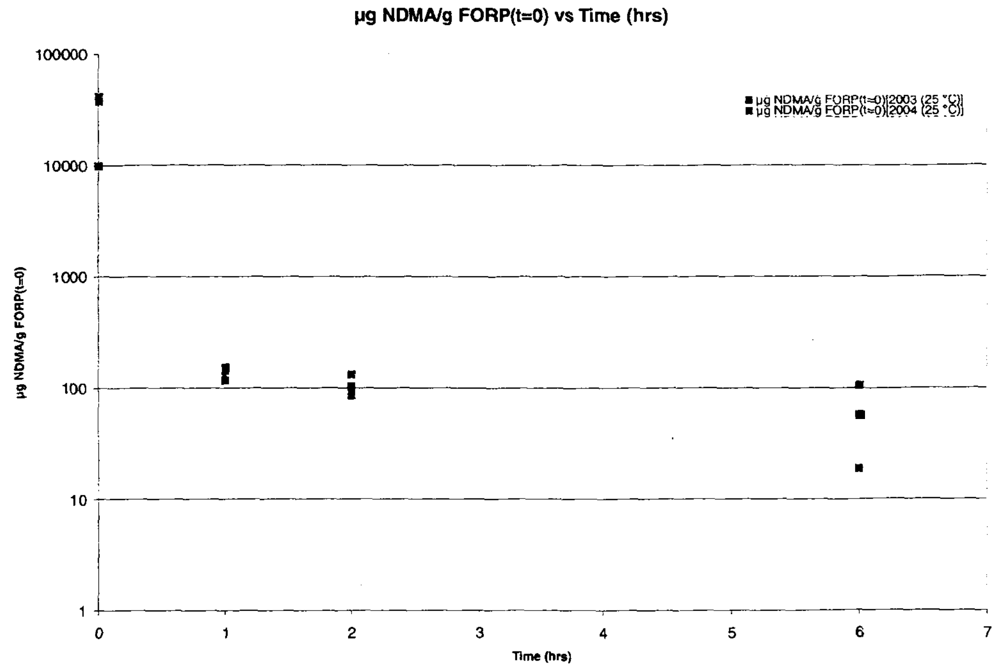

Figure 7. Concentration of NDMA relative to the initial mass of FORP (µg NDMA/g FORP) for the 25° C case (zenith, hot case) decreases rapidly with time. Within 1 hour the concentration level has reached a plateau.

