

CONTAMINATION DETECTION AND MITIGATION STRATEGIES FOR UNSYMMETRICAL DIMETHYLHYDRAZINE/NITROGEN TETROXIDE NON-COMBUSTION PRODUCT RESIDUES*

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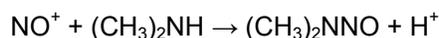
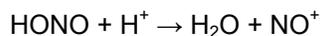
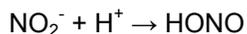
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ABSTRACT

Dimethylamine and nitrite, which are non-combustion reaction products of unsymmetrical dimethylhydrazine (UDMH) and nitrogen tetroxide (NTO) propellants, can contaminate spacesuits during extra-vehicular activity (EVA) operations. They can react with water in the International Space Station (ISS) airlock to form N-nitrosodimethylamine (NDMA), a carcinogen. Detection methods for assessing nitrite and dimethylamine contamination were investigated. The methods are based on color-forming reactions in which intensity of color is proportional to concentration. A concept color detection kit using a commercially available presumptive field test for methamphetamine coupled with nitrite test strips was developed and used to detect dimethylamine and nitrite. Contamination mitigation strategies were also developed.

INTRODUCTION

Unsymmetrical dimethylhydrazine (UDMH)/nitrogen tetroxide (NTO) propulsion systems on the International Space Station (ISS) generate non-combustion product residues that contain toxic chemical species. The product residue is conveniently referred to as UDMH Fuel Oxidizer Reaction Products (UFORP). Of the multitude of chemical species in UFORP, N-nitrosodimethylamine (NDMA) is a compound of major concern to NASA. There are different pathways for NDMA formation in UDMH/NTO propulsion systems. One pathway for NDMA formation is partial oxidation of UDMH. Another pathway for NDMA formation is the reaction of dimethylamine and nitrite with water. The latter reaction was of interest to this research because of a concern that non-volatile dimethylamine and nitrite species, probably salts, might contaminate a spacesuit during extra-vehicular activity (EVA) operations. Upon re-entry into the ISS airlock, NDMA could be formed:



As a result, astronauts could be exposed to NDMA formed in the airlock, and NDMA contamination in the airlock could potentially spread inside the ISS. Therefore, a need to detect dimethylamine and nitrite was identified. Additionally, a strategy for decomposing UFORP residues into less reactive, and less toxic, or more volatile products that could be evaporated in a space environment was also required.

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Due to space and power constraints, EVA Operations at NASA Johnson Space Center requested the detection methods to be based on readily observable color changes under no-flow conditions and cover a dynamic range of several orders of mass or concentration magnitude. In addition, the detection methods were requested to be applicable to spacesuit wipe samples to avoid contact of spacesuit surfaces with detection test chemicals. Finally, commercially available off-the-shelf (COTS) technology was requested.

EVA Operations also requested a mitigation strategy for gross UFORP contamination, should it be detected. The mitigation strategy was not constrained to the use of benign chemical methods.

NITRITE DETECTION

Typically available COTS nitrite test strips determine nitrite by the reaction of nitrite with a non-volatile acid to form nitrous acid, which then diazotizes an organic amine. The diazotized organic amine then reacts with a compound, such as N-(1-naphthyl)ethylenediamine, to form a red-violet azo dye. The intensity of the azo dye color is proportional to the concentration of nitrite. The concentration of nitrite in a test sample can be determined by comparing the color of the exposed nitrite test strip to a color comparison chart that expresses numerical nitrite or nitrogen concentrations corresponding to the appropriate developed colors. All of the reagents necessary for the color change are impregnated on a test zone of the COTS nitrite test strips. Initial screening of nitrite test strips showed there was no interference by nitrate.

DIMETHYLAMINE DETECTION

Dimethylamine is a small, secondary amine and its determination is normally made using instrumental methods. Many sophisticated methods requiring digestions, sample clean up, analytical separations, and instrumental analysis methods were found but were not options within the constraints of the test requirements. No COTS colorimetric test methods specific for dimethylamine were found. A search of classical wet-chemical methods for amine detection using colorimetric methods yielded several options, many of which are employed in qualitative organic laboratory tests. Several candidate color-forming reagents and methods were screened for suitability of dimethylamine detection prior to the performance of the work reported herein. These included Simon's reagent (an aqueous sodium nitroprusside/acetaldehyde solution and an aqueous sodium carbonate solution);¹ 7-chloro-4-nitro-2-oxa-1,3-diazole (NBD Chloride) in acetone;² 1,3-dinitrobenzene (*m*-dinitrobenzene) in acetone;³ Fluorescamine in acetone;⁴ 2,4-dinitrofluorobenzene (DNFB) in anhydrous ethanol;⁵ dansyl chloride;⁶ and the Hinsberg Test with benzenesulfonyl chloride and sodium hydroxide.⁷ The candidate color forming reagents and methods were also screened with ammonia, methylamine, and trimethylamine in order to evaluate potential interferences with dimethylamine color detection. Though trimethylamine was not identified as a UFORP constituent it was included in the screening tests in order to evaluate the complete homologous series of amines.

Simon's reagent was the most promising of these reagents for the colorimetric determination of dimethylamine as it showed selectivity over ammonia, methylamine, and trimethylamine and formed a blue-purple color. Simon's reagent was further evaluated in this work, and the COTS method employed in this work was a color test for methamphetamine using Simon's reagent chemistry, which is used as a presumptive field test by law enforcement officials.¹ The methamphetamine test is used for qualitative and presumptive testing only and is typically not calibrated to measure concentration. The methamphetamine test is available as a COTS field test kit from forensic suppliers.

CONCEPT TEST KIT FOR NITRITE AND DIMETHYLAMINE

It seemed reasonable that a test for nitrite could be coupled with a test for dimethylamine to produce a concept test kit for the simultaneous determination of these analytes. We were aware of the possibility that amines used in the COTS nitrite test strips could interfere with dimethylamine determination and therefore ensure our experiments were able to detect if an interference occurred.

CONTAMINATION MITIGATION STRATEGIES

Earlier work performed at NASA Johnson Space Center White Sands Test Facility (WSTF) indicated that many UFORP constituents evaporate with time in a space-like vacuum environment.⁸ It was observed, however, that dimethylamine and nitrite persisted under vacuum, possibly because their species were non-volatile salts. EVA Operations requested a strategy for decomposing UFORP residues into less reactive, and less toxic, or more volatile products that could be evaporated in a space environment. The mitigation strategy was required to decontaminate gross amounts of UFORP and was not limited to use of benign chemicals. The strategy presented in the Discussion Section of this paper is based on previous work performed at WSTF and on applicable principles of decontamination.

In earlier studies,⁹ WSTF demonstrated that dilute aqueous solutions of propellant hydrazines (hydrazine, monomethylhydrazine (MMH), and UDMH) and their oxidation products (NDMA and N-nitrodimethylamine (DMN)) were decomposed by Raney^{®†} nickel generated by the dissolution of nickel-aluminum (Ni-Al) alloy in sodium hydroxide solution.

Hydrazine was decomposed to ammonia:



MMH was decomposed to methylamine and ammonia:



UDMH was decomposed to dimethylamine and ammonia:



NDMA was decomposed to dimethylamine and ammonia proceeding through a UDMH intermediate:



DMN was decomposed to dimethylamine and ammonia proceeding through NDMA and UDMH intermediates:



Other studies^{9,10} with synthetic solutions or with UFORP prepared in the WSTF laboratory showed that other UFORP species, in addition to NDMA and DMN, were decomposed by Raney nickel, with the following results:

[†] Raney[®] is a registered trademark of R. Grace & Company Corporation, New York, New York.

Nitrite in water was reduced from an initial solution concentration of 1000 ppm to 67 ppm after 300 min (> 93 percent reduction); the predicted product was ammonia. Nitrate was also decomposed, but its decomposition proceeded through nitrite as an intermediate with a predicted product of ammonia:



N,N-dimethylformamide in a UFORP solution was reduced by Ni-Al from an initial solution concentration of 36 ppm to 23 ppm after 245 min (> 36 percent reduction). Dimethylamine was a predicted decomposition product.

Tetramethyltetrazene in a UFORP solution was reduced by Ni-Al from an initial solution concentration of 145 ppm to 6 ppm after 245 min (> 95 percent reduction). Dimethylamine was a predicted decomposition product.

Bis-(dimethylhydrazone)ethanedial in a UFORP solution was reduced by Ni-Al nickel from an initial solution concentration of 51 ppm to less than 1.8 ppm after 245 min (> 96 percent reduction). Ethylenediamine and dimethylamine were predicted decomposition products.

Dimethylaminoacetonitrile in a UFORP solution was reduced by Ni-Al nickel from an initial solution concentration of 11 ppm to less than 1.8 ppm after 245 min (> 83 percent reduction). N,N-dimethylethylenediamine was a predicted decomposition product.

This work demonstrated the feasibility of reductive decomposition of UFORP constituents to less toxic or more volatile products and forms a basis for some of the contamination mitigation strategy proposed in the Discussion Section of this report.

