Crowd-Sourced Technology Challenge for Improving Visual Color Detection of Hydrazine and Monomethylhydrazine Vapors in Spacecraft Environments*

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ABSTRACT

NASA currently uses a visual colorimetric detection method for potential hydrazine, monomethylhydrazine (MMH), or unsymmetrical dimethylhydrazine (UDMH) contamination in the International Space Station. Astronauts exposed to propellants or their residues during extravehicular activities may transfer contaminants into the airlock. The colorimetric detection method employs the Contamination Detection Kit (CDK), which uses a potassium tetrachloroaurate redox reaction with the propellant hydrazine vapors and a color comparison card to determine airborne concentrations. Seeking ideas for improvement, the NASA Tournament Lab (NTL) crowdsourced a way to tackle the challenge of detecting hydrazine and MMH vapors using colorimetric detection methods. This *Rid the Rocket* competition drew over 200 participants and 20 submissions from around the world proposing innovative ways to develop a new chemical colorimetric detection method for hydrazine and MMH vapors on spacecraft. Using a phased approach to evaluate contestants, NASA eventually narrowed the field to five finalists from the United States, Romania, Taiwan, and India. Concept papers and hardware submissions were judged on feasibility, creativity, and ability to detect hydrazine and MMH vapors before being sent to the NASA White Sands Test Facility for laboratory evaluation. Finalists employed variations of sampling methods and color-detection chemistry using a variety of sampling pumps and indicator pads or solutions—including those employing potassium or hydrogen tetrachloroaurate, *para*-dimethylaminobenzaldehyde (PDAB), and modifiers including sodium metasilicate and cetyltrimethylammonium bromide—to enhance gold nanoparticle formation and surface plasmon resonance (SPR) resulting in visual blue to purple color development. This paper presents a summary of the crowdsourced submissions and results of laboratory testing.

INTRODUCTION

The NASA Tournament Lab (NTL) facilitates the use of crowdsourcing to tackle NASA challenges. The NTL engaged Floor23 Digital LLC†, an open innovation platform managing and solving product, process, and public engagement problems through crowd-based challenges and announced, “The Rid the Rocket Challenge Aims to Crowdsource Solutions to Detect Hydrazine and Monomethylhydrazine (MMH) via Colorimetric Analysis.” The Rid the Rocket crowd-based competition sought submissions of innovative ways to build a new chemical detection method for hydrazine and MMH vapors through redox reactions aboard spacecraft. The detection of hydrazine and MMH vapor on spacecraft is a critical flight safety requirement on the International Space Station and is currently performed using the Contamination Detection Kit (CDK). The goal of this challenge is to yield qualified

* Approved for public release. Distribution is unlimited.

† Floor23 Digital LLC. 5215 N Ironwood Rd, Suite 202-36, Glendale, WI

solutions to be tested at the NASA White Sands Test Facility (WSTF) in Las Cruces, New Mexico. Floor23 executed a three-phase (Concept, Prototype, and Demonstration) challenge and prize competition to meet NASA's need for new screening methods to detect hydrazine and MMH. The total competitive prize purse for this challenge was $47,000 in cash awards, with $10,000 to the first-place winner and $1,000 to second and third places.

During the Concept Phase, competitors were invited to submit a concept proposal describing their new detection method. Phase-one winners advanced to the Prototype Phase, which required submission of a physical prototype for rigorous testing at WSTF. During the Prototype Phase, competitors were incentivized based on two milestones. The first milestone was the *Preliminary Review*, where selected participants submitted their readiness and plan to complete their prototypes. The second was the *Readiness-to-Ship*, where participants shipped their products to WSTF before the deadline. The final phase was the Demonstration Phase. Demonstration marked the testing stage of the challenge. Competitors submitted their prototypes to the WSTF for rigorous testing, evaluating their viability and effectiveness in space safety. Winners of this phase not only received monetary rewards but earned recognition for their contributions to space safety.

Participants were given requirements to deliver a prototype design and interface of gold salt coupons and a hand-held pump. Participants were required to establish clear objectives and target optimization parameters, as well as evaluate the device's suitability for flight operations. Evaluation would determine:

- Optimal sampling flow rate
- Potential cross interferences
- Temperature (293 K +)
- Humidity (0-100% relative humidity)
- Shelf life
- Limit of detection
- Saturation level
- Coupon material and gold salt solution concentration

The prize award structure is shown in Table 1.