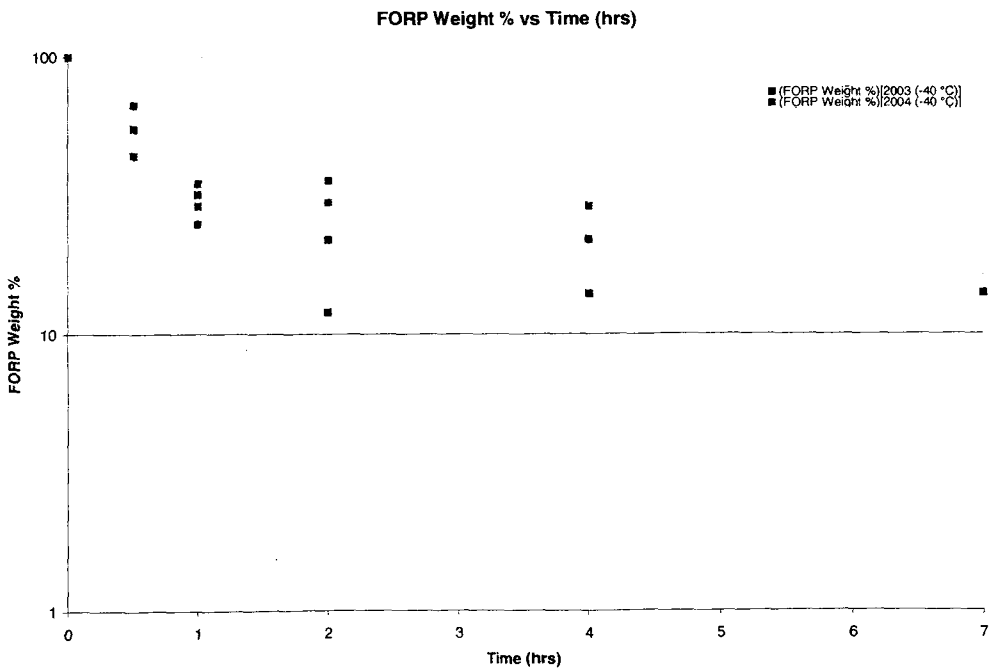

Figure 8. FORP weight (%) vs time for the -40° C case (nadir, cold case). FORP volatilizes rapidly to a stable mass that persists for a longer period of time.

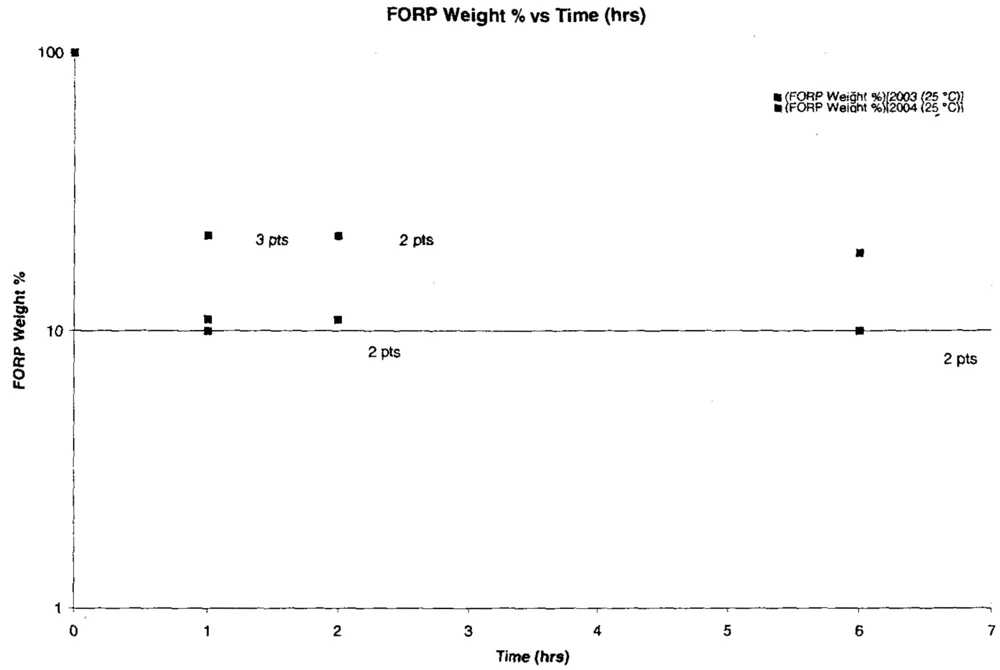

Figure 9. FORP weight (%) vs time for the 25° C case (zenith, hot case). FORP volatilizes rapidly to a stable mass that persists for a longer period of time.

