

EVAPORATION RATE STUDY AND NDMA FORMATION FROM UDMH/NO₂ REACTION PRODUCTS*

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ABSTRACT

Laboratory samples of *uns*-dimethylhydrazine (UDMH) fuel/oxidizer (nitrogen dioxide) non-combustion reaction products (UFORP) were prepared using a unique permeation tube technology. Also, a synthetic UFORP was prepared from UDMH, N-nitrosodimethylamine (NDMA), dimethylammonium nitrate, sodium nitrite and purified water. The evaporation rate of UFORP and synthetic UFORP was determined under space vacuum ($\sim 10^{-3}$ Torr) at -40 °C and 0 °C. The material remaining was analyzed and showed that the UFORP weight and NDMA concentration decreased over time; however, NDMA had not completely evaporated. Over 85% of the weight was removed by subjecting the UFORP to 10^{-3} Torr for 7 hours at -40 °C and 4 hours at 0 °C. A mixture of dimethylammonium nitrate and sodium nitrite formed NDMA at a rapid rate in a moist air environment. A sample of UFORP residue was analyzed for formation of NDMA under various conditions. It was found that NDMA was not formed unless nitrite was added.

INTRODUCTION AND OBJECTIVE

The International Space Station (ISS) Program Office requested testing of contamination being deposited on the surface of the service module. This contamination is a reaction product of *uns*-dimethylhydrazine (UDMH)/nitrogen dioxide. Astronauts may inadvertently bring this UDMH fuel/oxidizer reaction product (UFORP) into the airlock after an extravehicular activity (EVA). Earlier work established that a major ingredient of the UFORP was N-nitrosodimethylamine (NDMA), a potent carcinogen.¹ This laboratory was tasked to (1) determine the evaporation rate of the volatile components in a simulated space vacuum at selected temperatures and (2) to determine if NDMA is formed upon exposure of the nonvolatile UFORP residue to moist air. NDMA has been known to form in aqueous solutions containing dimethylamine and nitrite ion.² This data will allow Johnson Space Center (JSC) and Boeing to determine time requirements for evaporation of the volatile UFORP components and to assess the hazard potential if nonvolatile UFORP components are introduced into the airlock.

EXPERIMENTAL

PREPARATION OF UFORP

The UFORP was prepared by combining vapor streams from permeation tubes filled with liquid *uns*-dimethylhydrazine (UDMH) and oxidizer (N₂O₄) in a centrifuge tube chilled to 0 °C in accordance with the procedure described in earlier work.¹ UFORP prepared this way is a yellowish-orange liquid as shown in Figure 1, and consists of NDMA (approximately 0.8%) and other organic compounds.

*Approved for public release, distribution is unlimited.



Figure 1. UFORP residue before exposure to 10^{-3} Torr (0.5075g)

PREPARATION OF SYNTHETIC UFORP

Synthetic UFORP was prepared by mixing 2.5 mL of neat UDMH, 2.0 mL of neat NDMA, 0.43 g of dimethylammonium nitrate, 0.33 g sodium nitrite and 0.8 mL of purified water. Not all of the nitrate and nitrite salts were in solution.

PREPARATION OF DIMETHYLAMMONIUM NITRATE/NITRITE

Dimethylammonium nitrate was formed using an anion exchange resin (J. T. Baker, IONAC A-554 Cl⁻ Form, Type II Beads (16-50 Mesh)). Aqueous sodium nitrate was first passed through the column to convert the resin from the chloride to the nitrate form. Then aqueous dimethylammonium chloride (Aldrich) was passed through the resin to convert the dimethylammonium chloride to the nitrate. The aqueous effluent was evaporated using a rotary evaporator (Büchi) to recover the dimethylammonium nitrate. This was then repeated using new anion exchange resin and aqueous sodium nitrite. Dimethylammonium nitrite could not be formed using this method. Aqueous sodium nitrite was used with the dimethylammonium nitrate as a substitute for dimethylammonium nitrite.

PREPARATION OF UFORP RESIDUE

UFORP (1.0354 g) in a quartz bowl was placed inside a vacuum system at ambient temperature, as shown in Figure 2. The UFORP was subjected to 10^{-3} Torr for 5 days. The UFORP residue was removed and weighed 9.85×10^{-2} g.