EXPERIMENTAL

NITRITE DETECTION

Nitrite solutions at different concentrations were prepared from GFS Chemicals (Powell, Ohio) or Aldrich (Saint Louis, Missouri) ACS reagent grade sodium nitrite and deionized water. Nitrite test strips obtained from EMD Chemicals™[‡] were EM Quant^{®§} Nitrite Test Strips (category number 10007) with a detection range from 2 to 80 ppm nitrite and EM Quant[®] Nitrite Test Strips (category number 10022) with a detection range from 100 to 3000 ppm nitrite. Combination nitrate/nitrite test strips were WaterWorks™^{**} Nitrate/Nitrite Water Quality Test Strips (part number 4890009) obtained from Industrial Test Systems, Incorporated (Rock Hill, South Carolina) with a detection range from 0 to 10 ppm nitrite-nitrogen. In most tests the nitrate zone of the WaterWorks test strips were ignored or physically cut off of the strips before tests. To evaluate quantitation of nitrite on a simulated wipe sample, laboratory wipe tissues were wetted with freshly prepared sodium nitrite solutions of varying concentrations. The strips were applied to the wetted wipe surface and the color allowed to develop, then read against their color comparison scale in accordance with the manufacturer's instructions. Because the color comparison scale of the WaterWorks test strips correlated to nitrite-nitrogen (N) concentration, the sample test strip was matched with the closest color on the color comparison scale and the corresponding nitrite-N concentration was multiplied by 3.3 (gravimetric factor of nitrite/N) to obtain the equivalent nitrite concentration.

[‡] EMD Chemicals™ is a trademark of Merck KGaA, Frankfurt, Germany.

[§] EM Quant[®] is a registered trademark of Merck KGaA, Frankfurt, Germany.

^{**} WaterWorks™ is a trademark of Industrial Test Systems, Incorporated, Rock Hill, South Carolina.

DIMETHYLAMINE DETECTION

Dimethylamine solutions were prepared from dimethylamine hydrochloride (99 percent obtained from Aldrich) and deionized water.

Simon's reagent consisted of Solution A and Solution B.¹ Solution A (aqueous sodium nitroprusside/acetaldehyde solution) was prepared by dissolving 1 g sodium nitroprusside (ACS reagent grade sodium nitroferricyanide(III) dihydrate obtained from Aldrich) in 50 mL distilled water and adding 2 mL of acetaldehyde (ACS reagent grade obtained from Aldrich) to the solution with thorough mixing. Solution A was stored in an aluminum foil-covered glass bottle. Solution B (2 percent sodium carbonate) was prepared by dissolving 1 g of sodium carbonate (ACS reagent grade obtained from Aldrich) in 50 mL deionized water. For tests with Simon's reagent, different volumes of a dimethylamine solution were added to glass culture tubes. One drop of Solution A was added to a test solution followed by the addition of 2 drops of Solution B. The test solution was then agitated and the color was observed and recorded.

NARK^{®††} II Methamphetamine narcotic analysis reagent kits (part number NARK20015) were obtained from Sirchie Finger Print Laboratories, Inc (Youngsville, South Carolina). These test kits are a durable plastic pouch containing ampoules of reagents in a plastic holder. Although the composition of the reagents is proprietary, they utilize Simon's reagent chemistry. For tests with NARK II kits, different volumes of dimethylamine solution were pipetted onto one or more cotton swabs, which were then placed inside a NARK II field test kit pouch. After the pouch was sealed with its plastic clip, each of the ampoules was broken in accordance with the manufacturer's instructions. The solutions were mixed by gently shaking the pouch after breaking each ampoule. The resulting color was then observed and recorded.

CONCEPT TEST KIT FOR NITRITE PLUS DIMETHYLAMINE DETECTION

A WaterWorks nitrate/nitrite test strip with the nitrate test zone cut off or an EM Quant nitrite test strip were placed inside a NARK II field test kit pouch. Different volumes of nitrite and dimethylamine solutions were pipetted directly into the NARK II field test kit pouches. The pouches were then sealed with their clip in accordance with the manufacturer's instructions. The colors of the nitrite test zones were read and recorded as described earlier. The NARK II ampoules were then broken and the colors due to reaction of dimethylamine with the acetaldehyde, sodium carbonate, and sodium nitroprusside were observed and recorded.

UFORP PREPARATION AND CHARACTERIZATION

UFORP was prepared by the non-combustion vapor phase reaction of UDMH and MON-3 NTO.⁸ Prior to testing UFORP, dimethylamine and nitrite concentrations were determined by ion chromatographic analysis using a Dionex^{®‡‡} DX-600 ion chromatograph. Dilutions of UFORP were prepared in deionized water.

UFORP DETECTOR KIT AND UFORP DETECTION

A concept UFORP detector kit was assembled by inserting one or more nitrite test strips into a NARK II field test kit pouch.

Different volumes of aqueous UFORP solution (5100 µg UFORP/g deionized water) were pipetted into NARK II field test kit pouches to which a WaterWorks nitrate/nitrite test strip or EM Quant nitrite test strip had been previously inserted. The pouches were then sealed with their clip in accordance with the manufacturer's instructions. Nitrite concentrations were read and recorded. The ampoules were then

^{††} NARK[®] is a registered trademark of Sirchie Finger Print Laboratories Corporation, Youngsville, North Carolina.

^{‡‡} DIONEX[®] is a registered trademark of Dionex Corporation, Sunnyvale, California.

broken and their contents mixed in accordance with the manufacturer's instructions and the resultant colors were observed and recorded.

UFORP DECONTAMINATION

UFORP is a complex mixture of compounds whose composition has been characterized elsewhere.^{8, 11} Some of the major UFORP constituents have been shown to chemically decompose under laboratory conditions.^{9, 10} Other UFORP constituents have been shown to evaporate under a space-like vacuum.⁸ Chemical logic is also applicable to the development of decontamination strategies.

RESULTS

NITRITE DETECTION

Nitrite test strips gave accurate results when a strip with the appropriate detection range was exposed to a wipe tissue wetted with nitrite solution. Results are shown in Table 1.

DIMETHYLAMINE DETECTION

Dimethylamine gave a purple color with Simon's reagent. The intensity of the purple color increased with concentration. Table 2 describes the colors resulting from the mass of dimethylamine in the solutions.

These results show Simon's reagent is very sensitive to the colorimetric determination of dimethylamine. The color of Simon's reagent is light brown and color of the complex formed with dimethylamine is purple. The results suggest a visual detection limit is 0.01 mg dimethylamine under the conditions of this test. The color change to purple was so intense that a mass of 0.2 mg dimethylamine could not be visually distinguished from a mass of 0.6 mg dimethylamine.

The NARK II kits produced a red color for a blank water sample. The kits produced a purple color with samples containing a detectable amount of dimethylamine. Table 3 shows the color resulting from testing different volumes of dimethylamine solutions. Figure 1 is a photograph of NARK II kits tested with dimethylamine. The results shown in Figure 1 suggest the visual detection limit for dimethylamine is 0.05 mg and a strongly detect color at 0.5 mg.

NITRITE PLUS DIMETHYLAMINE DETECTION

It was found that leaving the EM Quant 10022 test strip inside the field test kit produced a positive result (purple color) in the absence of dimethylamine; therefore, these test strips were eliminated from further testing. The EM Quant 10007 and WaterWorks test strips did not cause this interference and could be used successfully in combination with the NARK II kits. The results of the combined solution tests are shown in Table 4.

UFORP DETECTION

The nitrite and dimethylamine concentrations in the UFORP were 160,000 and 210,000 ppm by weight, respectively, as shown in Table 5. The diluted UFORP solution used for testing contained nitrite and dimethylamine concentrations of 820 and 1100 ppm by weight, respectively.

The results of the WaterWorks nitrite strips and NARK II Field Test Kits analysis of the diluted UFORP solution are shown in Table 6. The results of the EM Quant 10007 nitrite strips and NARK II Field Test Kits analysis of the diluted UFORP solution are shown in Table 7. Photos were obtained and are shown in Figures 2 through 5.

Table 1. Test Strip Exposure to Nitrite Solutions

| NO ₂ ppm | RESULTS | | | | | |
|------------------------|--------------------------------|------------------|--------------------------------|--------|----------------------------|--------|
| | EM Quant 10022 Color Change | ppm ^a | EM Quant 10007 Color Change | ppm | WaterWorks Color Change | ppm |
| Blank (0) | no change | ND ^b | no change | ND | no change | ND |
| 0.5 | NA ^c | NA | off white | > 0.0 | faint pink | 0.5 |
| 2.0 | NA | NA | faint pink | 2.0 | light pink | 1.5 |
| 33.0 | yellow | < 100.0 | med. purple | < 40.0 | dark pink | 33.0 |
| 80.0 | dark yellow | < 100.0 | dark purple | 80.0 | dark pink | > 33.0 |
| 100.0 | dark yellow-orange | 100.0 | deep purple | > 80.0 | NA | NA |
| 3000.0 | deep red | 3000.0 | deep purple | > 80.0 | NA | NA |

^a ppm from color comparison scale.

^b ND – not detected.

^c NA - not applicable; nitrite concentration was outside detection range of strip and was not tested.