Table 1. Prize Award Structure

Competition Phase	Winners	Prizes
Concept Phase	Up to 5	$20,000 pool (Guaranteed min. of $2,500/winner)
Prototype Phase	Up to 5 Preliminary Review Milestone Up to 5 (Early Ship Milestone)	$10,000 pool (Preliminary Review Milestone) $1,000/winner (Early Ship Milestone)
Demonstration Phases	Up to 3	1st Place: $10,000 Runners Up (2): $1,000

BACKGROUND

The challenge sought participant innovation to enhance and improve the hydrazine and MMH fuel detection technology NASA CDK as specified by JSC-65129C (2015). Basic reactions of the $KAuCl_4$-based colorimetric determination of the propellant hydrazines can be written:

$4KAuCl_4 + 3N_2H_4 \rightarrow 4Au + 3N_2 + 12HCl + 4KCl$
$4KAuCl_4 + 3N_2H_3CH_3 \rightarrow 4Au + 3N_2 + 9HCl + 4KCl + 3CH_3Cl$
$2KAuCl_4 + 3(CH_3)_2N\text{-}NH_2 \rightarrow 2Au + 3(CH_3)_2N{=}NH^+Cl^- + 3HCl + 2KCl$

The observed color of gold nanoparticles (AuNPs) resulting from reduction of tetrachloroaurate in solution or on surfaces is attributed to surface plasmon resonance (SPR), a light/electron charge density effect. Amendola et al. (2017) present an extensive review of SPR in AuNPs. AuNPs have been exploited for centuries for their intense color and in the last two decades have been the subject of a growing number of scientific investigations related to their SPR properties. While traditional research concerns optical sensing, surface-enhanced resonance spectroscopy (SERS), and photothermal phenomena, new fields such as nonlinear optics (NLO) response, optical trapping, chiroptical effects, magneto-plasmonics, and plasmon-enhanced catalysis are emerging.

The characteristic bright red color of spherical AuNPs has attracted interest since ancient time. Nanoalloys can be found in ornamental cups such as the Lycurgus Cup (ca. 4th century), red ruby glass colored with the purple of Cassius (Middle Ages), and luster plates (15th–16th century). One of the oldest samples is represented by a gold-plated Egyptian ivory dating back to the 8th century BC, where AuNPs accidentally formed a purple staining by the diffusion of gold from a thin foil into the porous ivory substrate. Size and assembly are important factors in observed AuNP color. Plasmons are collective oscillations of free electrons in metals occurring at well-defined frequencies. Azzazy et al. (2012) note the typical structure of AuNPs is spherical, but AuNPs can also be composed of a thin gold shell surrounding a dielectric core, such as silica. SPR is the phenomenon behind the optical properties of AuNPs.

AuNPs range in size from 0.8 to 250 nm and are characterized by high absorption coefficients. Electromagnetic radiation of a wavelength much larger than the diameter of the AuNPs induces coherent, resonant oscillations of the metal free electrons across the nanoparticles. These oscillations are known as the SPR, which lie within visible frequencies and result in strong optical absorbance and scattering properties of the AuNPs. A colloidal gold solution of 20 nm particles exhibits an SPR band with an absorption maximum of 520 nm, generating the solution's distinct red color. Typically, SPR absorption maxima between 517 and 575 nm are exhibited by AuNPs whose diameters range from 9 to 99 nm. AuNPs with core diameters less than 2 nm fail to exhibit SPR. The SPR band is affected by several factors including the distance between AuNPs, the particle shape, and to a lesser extent the size of AuNPs and the refractive index of the medium. As the core/shell ratio increases, the SPR band exhibits a red-shift and when AuNPs aggregate, interaction of locally-adjacent AuNPs (plasmon-plasmon interaction) shifts their color to blue. The strong absorption of AuNPs can be used for colorimetric detection. The color of the AuNPs resulting from the reduction of $KAuCl_4$ by propellant hydrazine vapors is the basis for the CDK.

Colorimetric methods such as reaction of hydrazines with *para*-dimethylaminobenzaldehyde (PDAB) are based on ultraviolet-visible optical properties of the resultant *para*-dimethylaminobenzaldehyde azine with hydrazine or the *para*-dimethylaminobenzaldehyde hydrazones with MMH and UDMH, which absorb in the 450 nm range. PDAB colorimetry is a standard method for the detection of hydrazine, though it is less sensitive to MMH and UDMH. The use of PDAB detection methods for hydrazine determination is well established, dating back to the spectrophotometric method of Watt and Chrisp (1952) and later the ASTM D1385 (2018), which was first issued in 1978. The mechanism of reaction between hydrazine or MMH and PDAB involves the nucleophilic addition of the nitrogen base to the PDAB aldehyde group to form an intermediate imine followed by the elimination of water to form an azine with hydrazine or hydrazone with MMH and UDMH. This reaction is frequently acid-catalyzed by protonation of the carbonyl. While ASTM D1385 uses hydrochloric acid for the determination of hydrazine in water, badge or vapor sampling applications typically employ a non-volatile acid such as citric acid as described by Crossman et al. (1990). PDAB turns from colorless to yellow on exposure to hydrazine in solution and coated dosimeters develop an orange-red color upon exposure to the hydrazines. Use of PDAB for hydrazine detection in water is prevalent in standard methods and is found in commercially available test kits.

Another colorimetric method proposed was based on the reaction of 3,3',5,5'-tetramethylbenzidine (TMB) with excess $KAuCl_4$ remaining after exposure to a hydrazine. TMB is a pale yellow to white solid used in immunoassay staining procedures that is oxidized to the blue nitrogen analog quinone-type structure 3,3',5,5'-tetramethylbenzidine diimine. Blue on yellow ($KAuCl_4$) appears green. Gu et al. (2020) have reported the use of 3,3',5,5'-tetramethylbenzidine oxidation on paper devices for peroxidase-based assays including immobilized peroxidase-like platinum nanoparticles (PtNPs).