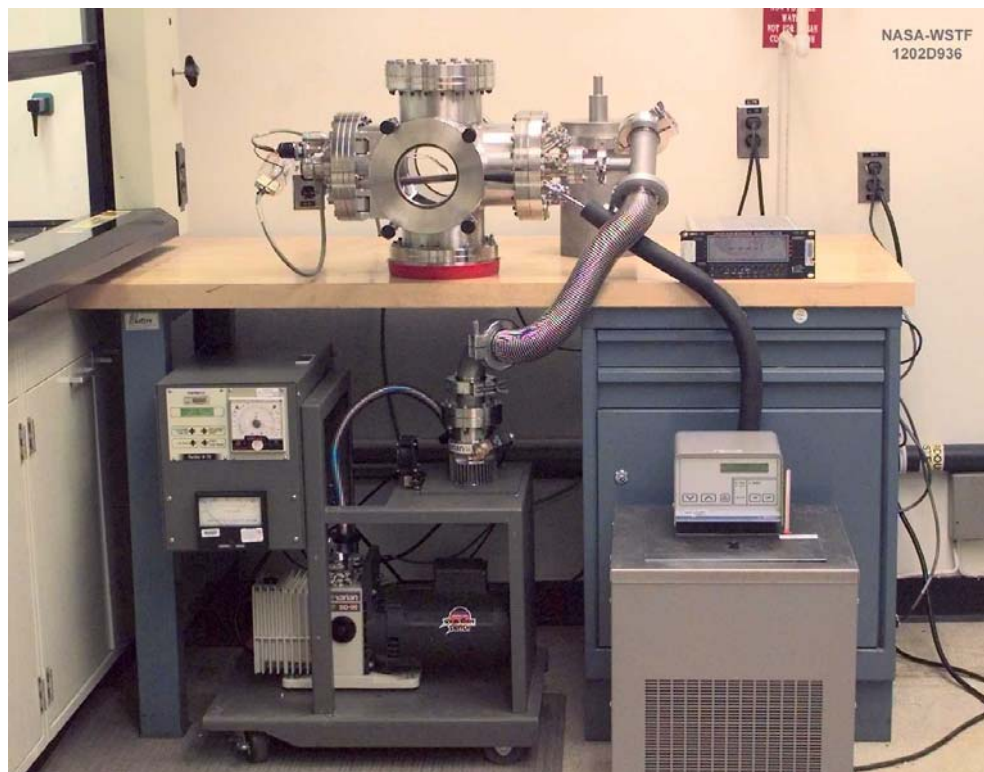


Figure 2. UFORP Evaporation Rate Vacuum System

EVAPORATION RATE TESTING

The vacuum system was evacuated to $\sim 10^{-3}$ Torr as indicated on the thermocouple gauge, then back-filled with nitrogen gas. The copper cold plate inside the vacuum chamber was cooled to -40 °C by running a chilled methanol and water mixture through a tube welded to the copper plate. Five glass slides were numbered 1 to 5 with an engraving tool and tared. A 250 μ L syringe was filled with 200 μ L UFORP, capped and weighed. The UFORP in the syringe was placed onto the first glass slide, which was immediately placed on the cooled copper plate. The syringe was capped and weighed again. The process was repeated for the remaining four glass slides. Ten minutes after the last slide was placed on the copper plate to allow it to cool to -40 °C, the vacuum system was started. The slides were removed from the vacuum chamber at selected time intervals. Each slide was placed into a desiccator and allowed to warm to room temperature before it was reweighed. The slides were then rinsed with two 1 mL aliquots of dichloromethane and collected into separate sample vials. The dichloromethane rinses were analyzed by gas chromatography-mass spectroscopy (GC-MS, Agilent model 6890N GC equipped with an Agilent model 5973 *Network* mass selective detector).

The process was repeated for the synthetic UFORP. The copper plate was then set to 0 °C, and the process was repeated for UFORP and synthetic UFORP.