Table 2. Dimethylamine Tests With Simon's Reagent

| Dimethylamine Mass (mg) | Color Observed |
|----------------------------|----------------|
| 0.0 | light brown |
| 0.01 | light purple |
| 0.2 | dark purple |
| 0.6 | dark purple |

Table 3. NARK II Field Test Kits With Dimethylamine Solutions

| Dimethylamine Mass (mg) | Color Observed |
|----------------------------|----------------|
| 0.5 | red |
| 0.05 | Reddish-purple |
| 0.5 | purple |

Table 4. NARK II Field Test Kits and Nitrite Test Strips With Dimethylamine and Nitrite Solutions^a

| Dimethylamine (mg) | Nitrite (ppm) | Nitrite Strip (ppm) | Color Observed |
|-----------------------|------------------|------------------------|----------------|
| 0.0 | 0.0 | 0.0 | red |
| 0.03 | 1.0 | 0.5 | reddish-purple |
| 0.5 | 60.0 | 40.0 | purple |

^a Dimethylamine by mass; nitrite by concentration.

Table 5. UFORP Analysis IC Results

| Ionic Species | Weight % mg (Ionic Species/UFORP) |
|------------------|--------------------------------------|
| Ammonium | 0.29 % |
| Methylammonium | 0.49 % |
| Dimethylammonium | 21.0 % |
| Nitrite | 16.0 % |
| Nitrate | 24.0 % |

Table 6. NARK II Field Test Kits and WaterWorks Test Strips With UFORP Solution^a

| Dimethylamine (mg) | Nitrite (ppm) | Nitrite Strip (ppm) | Color Observed |
|-----------------------|------------------|------------------------|----------------|
| 0.0 | 0.0 | 0.0 | red |
| 0.005 | 8.0 | 5.0 | red |
| 0.05 | 80.0 | > 10.0 | purple |

^a Dimethylamine by mass; nitrite by concentration.

Table 7. NARK II Field Test Kits and EM-Quant 10007 Test Strips With UFORP Solution^a

| Dimethylamine (mg) | Nitrite (ppm) | Nitrite Strip (ppm) | Color Observed |
|-----------------------|------------------|------------------------|----------------|
| 0.0 | 0.0 | 0.0 | red |
| 0.05 | 80.0 | 80.0 | purple |
| 0.5 | 800.0 | > 80.0 | dark purple |

^a Dimethylamine by mass; nitrite by concentration.



Figure 1: Detection of Dimethylamine with NARK II Test Pouches

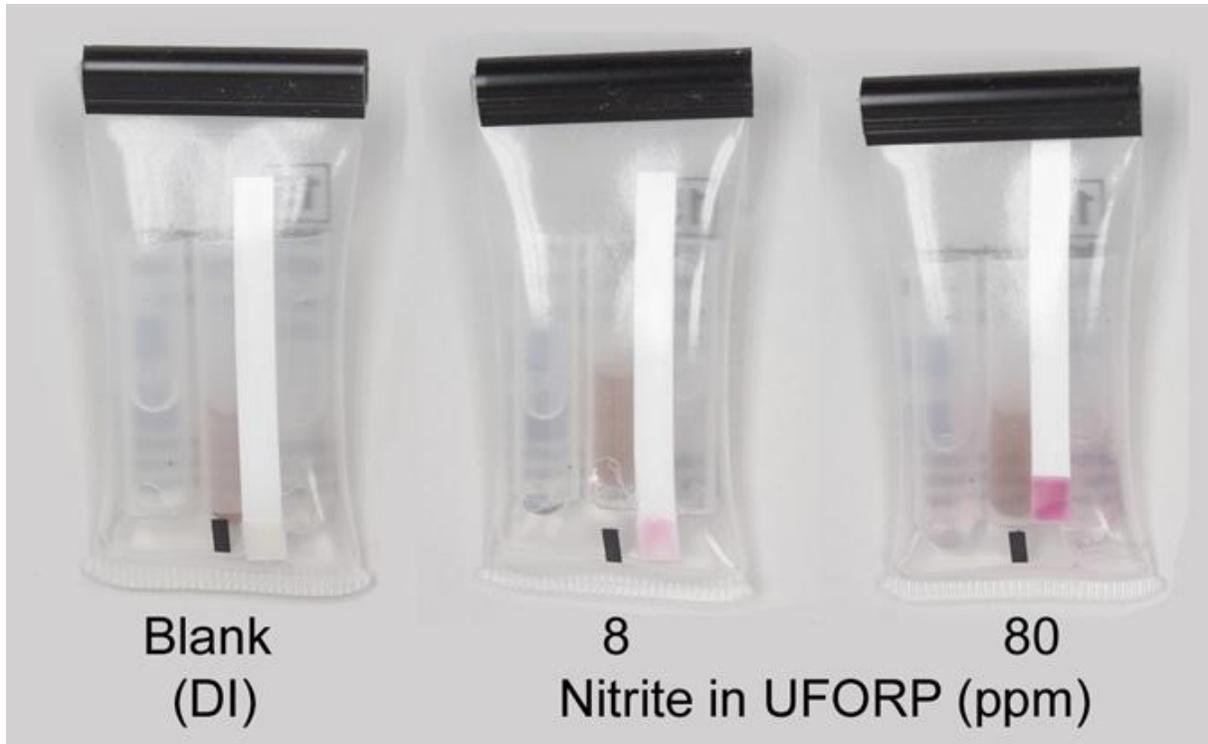


Figure 2. Detection of Nitrite in UFORP Using WaterWorks Nitrite Test Strips in NARK II Test Pouches



Figure 3: Detection of Dimethylamine in UFORP with NARK II Test Pouches

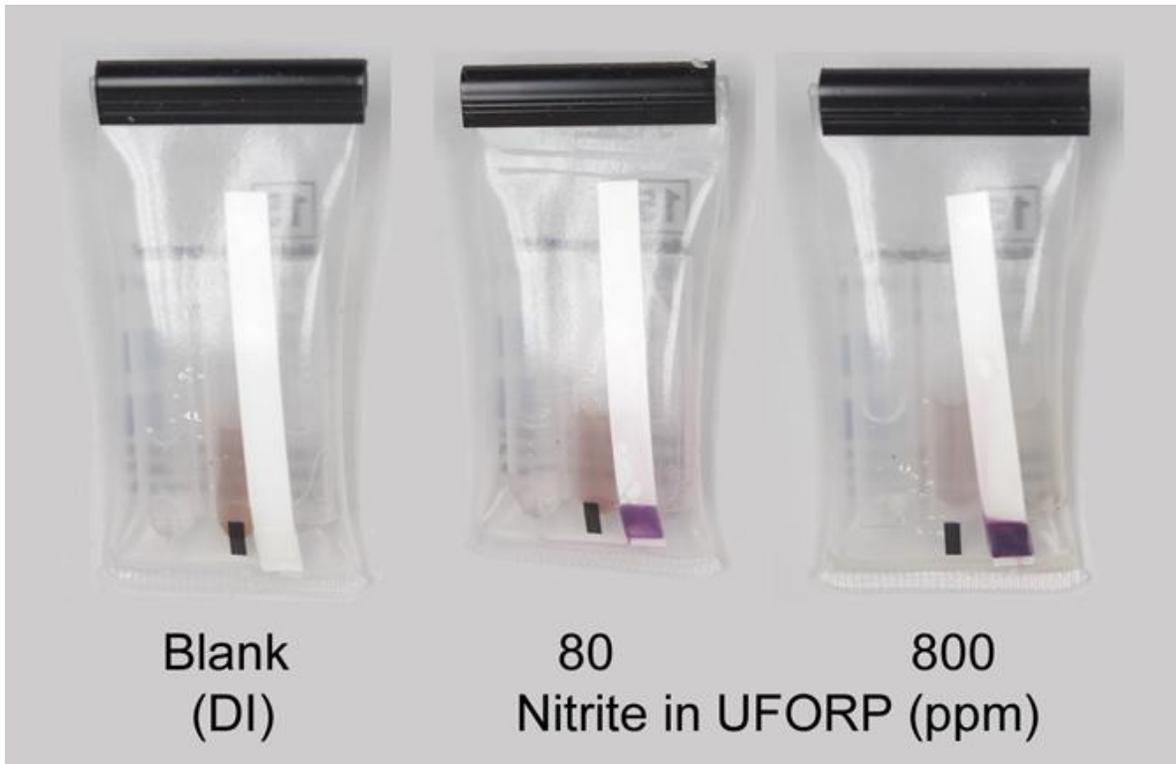


Figure 4. Detection of Nitrite in UFORP With EM Quant Nitrite Test Strips in NARK II Test Pouches