Use of cameras, including cell phone cameras and RGB apps to quantify hydrazine from various fluorophore and dye colorations is evidenced by increasing reports in the literature, for example Rajalakshmi et al. (2024).

OBJECTIVES

This manuscript presents an overview of a crowd-sourced competition and results of WSTF testing the finalists' submitted hydrazine vapor detectors with MMH.

SUMMARY OF PHASE ONE SUBMITTED PROPOSALS

Data collected indicated 315 registered participants, 17 Challenge Submissions, seven Unique Solvers, and five Solvers Selected. NASA received submissions from the United Kingdom, Brazil, Pakistan, India, Taiwan, Zimbabwe, the United States, Germany, Egypt, and Romania.

Concept Phase proposals are summarized in Table 2. Irrelevant or scientifically infeasible proposals, such as a global warming solution and a 3D scanner to detect the crystalline shape of MMH frozen at space temperatures using x-rays, are not included in this table. Concept Phase proposals were subject to change as the challenge progressed. The judges noted several participants did not have access to high-purity hydrazine or $KAuCl_4$ for evaluation. Some participants prepared hydrazine vapor, others used tetrachloroauric acid ($HAuCl_4$), and some reagents such as hydrazine sulfate were obtained through eBay®‡.

‡ eBay® is a registered trademark of eBay Inc., San Jose, California.

Table 2. Summary of Phase One Proposals

Concept	Summary	Comments/Feasibility
Colorimetric detection with picryl chloride (2-chloro-1,3,5-trinitrobenzene)	Uses picryl chloride supported on a pad in a heated chamber.	Picryl chloride has been used for derivatization and colorimetric detection of hydrazine, MMH, and UDMH in applications including spot tests. A heated chamber is not feasible in space.
ZnO nanoparticles/NiO nanosheets-based polymer for colorimetric hydrazines detection	Proposed enhancement by preparing nanoparticles and nanosheet coupons incorporating $KAuCl_4$	Concept proposal appeared derived from chemically modified electrode approaches. Quantifying hydrazine was not discussed.
$KAuCl_4$ redox platform for visual detection of MMH (Romania Finalist)	A hand pump assembly was used to draw air through $KAuCl_4$-impregnated pads made of suitable materials (quartz fiber, paper, porous polymers) and pretreated to promote gold nanoparticle formation resulting from chemical reduction. Excess tetrachloroaurate after hydrazine exposure could oxidize 3,3',5,5'-tetramethylbenzidine (TMB) to form a green-blue complex spot on the pad with a resultant color intensity inversely proportional to hydrazine concentration.	Pretreatment of pads to promote gold nanoparticle formation and use of RGB values to quantify hydrazine were novel concepts. Addition of 3,3′,5,5′-tetramethylbenzidine (TMB) solution with a syringe in a spacecraft is not feasible.
Screening device consisting of a built-in color chart, continuous tape to record redox reaction response. (United States-2 Finalist)	A hand pump measures precise amount of air and records stroke number. A continuously running tape coupled with a color intensity key enables hydrazine concentration determination.	Indicating tape composition was not specified and tape was manually rotated. Concept was feasible but incomplete.
Colorimetric detection of hydrazine by discs impregnated PDAB	A microcontroller, camera and discs within a tube are incorporated within the ISS air handler flow to constantly monitor for hydrazine without the need for crew intervention. Cabin air would constantly pass through this tube and PDAB detection discs. A camera monitors color changes discs.	Powered devices are not feasible but the concept to use a camera could facilitate comparison to a color chart and eliminate some subjectivity. Red/Green/Blue (RGB)/cell phone apps are reported in the literature to monitor fluorescence detection, but this was not stated.
Wolff-Kishner reduction	Aldehydes or ketones can be used in a spray containing sodium hydroxide and ethylene	The Wolff-Kishner reduction uses hydrazine in strong base to reduce aldehydes and

Concept	Summary	Comments/Feasibility
	glycol. The product hydrocarbon detected using a spectrometer indicates hydrazine was present.	ketones to alkanes. Liquid reagents and a powered spectrometer are not feasible on spacecraft and details or quantitation correlation was not specified.
Colorimetric methods to screen for hydrazine and MMH following redox reactions	The proposed method uses a hand-held pump to sample air, which is first filtered then mixed with a redox-active compound. A gold salt coupler is added to the reaction mixture, and the color intensity is measured. Reaction with potassium permanganate to form a brownish-yellow color detectable using a colorimeter was proposed. 1,2-Dimethyl-4-phenylazoimidazole was proposed to react with hydrazine and MMH to produce a red-colored compound. Colorimetric test strips and reference color charts, and use of GC-MS were also proposed.	Inadequate details on the gold salt coupler and the compound 1,2-dimethyl-4-phenylazoimidazole were given. Color fade of potassium permanganate is possible but use of solutions and powered instrumentation on spacecraft are not feasible.
Hydrazine detection system using PDAB (Taiwan Finalist)	A gas collection bag is used to collect air sample and a PDAB solution is subsequently injected and mixed. Color change is observed spectrophotometrically.	Injection of liquids and spectrophotometry on spacecraft is not feasible. Visual quantitation was not discussed.
Detection of hydrazine using silver oxide decomposition and a temperature sensor	Silver oxide decomposes hydrazine and MMH and a contact temperature sensor is used to detect the exothermic reaction.	While thermistor detection of hydrazine has been reported in the literature, insufficient detail was provided and mixtures or relative sensitivities of hydrazine or MMH to silver oxide were not discussed. Details on a contact temperature sensor and temperatures were not provided.
Detection of hydrazine with potassium permanganate	Reaction of hydrazine with potassium permanganate produces water, which is detected using copper sulfate color change. Detection of potassium hydroxide using litmus solution was also proposed. Use of manganese dioxide as a catalyst to	This proposal read like an artificial intelligence (AI)-generated approach and was not feasible as written.