SOLID PHASE MICROEXTRACTION

The headspace above the UFORP residue was sampled at various time intervals using a solid phase microextraction (SPME) injector equipped with a poly(dimethylsilane) on divinylbenzene fiber (Supelco^{®1}). The SPME needle was inserted through a septum located in the lid of the sample container and the fiber

¹ Supelco[®] is a registered trademark of the Sigma-Aldrich Co., Highland, Illinois.

was extended into the headspace gas for 1 minute. Then the fiber was removed and immediately analyzed by GC-MS.

RESULTS AND DISCUSSION

EVAPORATION RATE STUDIES

UFORP. The weight of the UFORP after being subjected to 10^{-3} Torr at $-40\text{ }^{\circ}\text{C}$ and $0\text{ }^{\circ}\text{C}$ was used to calculate the weight percent remaining. These residues, expressed as percent remaining, are shown in Figure 3. The concentration of NDMA remaining was calculated from 2 mL dichloromethane rinse solutions of the residues. The results are shown in Figures 4 and 5.

Figure 3 shows that the weight of the UFORP decreased with time. Over 85% of the weight was removed by subjecting the UFORP to 10^{-3} Torr for 7 hours at $-40\text{ }^{\circ}\text{C}$ and $0\text{ }^{\circ}\text{C}$. Figures 4 and 5 show that the NDMA concentration decreased with time at $-40\text{ }^{\circ}\text{C}$ and $0\text{ }^{\circ}\text{C}$, but still remained at low levels.

SYNTHETIC UFORP. The synthetic UFORP, prepared as described, contained 36% UDMH, 36% NDMA, 8% dimethylammonium nitrate, 6% sodium nitrite (equimolar to the nitrate), and 14% water. The quantity of UFORP residue remaining after selected time intervals at $-40\text{ }^{\circ}\text{C}$ and $0\text{ }^{\circ}\text{C}$ are shown in Figure 6.

Figure 6 shows the UFORP weight decreased significantly with time. Over 90% of the weight was removed by subjecting the UFORP to 10^{-3} Torr for 22 hours at $-40\text{ }^{\circ}\text{C}$ and for 30 minutes at $0\text{ }^{\circ}\text{C}$. The NDMA concentration immediately decreased from approximately 360,000 ppm to 140 ppm before the first measurement at $-40\text{ }^{\circ}\text{C}$ and to 10 ppm at $0\text{ }^{\circ}\text{C}$.

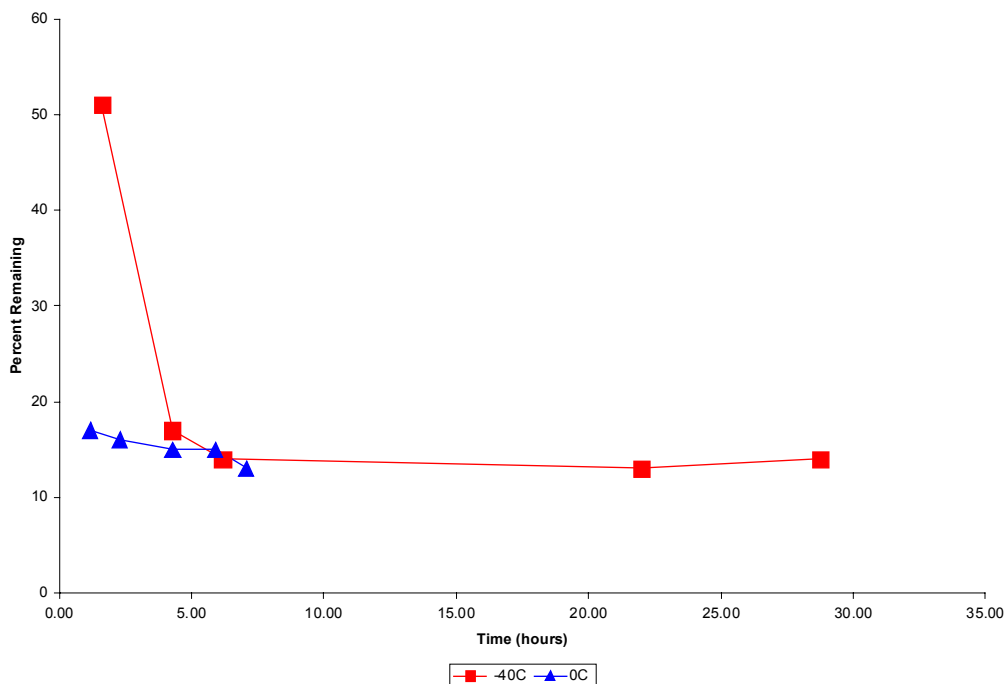


Figure 3. Weight percent remaining from evaporation of UFORP at $-40\text{ }^{\circ}\text{C}$ and $0\text{ }^{\circ}\text{C}$, 10^{-3} Torr