Figure 5. Detection of Dimethylamine in UFORP with NARK II Test Pouches

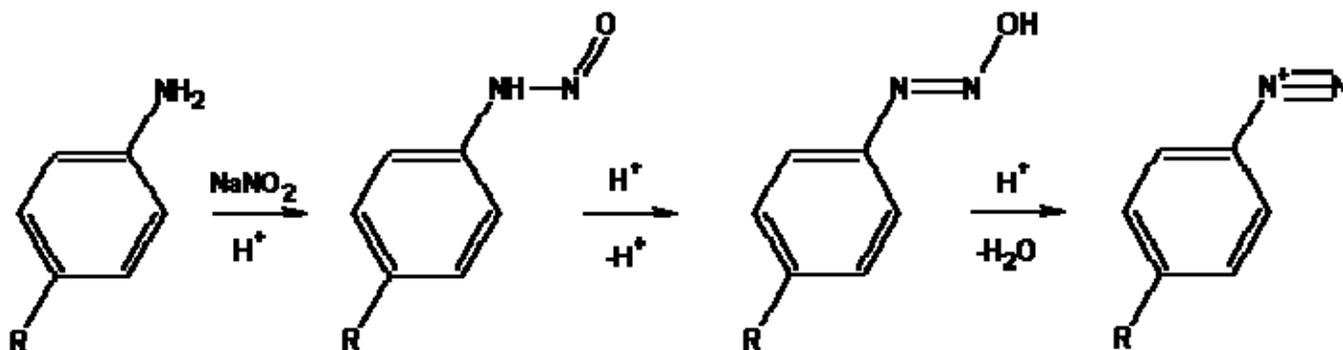
DISCUSSION

NITRITE DETECTION

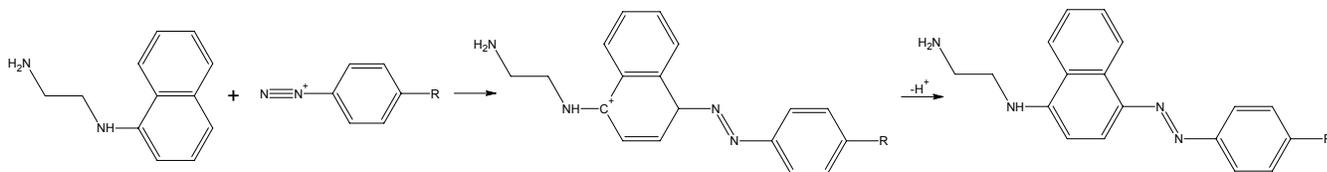
COTS test strips for nitrite were suitable for accurately detecting nitrite on wipe tissues under the given experimental conditions. No power or flow was required. Selection of the one or more nitrite test strips with the appropriate detection range will depend on EVA Operations requirements. The three test strips evaluated had a combined detection range from 0.5 to 3000 ppm, nearly five orders of magnitude. These could be used individually or together in order to determine nitrite over that concentration range on a wipe sample. The concentration values on the manufacturers' color comparison charts could also be calculated as a mass equivalent, depending on program requirements. COTS test strips and color comparison charts would likely need to be evaluated for storage concerns, such as shelf life and stability. Additionally, the ability to handle these strips in the attire normally worn by astronauts under their use conditions would likely need to be evaluated and their configuration modified as appropriate.

The nitrite test strips use an azo coupling reaction to form a colored dye species. A sequence of reactions consistent with this is as follows:

Initially an aryl diazonium ion is formed:



The aryl diazonium ion then reacts with N-1(naphthyl)ethylenediamine to form a colored dye species.

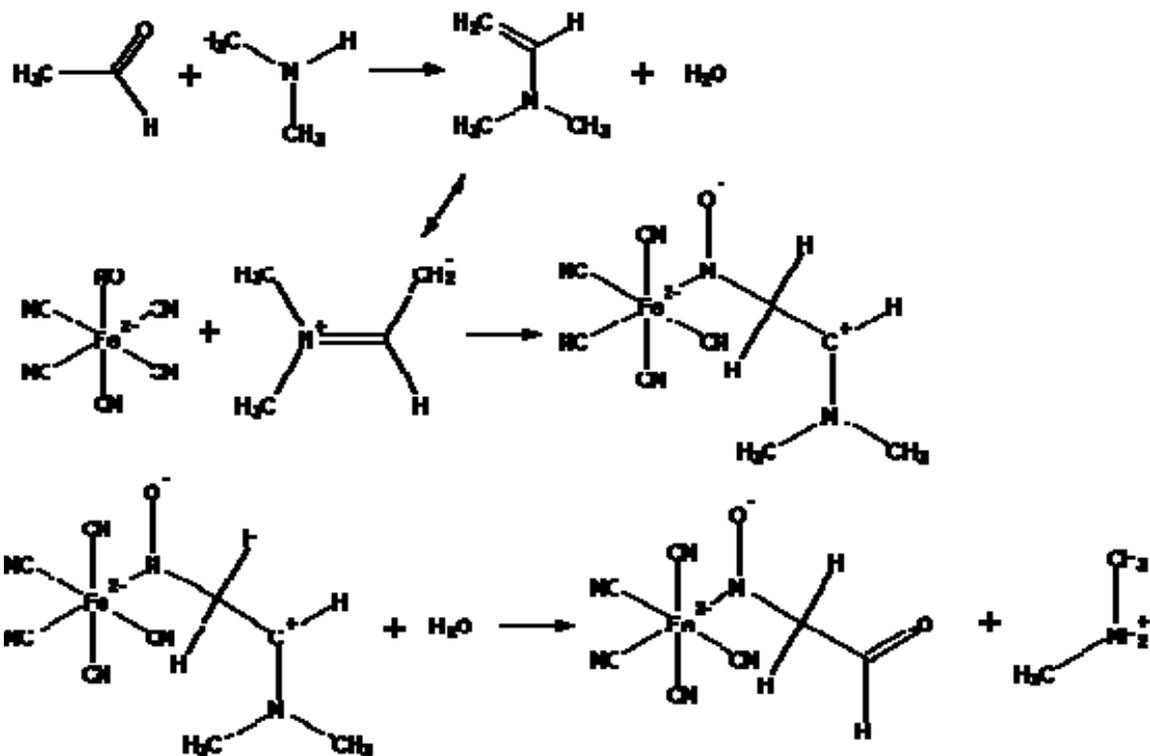


DIMETHYLAMINE DETECTION

Dimethylamine was readily detected by Simon's reagent. The results suggest a color comparison chart could be developed. However, because of the intensity of the purple color above a detectable mass (in the range of 0.01 to 0.05 mg with Simon's reagent and with NARK II field test kits) only a limited range of quantitation may be possible. Consequently, the visual test may only be useful for the semiquantitative determination of dimethylamine at low levels. This is consistent with the use of this reagent for presumptive rather than quantitative testing of methamphetamine.¹

Simon's reagent uses a color-forming reaction that is selective to secondary amines. Dimethylamine is detected colorimetrically by the reaction of the basic amine (sodium carbonate is used to make the solution basic) with acetaldehyde to form an enamine. The resultant enamine reacts with sodium nitroprusside to form a colored complex. A sequence of reactions consistent with those proposed by

Butler and Glidewell¹² for the reaction of piperidine is as follows, though it was not known which of the iron species accounts for the characteristic color formation:



Observation of a blue or purple color is indicative of a secondary amine. Because stable enamine formation occurs only with secondary amines, interference by methylamine is not of particular concern because methylamine is a minor component of UFORP compared to dimethylamine. Similar considerations to the use of the COTS nitrite test strips apply to Simon's reagent and NARK II field test kits.

UFORP DETECTION KIT AND UFORP DETECTION

A concept kit was made by combining COTS nitrite test strips and NARK II field test kits. Because the high range nitrite test strips (EM Quant 10022) caused a positive interference with the dimethylamine test, the strips were not suitable for the combination test kit using the NARK II test kits for dimethylamine. Equipped with a suitable nitrite test strip, feasibility of the test kit for the detection of nitrite and dimethylamine was demonstrated. Similar considerations to the use of the COTS nitrite test strips and NARK II field test kits apply to the concept UFORP detection kit.

UFORP CONTAMINATION MITIGATION STRATEGY

General steps for contamination mitigation include:

- Removal of gross contamination
- Removal of trace contamination
- Chemical or physical treatment of contamination
- Verification of contamination mitigation
- Disposal and cleanup of waste

Removal of Gross Contamination

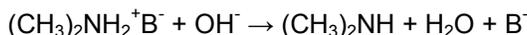
Removal of gross contamination from a spacesuit might be accomplished by scraping or wiping the bulk material with a suitable, non-abrasive device. This method must not spread contamination further on the spacesuit. Residues left on the spacesuit may ultimately need to be treated.

Water Application

Water may dissolve and rinse away UFORP residues. Additionally, it may cause an increase in the rate of reaction of non-volatile salt components, such as dimethylamine- and nitrite-containing species that form NDMA. Mechanisms for applying water and controlling effluent under zero gravity conditions need to be evaluated. These may include wet wipes or spray devices. Controlling humidity to sufficiently high values in the ISS airlock may be another option to promote dissolution of non-volatile salts.

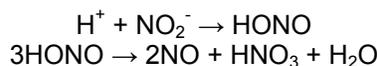
Control of pH

A strong base should release dimethylamine from non-volatile salts and decompose nitrite. For example, a non-volatile salt of dimethylamine with "B⁻" as a counter ion could react with hydroxide (OH⁻) as follows:



Dimethylamine is volatile and could evaporate in a space-like vacuum.

A strong acid will decompose nitrite as follows:

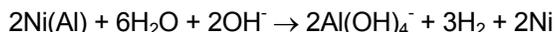


This is because protonation of nitrite forms unstable nitrous acid that decomposes to NO, nitric acid, and water. NO and nitric acid are volatile and could evaporate in a space-like vacuum.

Mechanisms for applying acid and controlling effluent under zero gravity conditions need to be evaluated. These may include wet wipes or spray devices. Some of the concerns for using strong acid in the ISS airlock include storage, handling, and excess acid clean-up. Appropriate choices of base or basic buffers would need to be evaluated.