Concept	Summary	Comments/Feasibility
	supplement oxygen supplies for astronauts was purported.	
Detection of hydrazine with platinum salts (India Finalist)	Use of platinum salts including platinum(IV) chloride and platinum(II) acetylacetonate offering enhanced color sensitivity to replace copper salts were proposed. A handheld air sampler pump equipped with an electric motor and a spiral centrifugal fan, electronic speed control, and a lithium polymer battery was proposed. The pump was capable of being modified to be spring powered. The air pump has a storage compartment for sample badges. Detection limit data was provided.	This proposal had potential flaws. Color changes from orange Pt(II) salts to brown/black Pt(0) may not contrast well. Pt(IV) chloride is brown/black and reduction may not produce a color contrast as useful as yellow to blue with Au(III) to Au(0). The comparison to copper salts was not correct as the CDK uses $KAuCl_4$. The handheld air pump would be required to operate without battery power.
Detection of hydrazine and MMH by redox reaction with palladium-coated gold salt coupons	Finely divided palladium (Pd) is added to gold salt coupons as a catalyst. Pd adsorbs gaseous hydrazine/MMH from the sampled air to facilitate oxidation with the gold salt on the coupon. Palladium accelerates the reaction kinetics to minimizing the analysis time. The device includes an air sampler with a handheld piston-like structure graduated for different external pressures and a magnifier lens for observation of color.	The palladium catalyst was untested.
Colorimetric sensor cartridge for improved detection of hydrazine and MMH (United States-1 Finalist)	A sensor cartridge housing a $KAuCl_4$ sensing pad which changes color upon exposure to hydrazines was proposed. Airflow over the sensing element is provided by a manually operated lightweight plastic bellows pump through manual actuation. Pre-wetting the sensing pad to promote hydrazinium and methylhydrazinium formation to eliminate effects of varying air sample humidity, and pre-seeding a sensing pad with 2-5 nm gold/silver nanoparticles to supply nucleation sites for faster and larger nanoparticle growth was proposed. The	This concept provided no data. $KAuCl_4$ was used as in CDK. Silver nitrate (colorless) premised to turn yellow-green is not an accurate supposition as silver nitrate reduces to black silver and black against white does not provide suitable contrast. Silver salts require pH adjustments for optimal reaction to occur. No pH conditioning is required for gold salts. Use of a camera with image processing software was mentioned but not elaborated. Cell phone RGB apps have potential, but this was not discussed. Wetted sensing pads is not

Concept	Summary	Comments/Feasibility
	sampling and detection system was purported to be portable, lightweight, and equipped with a transparent window to visualize color change. Intensity of the color change on the sensing pad will be determined with a camera using image processing software. Other features included single use and disposable individual, hermetically sealed packaging of sensing pads, a Luer-lock fitting between the bellows pump and the sensor cartridge to prevent leakage. Silver nitrate on the sensing pad to provide a different or more sensitive color change to the human eye in additional to gold salts was proposed.	feasible. Seeding is conceptually an enhancement but was untested as of the submission.

Finalists shipped their products to WSTF where they were evaluated using hydrazine and MMH vapor streams. Participants also posted visual displays including video demonstrations of their concepts and submittals on platforms such as Google Drive™.[§]

EXPERIMENTAL

Submitted prototypes were evaluated at WSTF using MMH target concentrations of 1 ppm and 200 ppb in air. MMH streams were produced using MMH permeation tubes placed in glass vials, which were placed in heated blocks at 43 °C. Gaseous nitrogen and air was supplied as a diluent using a rotameter to measure flow rate. A Miller-Nelson flow-temperature-humidity control system standard atmosphere generator was used to condition gas streams of hydrazine, MMH and UDMH to known relative humidity. Vapor phase MMH concentrations were confirmed by sampling the effluent stream for 10 min at 1L/min with acidified acid-washed diatomaceous (firebrick), eluting the firebrick, and analyzing by high performance liquid chromatography (HPLC). Results were back-calculated to permeation stream gas-phase concentrations. This was the same experimental configuration used to validate the CDK gold salt hydrazine detection pads.