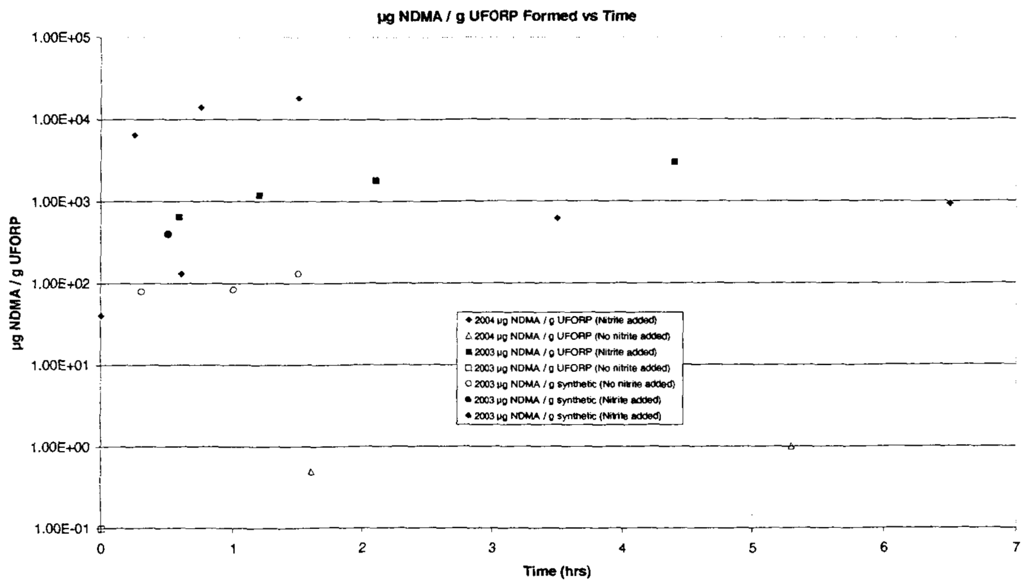

Figure 10. NDMA concentration (µg NDMA/g FORP) vs time measured during the NDMA formation test. It can be seen that the NDMA forms rapidly.

FORP Remaining 2 hrs after Service Module Thruster Firing (-40° C case)

FORP (g/cm²) remaining vs position on SM from roll thruster (m) for –40° C case 2 hrs after SM thruster firing (45 sec firing) (2.6 kg of propellant).

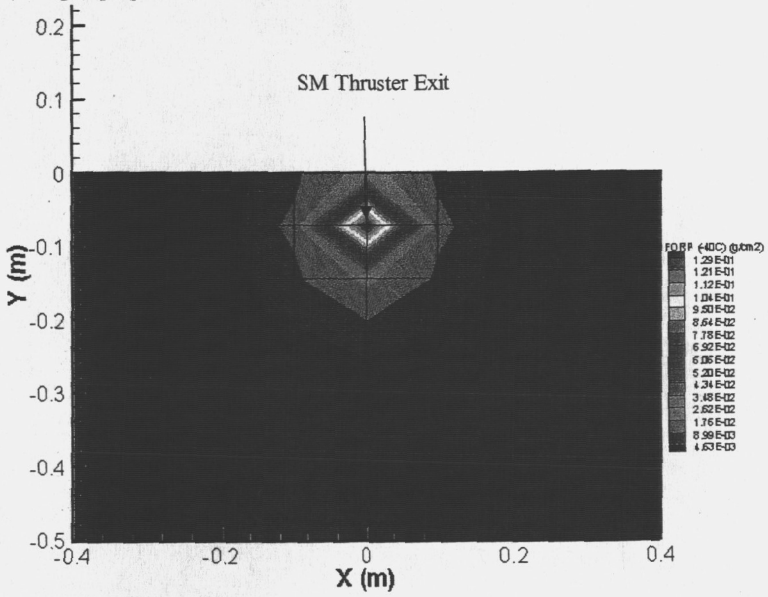

Figure 12. Map of the FORP predicted to remain after 2 hours on the surface around the SM roll thrusters after a 45 sec roll thruster firing. It can be seen that the FORP concentration drops rapidly with distance from the thruster.