Reductive Raney Nickel Decomposition

Reductive hydrogenation reactions typically cleave N-N bonds to N-H bonds and reduce N-O bonds to N-H. Earlier work at WSTF showed that several UFORP compounds were reduced by Raney nickel.^{9,10} Raney nickel was generated from the reaction of nickel-aluminum alloy in base:



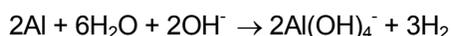
Results showed that NDMA was reduced to dimethylamine and ammonia. Other UFORP constituents were also reduced. Since NDMA is a contaminant of concern due its formation from dimethylamine and nitrite, NDMA could be reacted to form dimethylamine and ammonia that are volatile species of lower toxicity and could evaporate in a space-like vacuum.

Other work at WSTF showed that nitrite was sufficiently reduced by Al in base; though a product study was not performed, the predicted reduction product of nitrite is ammonia.⁹ Under neutral or basic conditions ammonia is a volatile species and could evaporate in a space-like vacuum. Elimination of nitrite would avoid the possibility of NDMA formation by reaction of nitrite with dimethylamine.

Mechanisms for using Raney nickel solutions and controlling effluent under zero gravity conditions would need to be evaluated. These methods could include the development of a Ni-Al scrub pad impregnated with NaOH in a manner that when wetted, the above reaction allows decontamination and mechanical removal of contaminant when applied to a spacesuit material. A similar concept was demonstrated when a spill pillow containing Ni-Al and NaOH was tested with UDMH (ammonia and dimethylamine were formed).⁹ Water could be used to activate the spill pillow or an analogous kit, if developed.

Other Reductive Hydrogenation Reactions

Other hydrogenation reactions may have promise as previously demonstrated by WSTF.^{9,10} Addition of Al powder to the basic solutions results in the following reaction:



Hydrogen and an active aluminum surface are effective for limited, non-catalytic reductive hydrogenation. For example, NDMA was reduced to UDMH. Under neutral or basic conditions UDMH is a volatile species and is predicted to evaporate in a space-like vacuum.

Hydrogen gas bubbled through UFORP solutions at ambient temperature had little or no effect on reducing UFORP constituents.¹⁰ It was believed heat and the presence of an active metal (Al) and catalyst (Ni) was required for effective reduction to occur. Hydrogen gas does not appear to have utility in UFORP contamination mitigation.

Mechanisms for using Al in base and controlling effluent under zero gravity conditions need to be evaluated. Similar considerations apply to those suggested above for Ni-Al alloy in base.

Oxidative Decomposition

Oxidation is commonly employed in many pollutant remediation methods. For example mild oxidation can convert nitrite to nitrate:



Elimination of nitrite would remove the possibility for dimethylamine to react to form NDMA. Additionally, a variety of oxidizing agents for nitrite could be substituted for oxygen, though oxygen is benign and readily available on the ISS.

Assisted Ultraviolet Light Treatment

Ultraviolet (UV) light has been instrumental in oxidation of many pollutants in water and air. Addition of oxidizing agents, such as ozone, hydrogen peroxide, and potassium persulfate, has been found to increase the effectiveness of UV oxidation for a number of pollutants.

UV light has been demonstrated to decompose NDMA in aqueous solution.¹³ The major products of decomposition are dimethylamine and nitrite (which unfortunately are precursors to NDMA) and the minor products are nitrate, formaldehyde, and formic acid. UV light has also been reported to decompose NDMA in the atmosphere.¹⁴ UV light sources placed in the ISS interlock may have utility in decomposing NDMA. Vacuum-UV conditions may have increased utility in this process as volatile products would readily evaporate. Studies to evaluate this, however, are required.

Contamination Mitigation Kits

As appropriate, the desired decontamination method(s) need to meet space, storage, and other flight-qualification requirements. This will depend on the method(s) selected. The users will need training in contamination mitigation, as well as in clean up and disposal procedures. First, the method(s) would

need to be determined. Next, laboratory evaluations would need to be performed and evaluated. A prototype kit would need to be designed, assembled, and tested. Finally, a kit would need to be flight-qualified. Procedures for use and training would need to be established for contamination mitigation kits and for clean-up and disposal.

Post-mitigation Contamination Evaluation

Other work performed on this project has shown promise in the determination of nitrite and dimethylamine. Assessment of pre- and post-treatment contamination could be performed using the detection methods previously described. Use of pH paper could be used for evaluation residual acid and base, should they be used.

CONCLUSION

Detection of UFORP as dimethylamine and nitrite using commonly available methods and COTS test items was demonstrated. UFORP contamination mitigation strategies were also discussed. This work is directly applicable to EVA operations on the ISS.

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CONTAMINATION DETECTION AND MITIGATION STRATEGIES FOR UNSYMMETRICAL DIMETHYLHYDRAZINE/NITROGEN TETROXIDE NON-COMBUSTION PRODUCT RESIDUES

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Overview

This presentation reports:

- Analytical methods for the visual detection of selected UDMH Fuel Oxidizer Reaction Products (UFORP) and NTO constituents using commercially-available off-the-shelf (COTS) technologies
- Mitigation strategies for gross UFORP decontamination



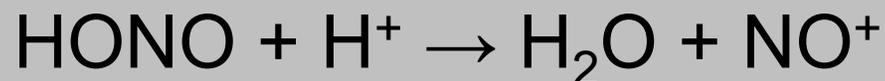
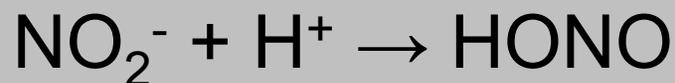
INTRODUCTION

- UFORP propellant residues on the International Space Station (ISS) may contaminate space suits during extra-vehicular activity (EVA) operations
- Many of the known product residues are volatile and will evaporate in space
- WSTF has shown that non-volatile residues from synthetic UFORP may react with water to form N-nitrosodimethylamine



INTRODUCTION

- A reaction known to produce NDMA is between nitrite and dimethylamine in the presence of water:



- The source of nitrite and dimethylamine may be non-volatile salts



INTRODUCTION

- WSTF Laboratory developed means to detect dimethylamine and nitrite visually based on:
 - Readily observable color changes
 - No-flow conditions
 - A dynamic range of several orders of mass or concentration magnitude
 - Applicability to space suit wipe samples to avoid contact of space suit surfaces with detection test chemicals
 - COTS technology



INTRODUCTION

- WSTF Laboratory also proposed contamination mitigation strategies
 - Mitigation strategies were required to decontaminate gross amounts of UFORP and were not limited to use of benign chemicals



Visual Detection of Nitrite

- COTS test strips for nitrite are accurate and widely available
- In the presence of an acid, nitrite reacts with an aromatic amine to form a diazonium salt
- The diazonium salt reacts with N-(1-naphthyl) ethylenediamine to form a red-violet azo dye
- The concentration of the dye is proportional to the color intensity
- Nitrate is similarly determined if the test zone contains Cd or Zn that reduces nitrate to nitrite

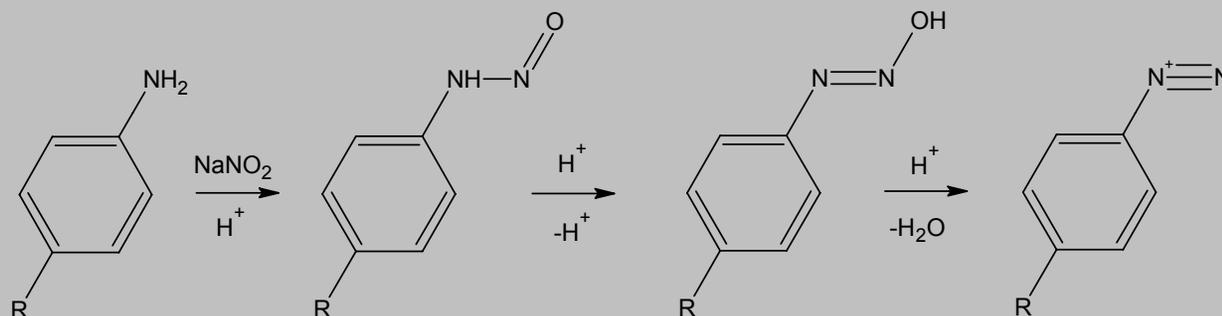


Visual Detection of Nitrite

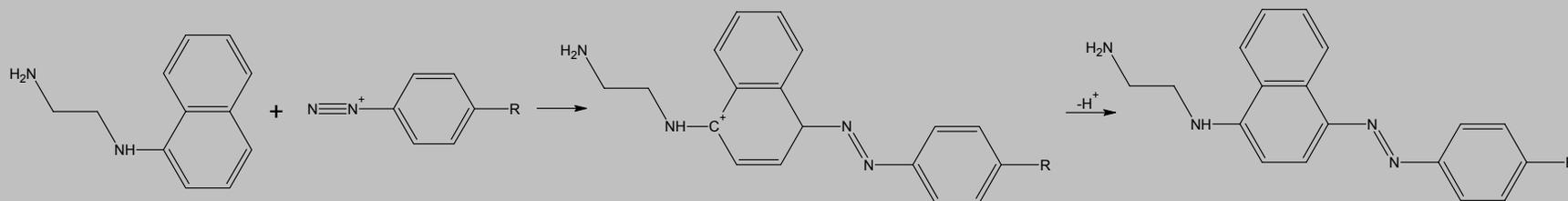
- Typical applications:
 - Groundwater, well water, and drinking water
 - Spring water and mineral water
 - Industrial water and wastewater
 - Water in aquariums
 - Pressed plant and fruit juices
 - Food, animal fodder
 - Soils and fertilizers