Final submissions were assessed using a predetermined judging rubric. The rubric included points awarded for response time, sensitivity of detection, method testing and evaluation, ease of detection/use, and stability (shelf life and potential cross-interferences). Results were pooled and ranked to determine the placement of the final submissions.

[§] Google Drive™ is a trademark of Google Inc., Mountain View, California.

RESULTS AND DISCUSSION

All submissions used manually-actuated sampling devices. Photos supplied by each finalist and summary results of WSTF testing with MMH are presented.

First Place: Colorimetric Sensor Cartridge for Improved Detection of Hydrazine and Monomethylhydrazine (United States-1 Finalist)

This device as shown in Figure 1 used a syringe hand pump interfaced with a sensing pad containing hydrogen tetrachloroaurate, which reduces to elemental AuNPs upon exposure to hydrazines. Color development by AuNPs is enhanced by pretreating pads with sodium metasilicate (Na_2SiO_3), which catalyzed AuNP formation and aggregation of nanoparticles providing a basic glass-like surface for crystal formation according to the reaction:

$[AuCl_4]^- + 4N_2H_5^+ \rightarrow Au + 2N_2 + 4NH_4^+ + 4H^+ + 4Cl^-$

The device was manually actuated to provide consistent sample volume and flow over the sensing pad with no electrical power required. A Luer lock fitting of syringe and sensor cartridge prevented leakage, and a pre-wetted sensing pad was purported to eliminate effects of varying air sample humidity. The participant emphasized basic sodium metasilicate helped drive the reaction, which produces acidic species (H^+ and NH_4^+), and that SPR of the AuNPs produced the characteristic purple color.

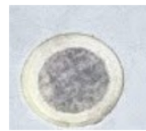
Sodium metasilicate was reported by Köhler, Wagner, and Albert (2005) as an effector for the formation of AuNPs from $HAuCl_4$ reduced by ascorbic acid and Fe(II) by facilitating aggregation.

Figure 1. United States-1 Finalist Challenge Submittal

WSTF test results showed a 1–2-liter sample volume was sufficient for color change with the sodium metasilicate pretreated pads as shown in Figure 2. Minimal reaction was observed without the sodium metasilicate pretreatment. Larger volumes of sample were required to observe a color change at 200 ppb than for 1 ppm. The response time was 1-2 minutes with 1 ppm and 200 ppb MMH with sodium metasilicate pretreatment and 4 minutes for 1 ppm MMH and 200 ppb MMH without sodium metasilicate pretreatment, indicating the sodium metasilicate treatment yielded a faster response time.

WSTF Pad
1 ppm MMH in Air
1 Liter Sample
Response: 1-2 min

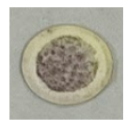
Contestant Gold
Salt Pad/No Sodium Metasilicate
1 ppm MMH in Air
1 Liter Sample
Response: 4 min



Contestant Gold
Salt Pad/Sodium Metasilicate
1 ppm MMH in Air
1 Liter Sample
Response: 1-2 min

WSTF Pad
200 ppb MMH in Air
2 Liter Sample
Response: 1-2 min

Contestant Gold
Salt Pad/No Sodium Metasilicate
200 ppb MMH in Air
2 Liter Sample
Response: 4 min



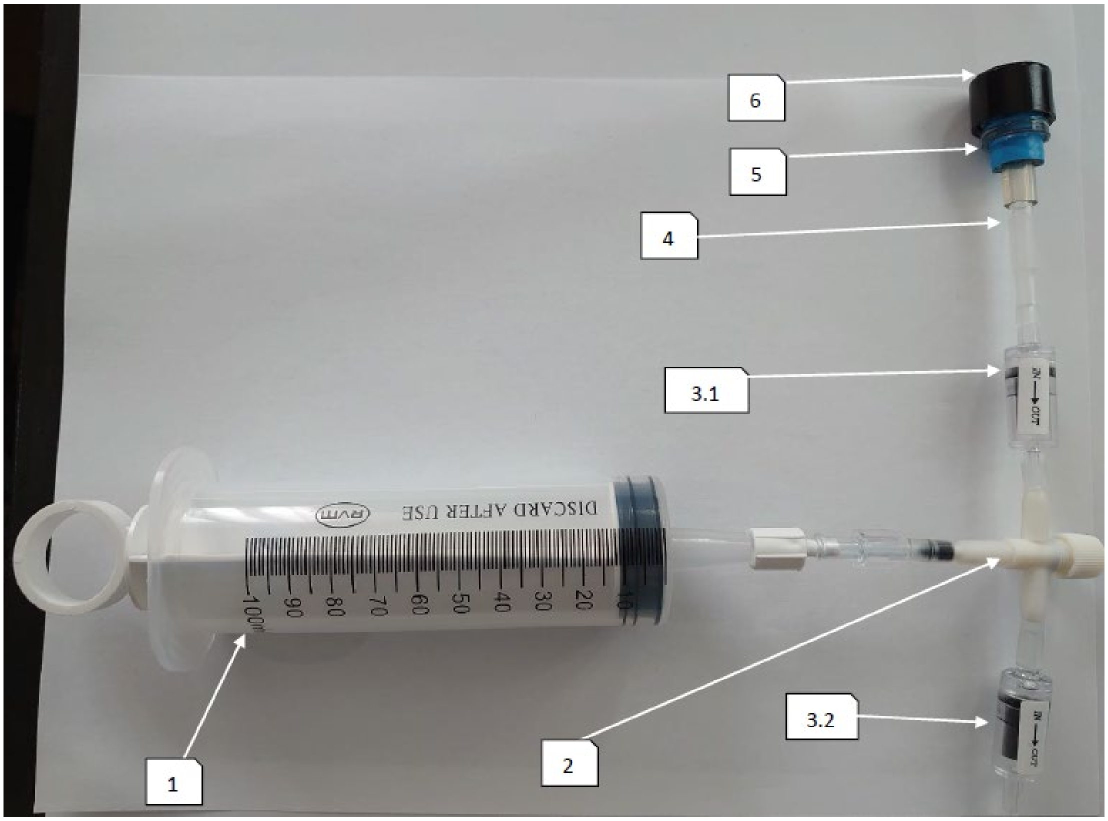
Contestant Gold
Salt Pad/Sodium Metasilicate
200 ppb MMH in Air
2 Liter Sample
Response: 1-2 min