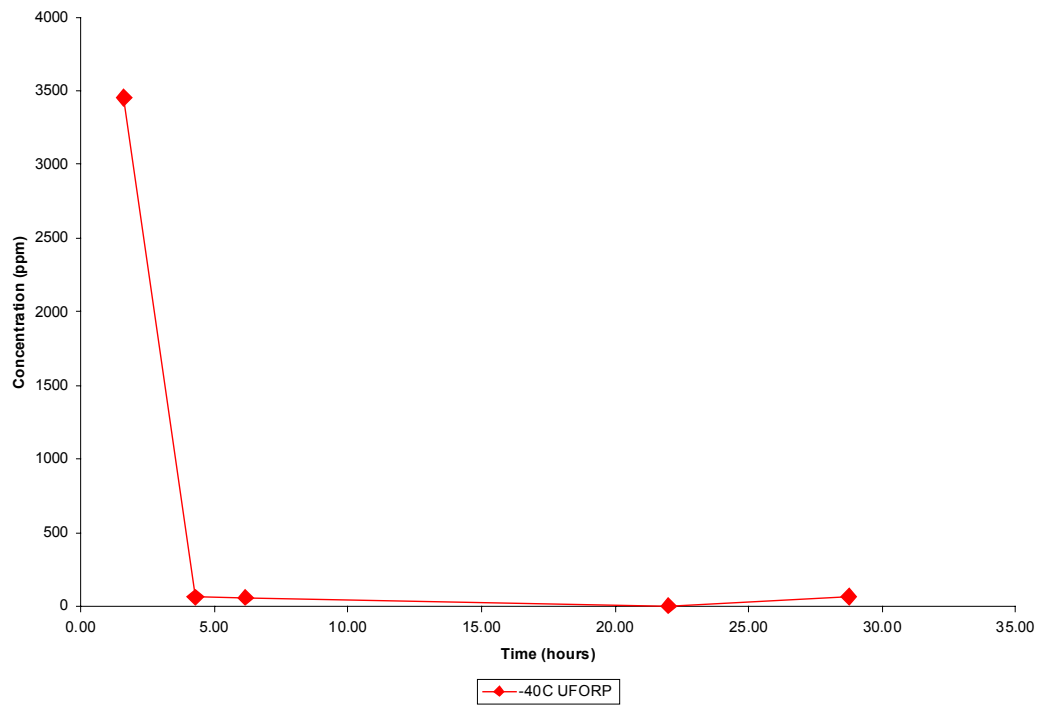


Figure 4. NDMA concentration from evaporation of UFORP at $-40\text{ }^{\circ}\text{C}$, 10^{-3} Torr. The starting NDMA concentration was approximately 8,000 ppm.