Visual Detection of Nitrite

- Preparation of an aryl diazonium ion

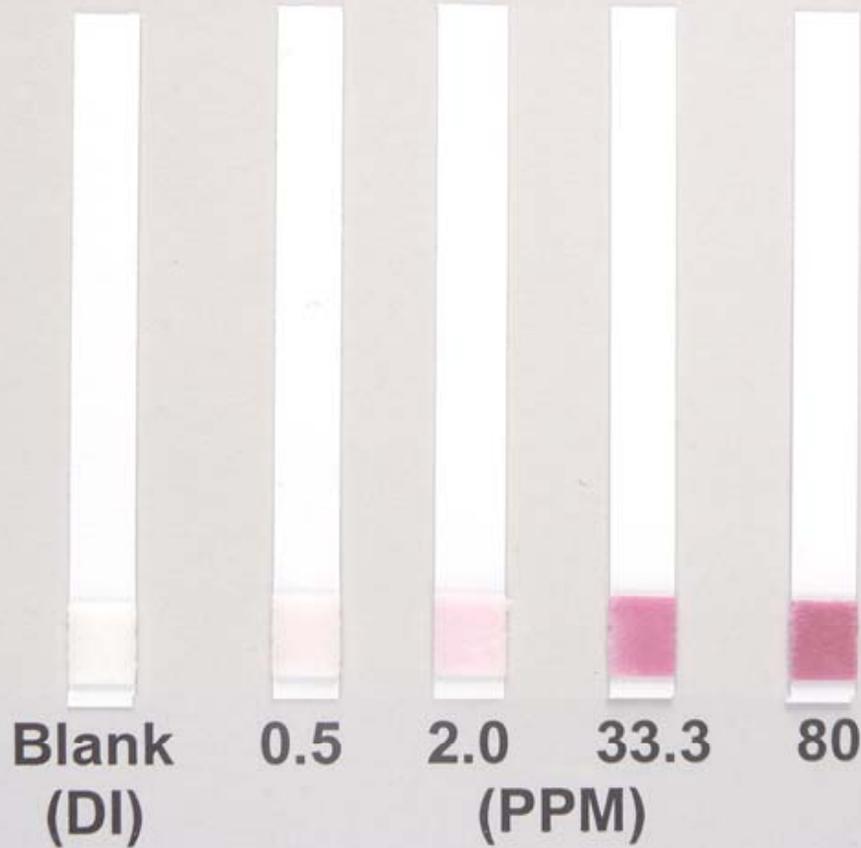


- Azo coupling reaction with N-1(naphthyl)ethylenediamine

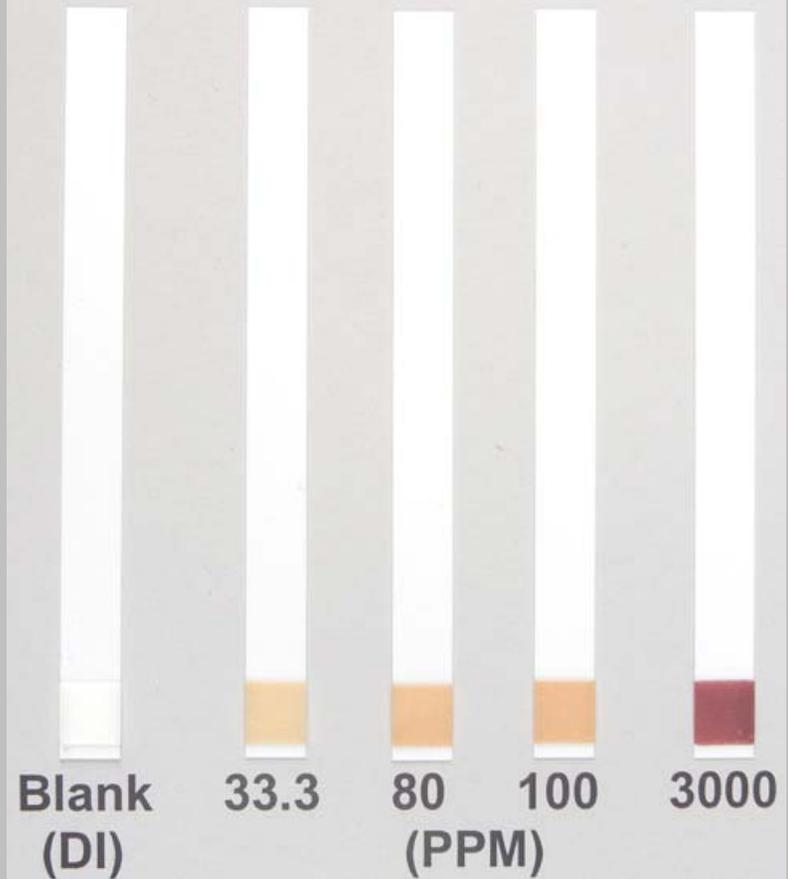


Visual Detection of Nitrite

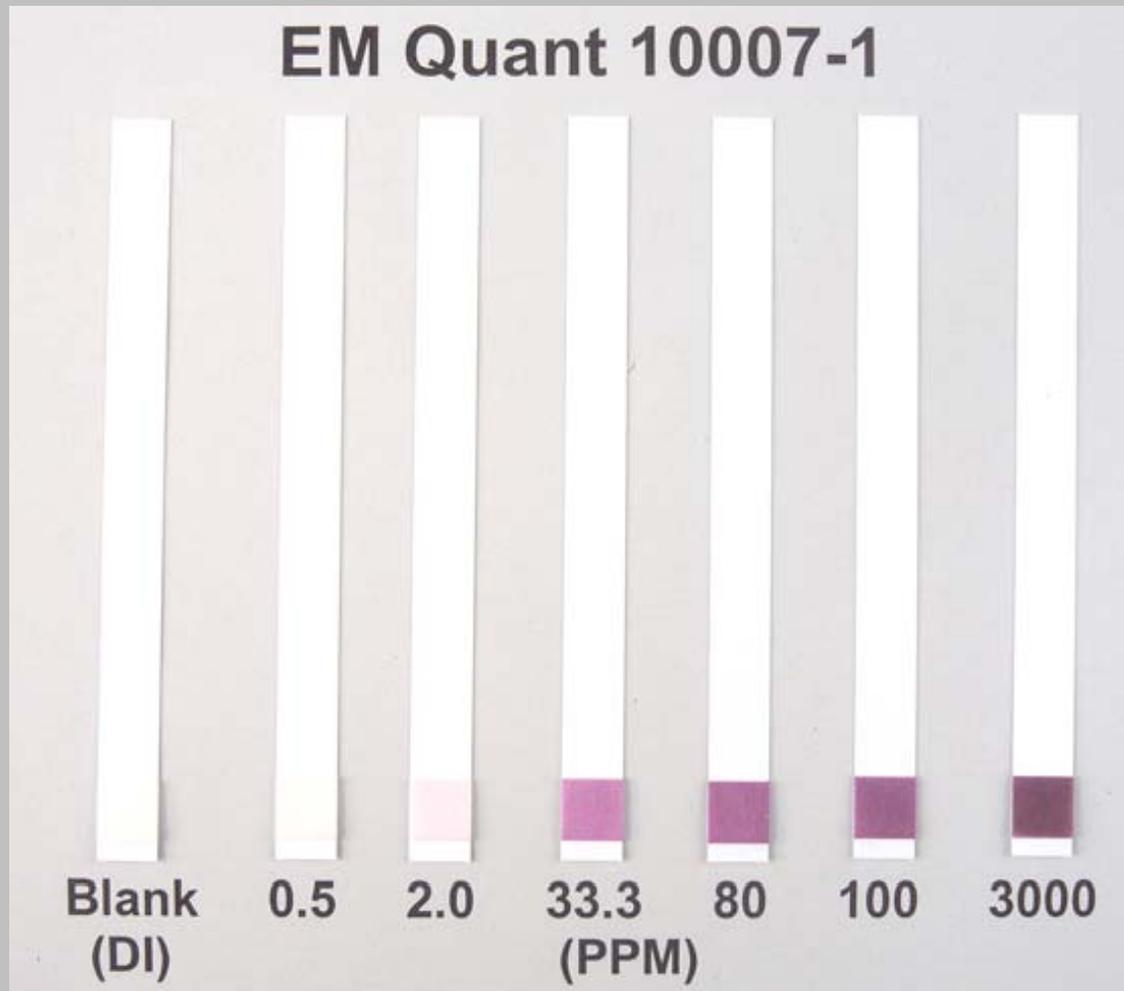
Water Works



EM Quant 10022-1



Visual Detection of Nitrite





Visual Detection of Dimethylamine

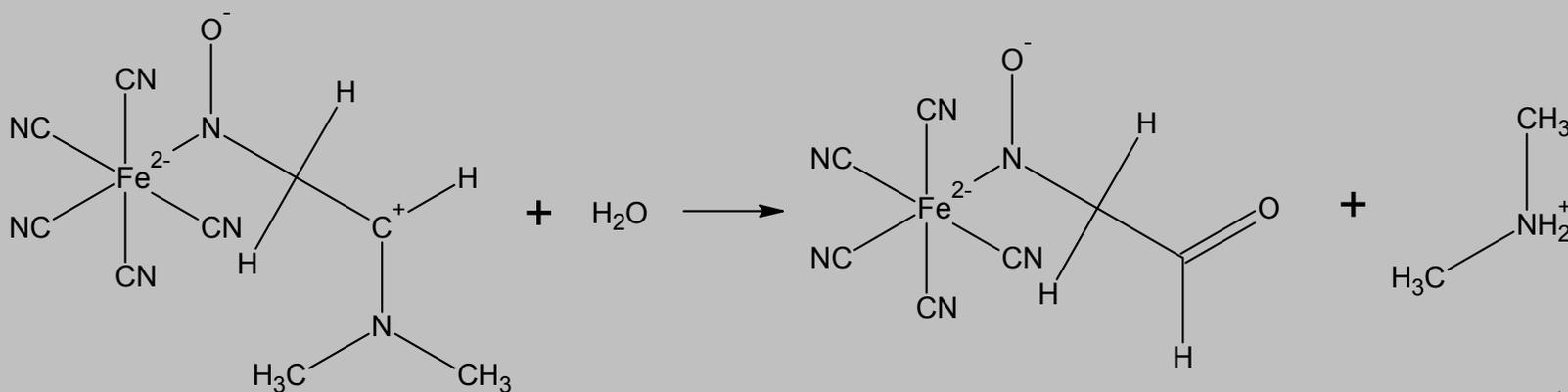
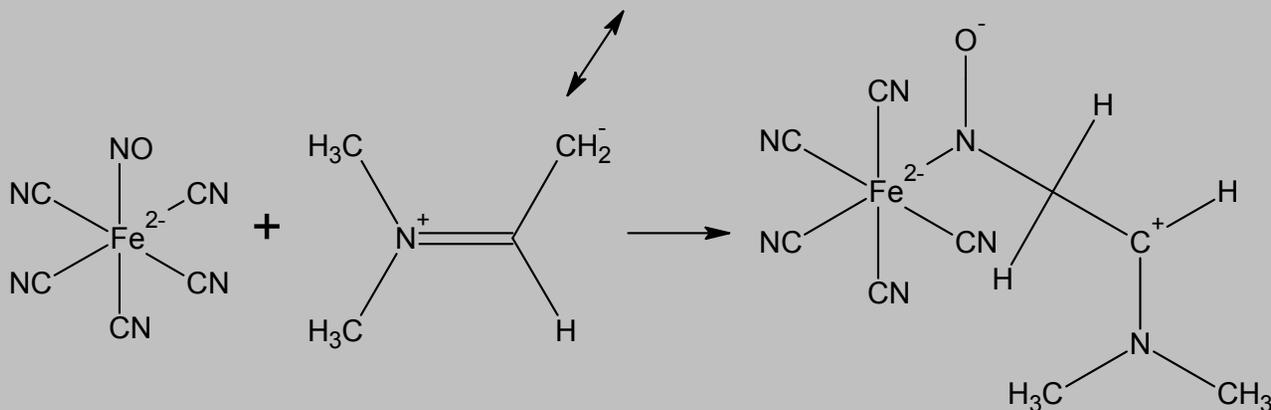
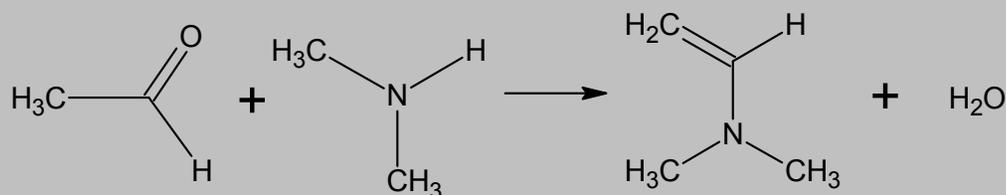
- Several reagents were screened with ammonia, methylamine, dimethylamine, and trimethylamine
 - Simon's reagent (an aqueous sodium nitroprusside/acetaldehyde solution and an aqueous sodium carbonate solution)
 - 7-chloro-4-nitro-2-oxa-1,3-diazole (NBD Chloride) in acetone
 - 1,3-dinitrobenzene (*m*-dinitrobenzene) in acetone
 - Fluorescamine in acetone
 - 2,4-dinitrofluorobenzene (DNFB) in anhydrous ethanol
 - Dansyl chloride
 - Hinsberg Test with benzenesulfonyl chloride and sodium hydroxide



Visual Detection of Dimethylamine

- Simon's Reagent
 - Simon's reagent was unambiguously the most promising candidate reagent
 - It was also the most difficult candidate method to find
 - Found by searching "secondary amine + color detection"
 - NOT "dimethylamine + color detection"
 - The reagent is used for the presumptive testing of methamphetamine and other drugs of abuse, e.g. Ecstasy in the field and in crime labs
 - The reagent is approved by the National Institute of Justice.
 - NIJ Standard-060401 "Color Test Reagents/Kits for Preliminary Identification of Drugs of Abuse." National Law Enforcement and Corrections Technology Center, Rockville MD. July 2000
 - Ammonia, methylamine, and trimethylamine did not interfere

Reaction of Dimethylamine with Simon's Reagent





Visual Detection of Dimethylamine

- Solution A (aqueous sodium nitroprusside/acetaldehyde solution) was prepared by dissolving 1 g sodium nitroprusside (sodium nitroferricyanide(III) dihydrate) in 50 mL distilled water and adding 2 mL of acetaldehyde