Figure 2. Colorimetric Sensor Cartridge

Note enhanced color of the gold salt pads treated with sodium metasilicate.

Second Place: Sampling Device Prototype with PDAB or $KAuCl_4$ reagents on Pads and Filters (Romania Finalist).

The device shown in Figure 3 was designed to sample air from a gas collection bag drawing the sample with a piston pump through a sampling pad or filter containing a color indicator. Color indicators included $KAuCl_4$ or PDAB on quartz, paper, sodium chloride/quartz, glass fiber, polytetrafluoroethylene (PTFE), or paper pads. One application used $KAuCl_4$ and 3,3′,5,5′-tetramethylbenzidine (TMB), where TMB added to hydrazine-exposed pads was oxidized by excess $KAuCl_4$ to form a green-blue complex spot on the pad with a resultant color intensity inversely proportional to hydrazine concentration. The participant emphasized validation work using a camera—including a smartphone camera—in association with image analysis software could provide results similar to spectrophotometric determinations. Validation work performed and presented used a standard smartphone to capture image for pre-loaded/exposed pads and commercial imaging software to obtain RGB color codes for areas of interest on pre-exposed and post-exposed pads. Detailed numerical and graphical data were presented.



Legend: 1 = Piston pump (100 mL); 2 = Flow controller T connector; 3.1/3.2 = Direction controllers; 4 = Connection tubes; 5 = Port filter; 6 = Pad/filter

Figure 3. Romania Finalist Challenge Submittal

WSTF test results showed 1-2 liter of sample volumes at 1 ppm and 200 ppb MMH were sufficient for color change as shown in Figure 4. Higher volumes are required at the lower concentration. Response times were 2-4 minutes for 1 ppm MMH and greater than 3 minutes for 200 ppb MMH. The participant's pad selection with tetrachloroaurate was similar to WSTF CDK pads. No reaction with PDAB was observed.

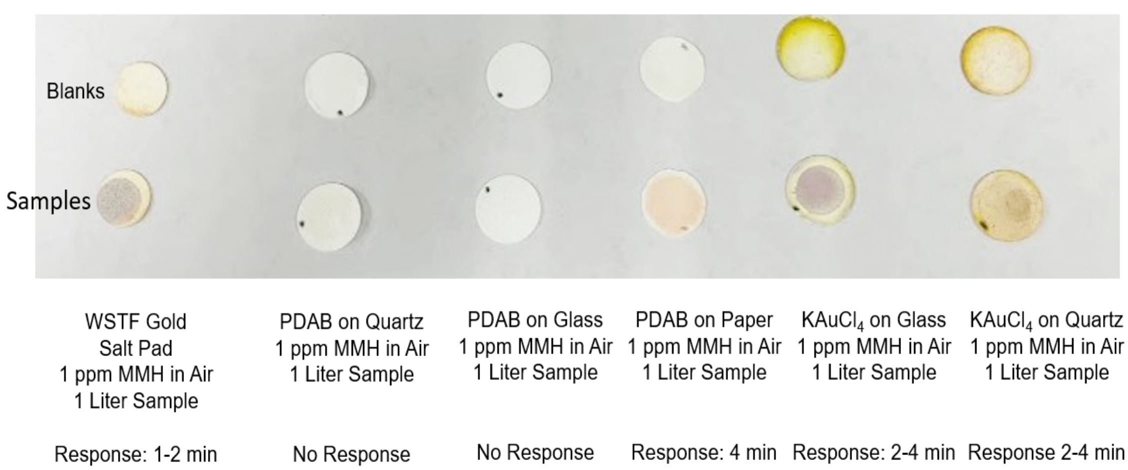


Figure 4. Sampling Device Prototype with PDAB or $KAuCl_4$ Reagent

Third Place: Hydrazine Detection System (Taiwan Finalist)

The device shown in Figure 5 samples air with a syringe and is injected into a sampling bag. Liquid PDAB reagent is then injected into the sampling bag and the developed color is observed. Submitters observed phosphoric acid was used in preparing the PDAB solution provided safety and performance advantages over sulfuric acid. The formulation of the reagents was 10 mL phosphoric acid and 30 mL distilled water added to 1.5 g PDAB in 10 mL distilled water as shown in Figure 6. Assuming concentrated (85%) phosphoric acid was the initial source, the phosphoric acid concentration in the PDAB/phosphoric acid solution is 17 percent. Use of citric acid, which has been employed in PDAB dosimeter badges, was not discussed.