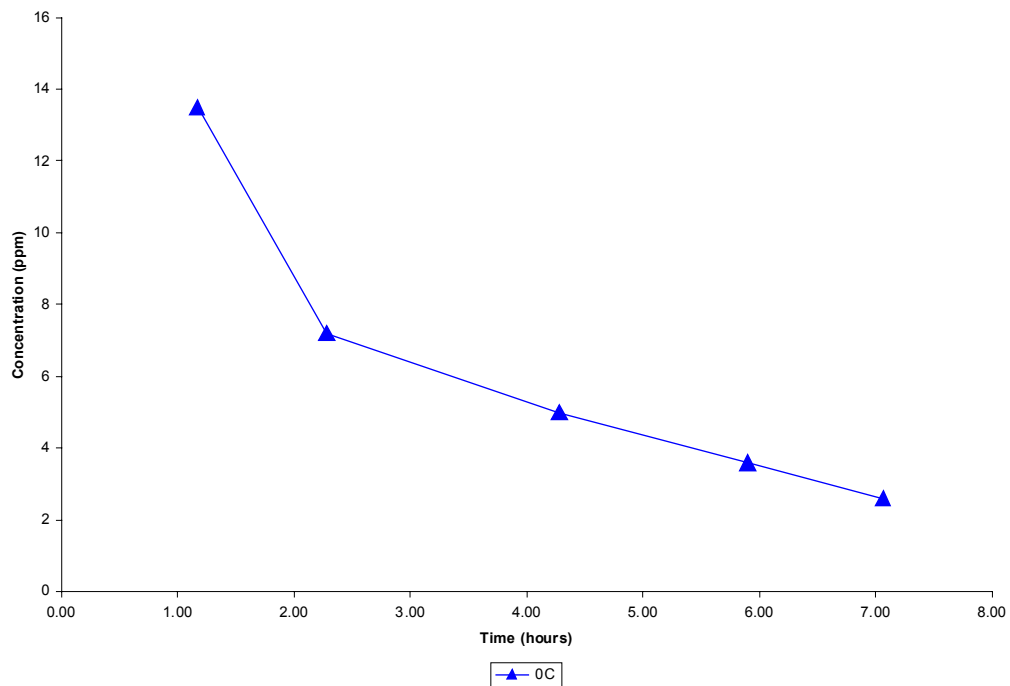


Figure 5. NDMA concentration from evaporation of UFORP at $0\text{ }^{\circ}\text{C}$, 10^{-3} Torr. The starting NDMA concentration was approximately 8,000 ppm.

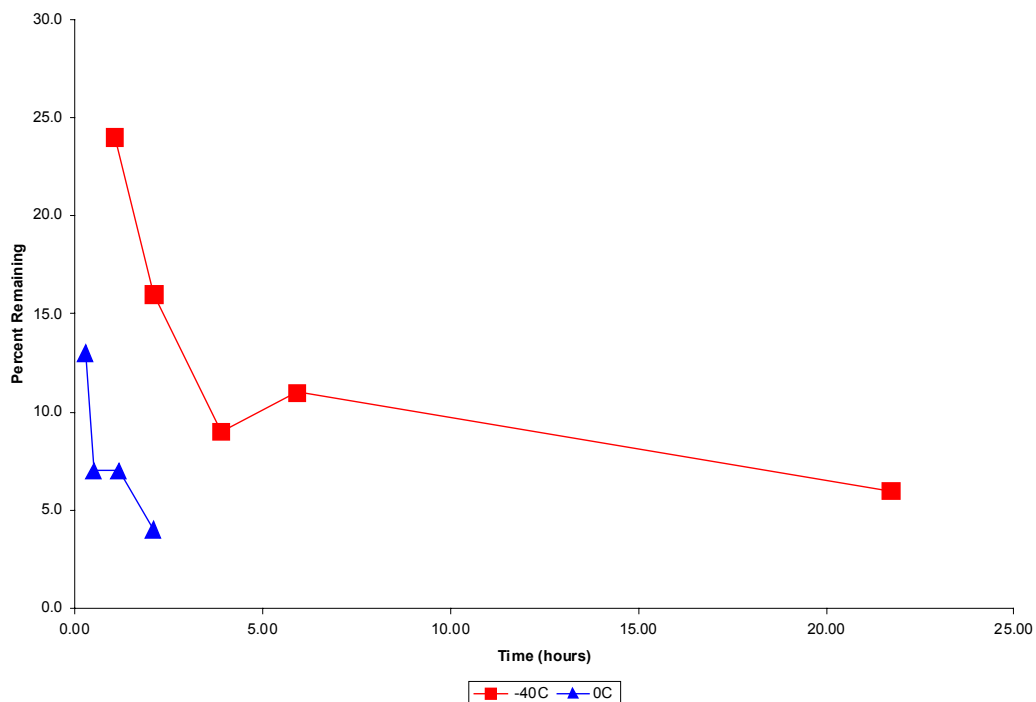


Figure 6. Weight percent remaining from evaporation of synthetic UFORP at -40 °C and 0 °C, 10^{-3} Torr

NDMA FORMATION TESTING

Three separate mixtures were studied in air under ambient temperature and pressure. The first mixture contained dimethylammonium nitrate (2.3 g), sodium nitrite (1.6 g) and 1 mL of purified water, which were all added simultaneously. An initial analysis of the headspace by SPME/GC-MS was performed immediately after mixing the components and 3400 ppm NDMA was found. After 27 hours, 9,000 ppm NDMA was found.