- Solution B was 2 percent sodium carbonate
- Different volumes of a dimethylamine solution were added to glass culture tubes
- One drop of Solution A was added to a test solution followed by the addition of 2 drops of Solution B
- The test solution was then agitated and the color was observed and recorded



Visual Detection of Dimethylamine

Results of Simon's Reagent Tests

| Dimethylamine Mass (mg) | Color Observed |
|----------------------------|----------------|
| 0.0 | light brown |
| 0.01 | light purple |
| 0.2 | dark purple |
| 0.6 | dark purple |

- Results suggest a detection limit of 0.01mg dimethylamine
- Above 0.2 mg the color was too intense to distinguish higher concentrations



Visual Detection of Dimethylamine

- Simon's Reagent Tests are available from forensic suppliers for methamphetamine field tests
- NARK[®] II Methamphetamine kits were obtained from Sirchie Finger Print Laboratories, Inc.
 - These consist of a durable plastic pouch containing ampoules of sodium nitroprusside, acetaldehyde, and sodium carbonate
 - A clip is removed to open the pouch, the test material is added, the pouch is closed and clipped, then the ampoules are broken in sequence, agitated, and the resultant color is observed
 - Purple is a positive presumptive test for a secondary amine

Visual Detection of Dimethylamine





Concept Kit

- Tests with nitrite strips and Simon's reagent formed the basis of a concept kit for the sequential determination of nitrite and dimethylamine:
 - Insert a nitrite test strip into a methamphetamine test pouch
 - Open and add test material
 - Close and agitate
 - Read nitrite color/concentration
 - Break ampoules and observe dimethylamine color indication
 - Dimethylamine detection is based on mass rather than concentration due to the volume of the reagents, though a dilution factor could be used in a color comparison chart