Figure 5. Taiwan Finalist Submittal

The Taiwan finalist was a collaborative effort between professor and students at the National Central University, Taiwan. WSTF test results showed 1-2 liter of 1 ppm or 200 ppb MMH was sufficient to obtain color change. The PDAB solution changed from pale yellow to dark yellow with vapor phase MMH. The response time was 1-2 minutes for 1 ppm MMH and 3 minutes for 200 ppb MMH.

PDAB/Phosphoric acid solution

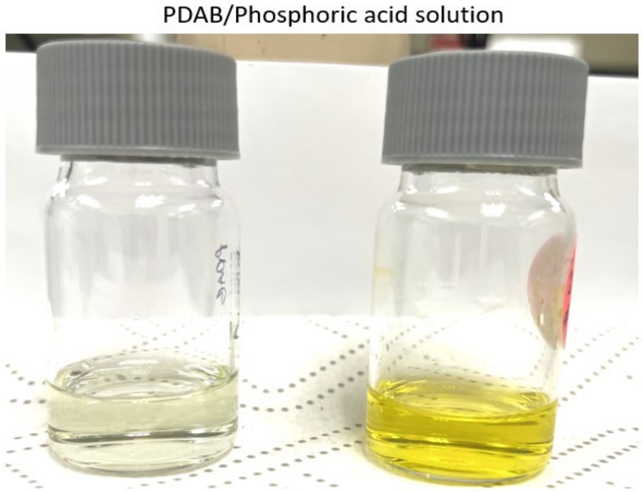


Figure 6. Hydrazine Detection System. Color Change for Taiwan Finalist PDAB Solutions with 1 ppm MMH (Right). Blank PDAB Solution (Left)

Runners-Up

Hand Pump with Stroke Counter Using Paper Tape. (United States-2 Finalist)

The 3D-printed device shown in Figure 7 and Figure 8 used a paper tape coated with potassium tetrachloroaurate. A tape driving system and an embedded color chart to measure hydrazine concentrations was included.

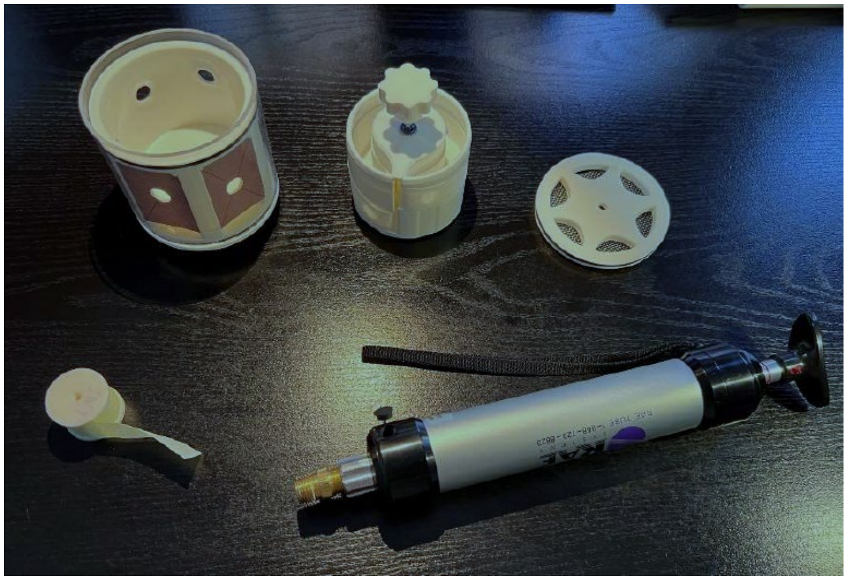


Figure 7. United States-2 Finalist Hand Pump with Stroke Counter Using Paper Tape

WSTF testing showed the prototype did not detect any concentration of MMH in the gas phase even with the bag tests. The tape had visible pores like cloth and for comparison, the CDK matrix is glass fiber 1 µM filter. Small pores provide increased surface area for color development. The hardware air sampling works as intended. The tape may be replaced with a different material, such as a 1 µm glass fiber filter, to optimize the reaction between hydrazines and $KAuCl_4$. The complexity of the engineering was appreciated, and efforts on the participant's part were highly focused on this aspect. The tape coated with $KAuCl_4$ may have been too porous for observing color change from a gas-phase reaction. Further focus on the redox chemistry and optimization of moving parts would be beneficial. The submittal is deemed suitable for further investigation.