To see whether NDMA formation was dependent on each component, a second mixture was made which at first contained only dimethylammonium nitrate (1.5 g). The dimethylammonium nitrate was analyzed at various time intervals and NDMA concentration stayed at approximately 700 ppm over a 5-hour period. After the addition of 1 mL of water, NDMA concentrations dropped to approximately 100 ppm. The mixture was monitored for 2 hours after the addition of water, then sodium nitrite (1.0 g) was added. The mixture formed NDMA rapidly. Figure 7 shows the rate of formation of NDMA from this mixture after sodium nitrite was added.

To determine the effect of the synthesized dimethylammonium nitrate, a third mixture containing only dimethylammonium chloride (2.0 g), sodium nitrate (2.0 g), and 1 mL of water, was analyzed over a 22-hour period and no NDMA was detected (detection limit = 25 ppm). After the addition of sodium nitrite (1.6 g), NDMA formed rapidly. Figure 8 shows the rate of formation of NDMA from this mixture after the addition of sodium nitrite.

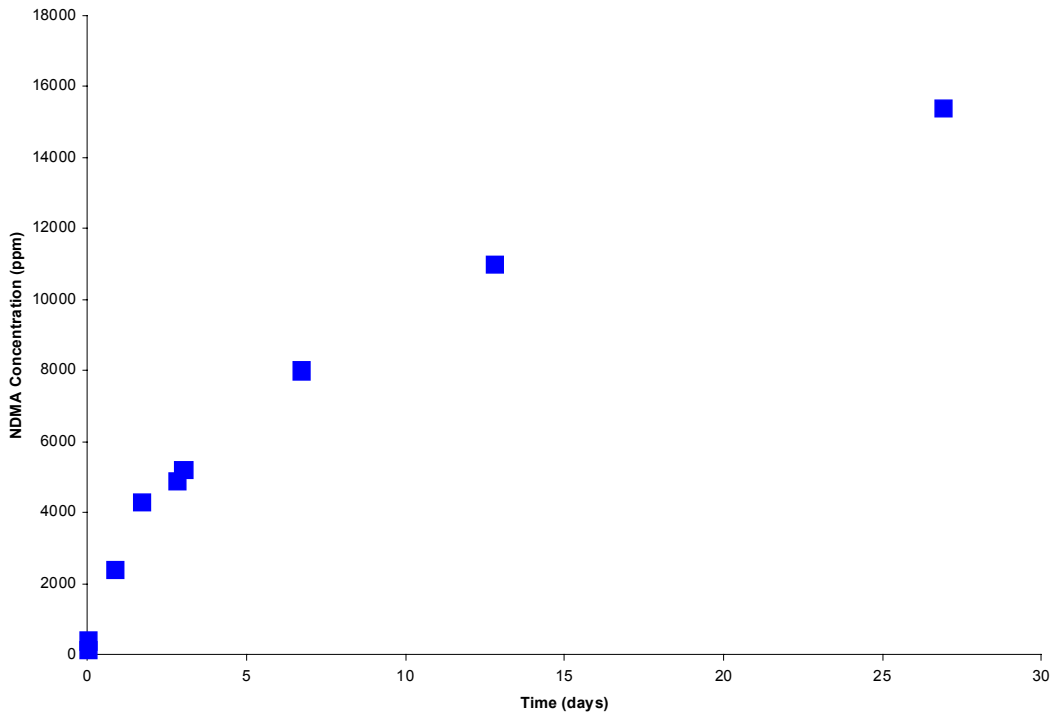


Figure 7. Formation of NDMA from mixture of dimethylammonium nitrate, water, and sodium nitrite