Concept Kit

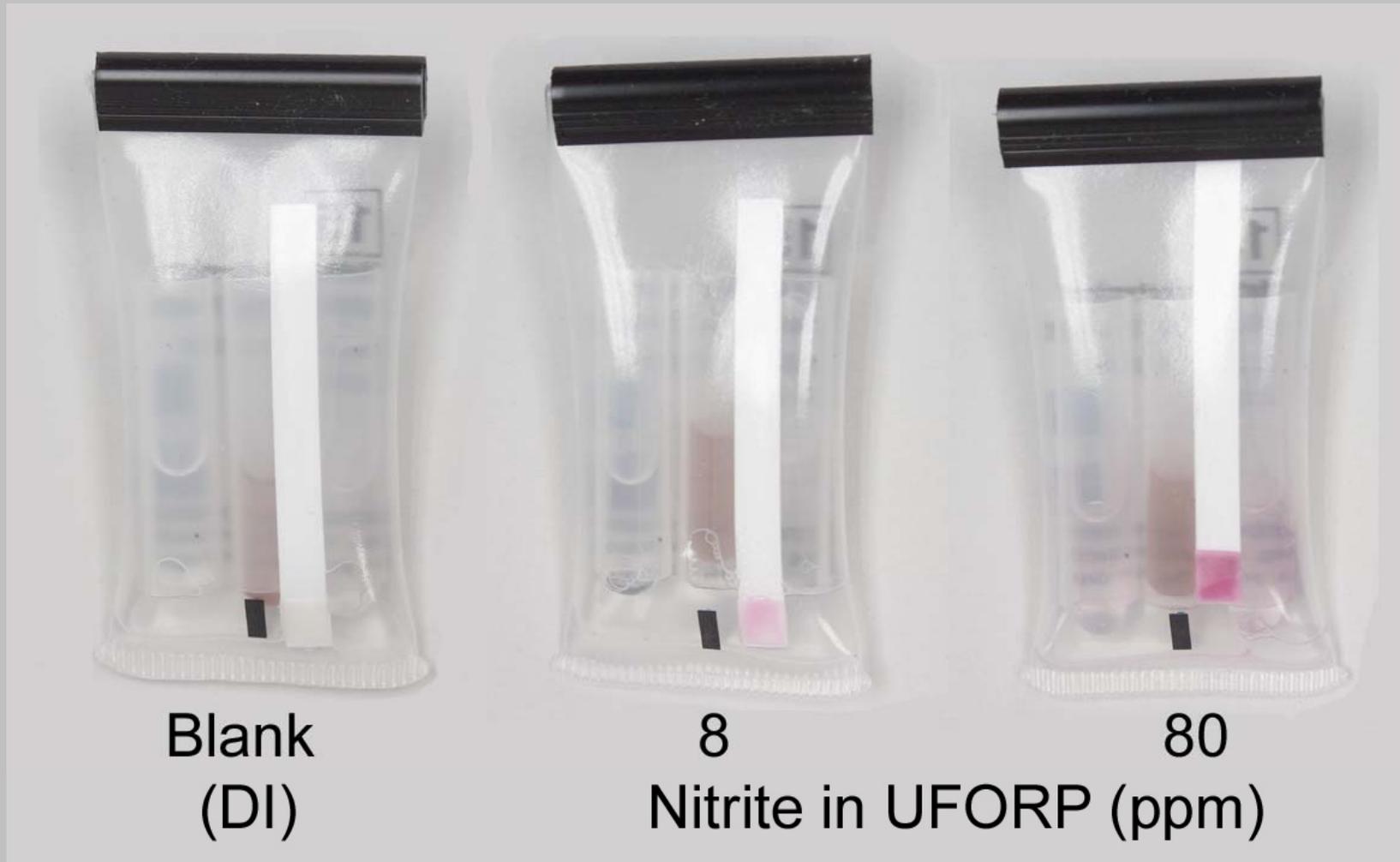
- The high range nitrite test strip ≤ 3 g/L caused a positive interference with the dimethylamine test
- This is believed to be due to the amine used in that test strip
- Concept kits tested thereafter did not have that interference
- The next phase of this work was to evaluate UFORP
- UFORP was prepared by the vapor phase reaction of UDMH and NTO at non-combustion concentrations



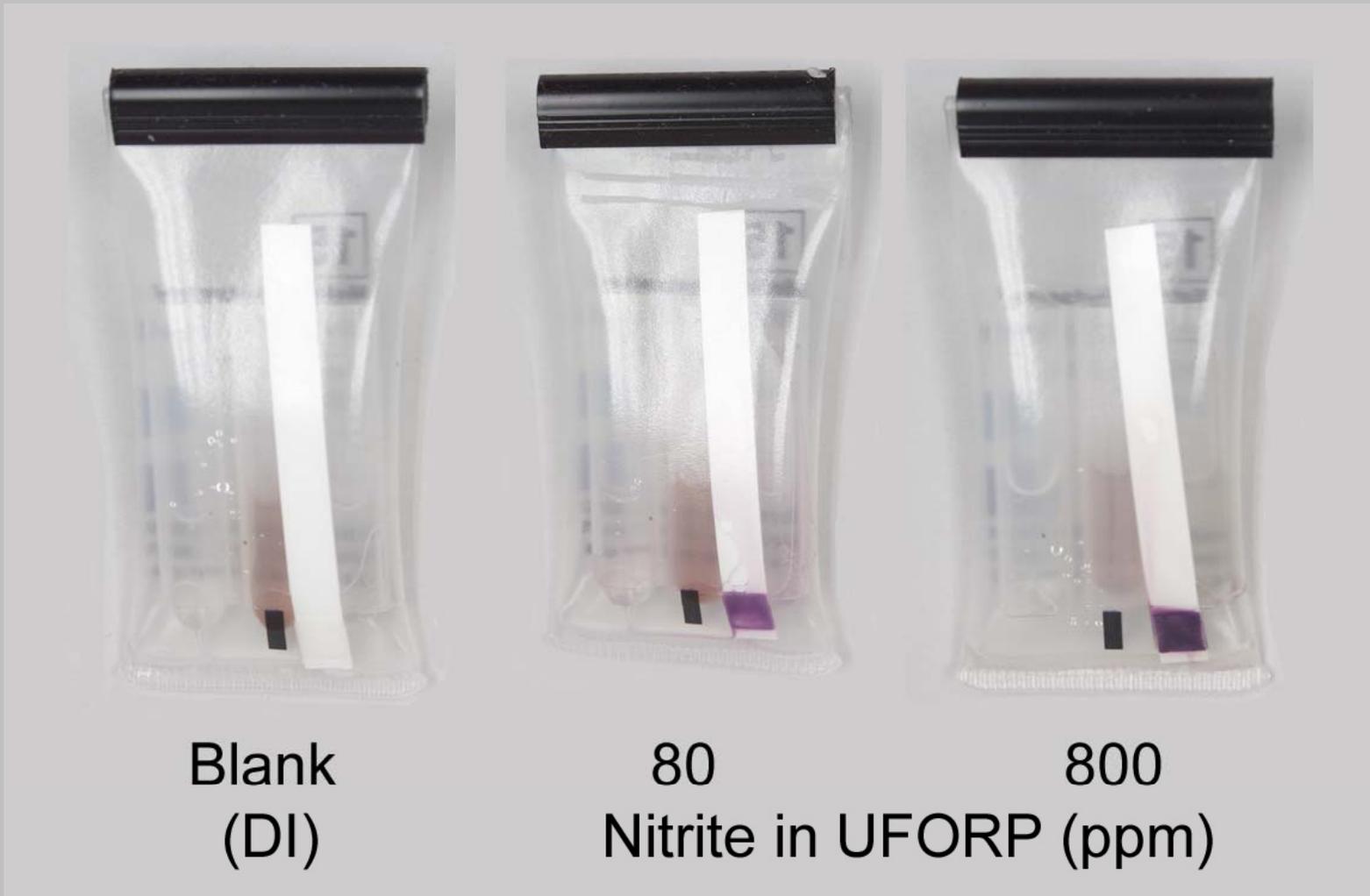
UFORP Composition

| Ionic Species | Weight Percent (mg ionic species/mg UFORP) |
|------------------|---|
| Ammonium | 0.29 % |
| Methylammonium | 0.49 % |
| Dimethylammonium | 21 % |
| Nitrite | 16 % |
| Nitrate | 24 % |

Concept Kit – Nitrite in UFORP



Concept Kit – Nitrite in UFORP



Concept Kit – Dimethylamine in UFORP



Concept Kit – Dimethylamine in UFORP





Contamination Mitigation Strategy

- General steps for contamination mitigation include:
 - Removal of gross contamination
 - Removal of trace contamination
 - Chemical or physical treatment of contamination
 - Verification of contamination mitigation
 - Disposal and cleanup of waste



Contamination Mitigation Strategy

- Previous work has shown:
 - Many UFORP constituents will evaporate in a space-like vacuum
 - Chemical reduction is effective toward decomposition of UFORP constituents
- Concepts for the mitigation of nitrite and dimethylamine precursors to NDMA are presented



Contamination Mitigation Strategy

Water Rinse

- Water may dissolve insoluble species and allow them to evaporate
- Water will increase the rate of NDMA formation from dimethylamine and nitrite in UFORP residues; however, NDMA is volatile and will evaporate in a space-like environment
- Direct water application or controlling humidity to sufficiently high values in the ISS airlock may be options



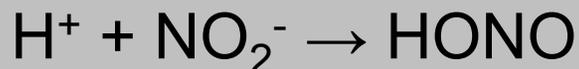
Contamination Mitigation Strategy

Control of pH

- Addition of base could liberate dimethylamine from a non-volatile salt:



- Dimethylamine is volatile and could evaporate in a space-like vacuum.
- Addition of acid could decompose nitrite:



Contamination Mitigation Strategy

Redox Chemistry

- Oxidation



- Reduction

- Raney[®] nickel or hydrogen generated from Al in base will decompose UFORP constituents having N-N and N-O bonds

- NO_3^- , NO_2^- , NDMA, DMN, DMF, tetramethyltetrazene, bis-(dimethylhydrazone)ethanedial, dimethylaminoacetonitrile



Contamination Mitigation Kits

- First, the method(s) would need to be determined
- Next, laboratory evaluations would need to be performed and evaluated
- A prototype kit would need to be designed, assembled, and tested
- Finally, a kit would need to be flight-qualified.
 - A flight unit needs to meet space, storage, and other qualification requirements
- Users will need training including clean up and disposal procedures



Post-mitigation Contamination Evaluation

- Methods described in this work for the determination of nitrite and dimethylamine could be applied
- Assessment of residual chemicals could be performed on a case-by-case basis, including use of simple pH paper for evaluation of residual acid and base



Conclusion

- A concept kit based on COTS was demonstrated for the determination of nitrite and dimethylamine, precursors to NDMA
- Design and evaluation of a prototype flight unit are recommended
- Several strategies for UFORP contamination mitigation were proposed
- Selected strategies could be incorporated into decontamination kits along with procedures for their use
- Design and evaluation of prototype flight unit(s) are recommended