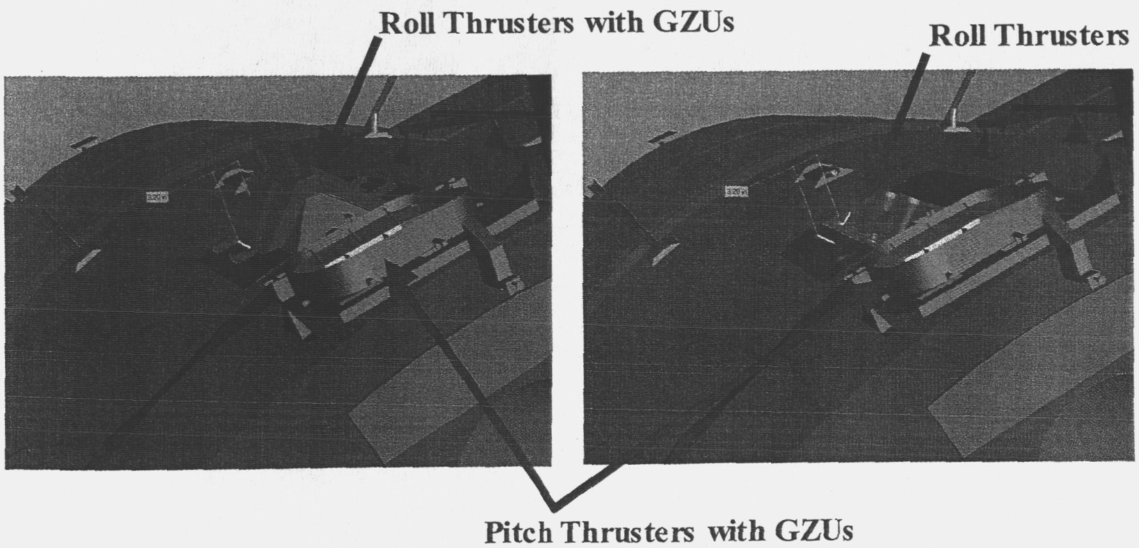

Figure 11. Zenith side of Service Module (SM). Gas Dynamic Protection Units (GZUs) constrain the thruster plume. The distance from the roll thruster to the closest SM surface outside the GZUs is ~3.2 in (~8 cm).

Ionic Species	Ammonium (%/wt[a])	Methylammonium (%/wt[a])	Dimethylammonium (%/wt[a])	Nitrate (%/wt[a])	Nitrite (%/wt[a])
CY 2003 Residue (10%)[b]	0.05	1.1	7.9	36	0.08
CY 2004	0.6	2	20	9	20
CY 2004 Residue (14%)[b]	0.3	1.7	13	48	0.6

[a] %/wt - Weight percent
[b] Ionic Species were analyzed after UFORP was subjected to vacuum for 5 days

Table 1. FORP Composition Ion Results

Distance (m)	FORP present (g/cm2)	NDMA released (g)	NDMA DC1 concentration (ppb)	NDMA ISS concentration (ppb)	
0.08	1.96E-02	3.57E-02	934	33	at GZU
0.15	6.22E-03	1.13E-02	296	10	
0.23	2.96E-03	5.39E-03	141	5	
0.30	1.72E-03	3.13E-03	82	3	
0.37	1.11E-03	2.03E-03	53	2	
0.44	7.77E-04	1.41E-03	37	1	

Table 2. NDMA concentration predicted to be released in the cabin for FORP transferred to the EVA suit one hour after the roll thruster firing at different distances from the roll thruster for the -40° C case (Nadir)

Distance (m)	FORP present (g/cm2)	NDMA released (g)	NDMA DC1 concentration (ppb)	NDMA ISS concentration (ppb)	
0.08	1.20E-02	2.18E-02	571	20	at GZU
0.15	3.80E-03	6.92E-03	181	6	
0.23	1.81E-03	3.30E-03	86	3	
0.30	1.05E-03	1.91E-03	50	2	
0.37	6.81E-04	1.24E-03	32	1	
0.44	4.75E-04	8.65E-04	23	1	

Table 3. NDMA concentration predicted to be released in the cabin for FORP transferred to the EVA suit one hour after the roll thruster firing at different distances from the roll thruster for the 25° C case (Zenith)