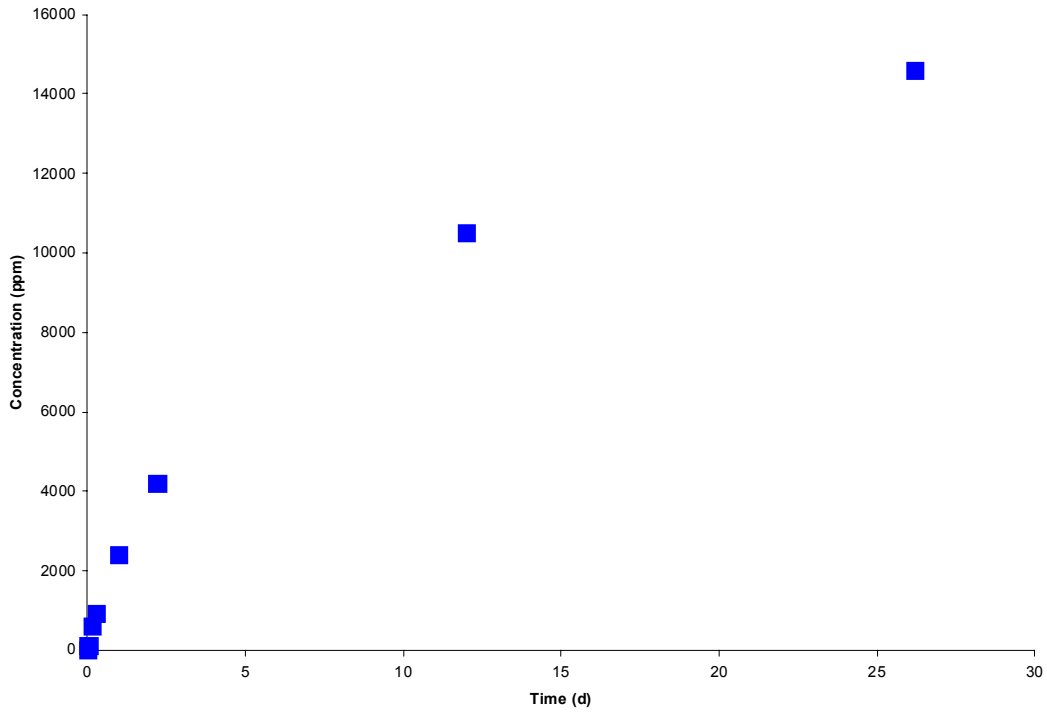


Figure 8. Formation of NDMA from mixture of dimethylammonium chloride, sodium nitrate, water, and sodium nitrite

UFORP Residue. When the UFORP residue was removed from the vacuum system, it appeared as a shiny, highly viscous liquid as shown in Figures 9 and 10. Most of the UFORP residue (60.9 mg) was placed into a tared 40 mL ICHEM vial using a spatula. The remaining UFORP residue was rinsed from the quartz bowl into a 40 mL ICHEM vial with 1 mL of water.



Figure 9. UFORP residue inside vacuum chamber at 10^{-3} Torr after 26 hours



Figure 10. UFORP residue (0.06 g) after 26 hours exposure to 10^{-3} Torr

The UFORP residue and the UFORP residue rinsed with 1 mL of water were analyzed by SPME/GC-MS for 2 days and no NDMA was found. The UFORP residue rinsed with water was spiked to 100 ppm NDMA and 100 ppm was recovered, ruling out a detection problem due to the matrix of the UFORP. The UFORP residue was monitored for a total of 4 days and no NDMA was detected in the headspace.

To determine why the UFORP residue was not forming NDMA, some UFORP residue (9.9 mg) was added to 1 mL of water. The sample was analyzed for nitrate and nitrite by ion chromatography (IC) using a Dionex^{®1} Model DX-600 ion chromatograph equipped with a conductivity detector and a Dionex AS14 anion exchange column. Ammonium, methylammonium, and dimethylammonium were determined using the same IC but with a Dionex CS16 cation exchange column. An analysis of the ions present in the UFORP water solution by IC showed there was minimal nitrite in the UFORP residue. Table 1 shows the IC results.

Sodium nitrite (3.3 mg) was added to the UFORP residue (22.1 mg) remaining in the 40 mL ICHEM vial to see if NDMA would form due to nitrite. The headspace above the mixture was analyzed by SPME/GC-MS at various time intervals. NDMA formed rapidly after the addition of sodium nitrite. The results are shown in Figure 11.

Table 1. IC results for UFORP residue in water

Component	Amount (µg)	Weight Percent
Nitrite	7.9	0.08%
Nitrate	3600	36%
Ammonium	5.3	0.05%
Methylammonium	110	1.1 %
Dimethylammonium	780	7.9%

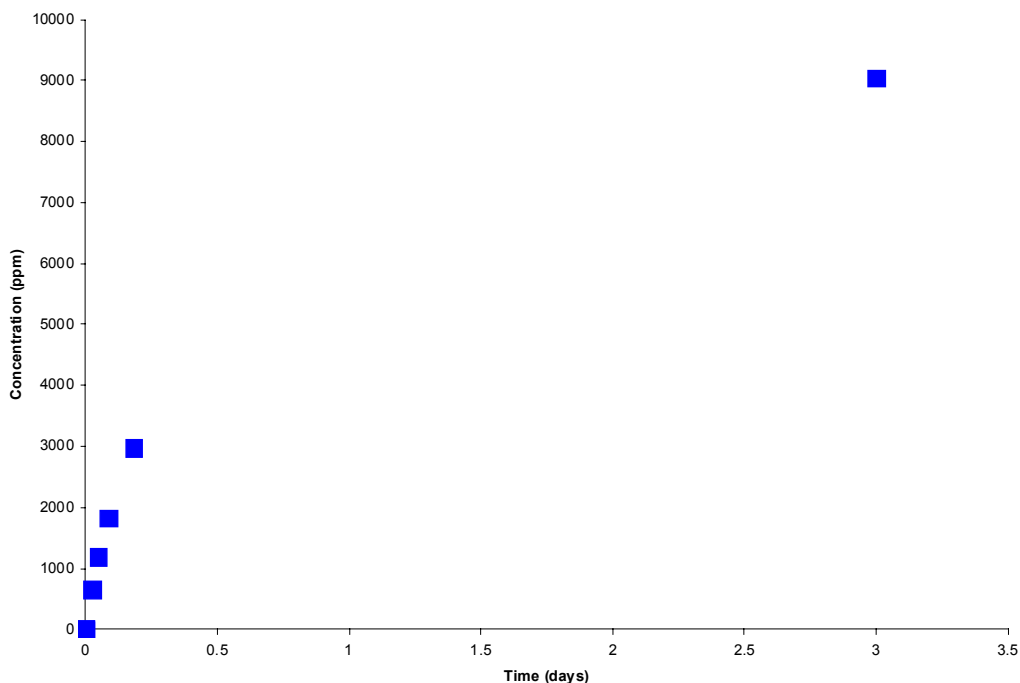


Figure 11. NDMA Formation from NaNO₂ and UFORP residue

¹ Dionex[®] is a registered trademark of the Dionex Corporation, Sunnyvale, California.

CONCLUSIONS

The analysis of UFORP and synthetic UFORP subjected to a simulated space vacuum showed that NDMA concentration decreased in a space environment even at $-40\text{ }^{\circ}\text{C}$. However, NDMA is not completely removed from UFORP after 29 hours in a space-like environment ($-40\text{ }^{\circ}\text{C}$, 10^{-3} Torr).

NDMA was readily formed when a mixture of dimethylammonium nitrate, water, and sodium nitrite are exposed to air in a laboratory environment. The same is true for the mixture of water, laboratory reagent-grade dimethylammonium chloride, sodium nitrate, and sodium nitrite. NDMA was not formed from UFORP residue alone, likely due to the low nitrite concentration. When sodium nitrite was added to the UFORP residue, NDMA began to form immediately and rapidly.

REFERENCES

1. Dee, L.A. and V.D. Davidson. *Laboratory Preparation and Characterization of UDMH/NO₂ Reaction Products*, WSTF-IR-0168-001-02, NASA Johnson Space Center White Sands Test Facility, Las Cruces, NM, April 29, 2002.
2. Liteplo, R.G. and M.E. Meek. *N-Nitrosodimethylamine*, <http://www.inchem.org/documents/cicads/cicads/cicad38.htm>.