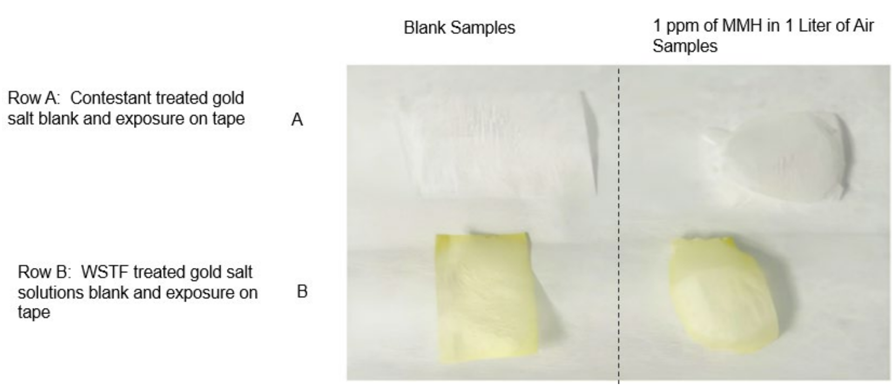


Figure 8. Air Sampling Device with Potassium Tetrachloroaurate(III)-Treated Pads (United States-2 Finalist)

Air Sampling Device with Hydrogen Tetrachloroaurate-Treated Pads (India Finalist)

The device was received with some damage and could not be operated as intended. Further, the color tape was developed when received and could not be tested.

The two-staged device shown in Figure 9 was a hand pump coupled with a $HAuCl_4$-treated sample badge and was equipped with a storage stage, spring housing and gear box for the pump, and end cap. The handheld air pump integrates a storage compartment specifically designed to accommodate the sample badge adapter. A sample badge is inserted into the uppermost sample badge adapter and secured with a rotation. Initiating a measure rotation of the spring housing facilitates gradual winding of the internal spring mechanism prompting engagement of a turbine and formation of a low-pressure zone in the dome. The low pressure zone causes an accurate and precise airflow through the sample badge. A modified $HAuCl_4$ solution coupled with cetyltrimethylammonium bromide was purported to provide enhanced visual color change.

Cetyltrimethylammonium bromide is a surfactant. Surfactants are important in the synthesis and functionalization of metal nanoparticles, including AuNPs as described by Li et al. (2020a, 2020b). Among the surfactants used in the preparation of metallic nanoparticles, cetyltrimethylammonium bromide—a quaternary ammonium cationic surfactant—has been the most typical representative to grow AuNPs with different morphologies. Morphologies of AuNPs are important because they affect color. AuNP morphologies include gold nanorods, hexagonal and triangular nanocrystalline gold plates, bimetallic nanoparticles, high-index faceted gold nanocrystals, gold nanocubes, and others. The proposed mechanism was related to assembly structure variation of cetyltrimethylammonium bromide on the surface of negatively charged AuNPs facilitating interfacial self-assembly of colloidal nanoparticles. Self-assembly is generally induced by neutralizing nanoparticle surface charge.

Figure 9. Air Sampling Pump for Interface of Sample-Treated Pad

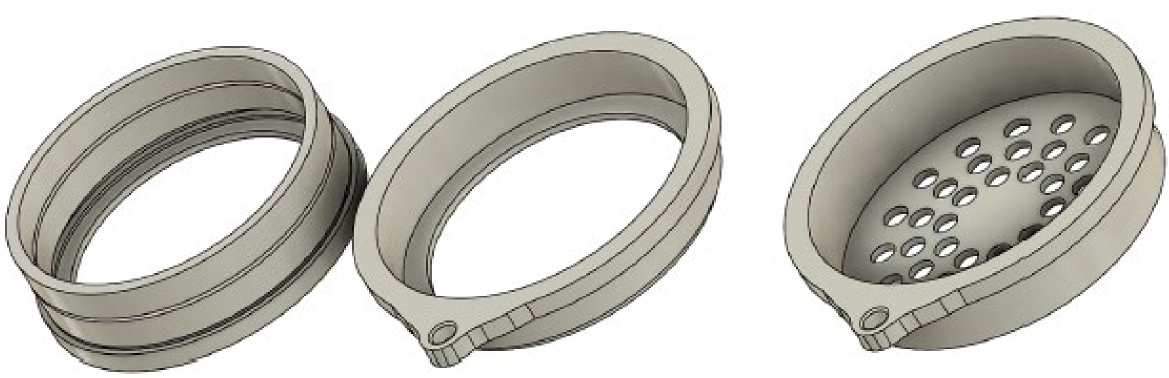


Figure 10. Air Sampling Device with Hydrogen Tetrachloroaurate-Treated Pads

WSTF noted the $HAuCl_4$ color pads provided were developed and had turned purple as received but were tested despite this. Color pads were exposed to 1 liter of air containing 1 ppm MMH at 1 liter/min. Color pads were also exposed to 1 ppm MMH for 2 hours at 1 liter/min. No additional color change above the as-received developed color was observed. Further optimization and formulation will be required to enhance the redox reaction between hydrazines and $HAuCl_4$. This air sampler prototype should work based upon its design and is considered suitable for further investigation.

CONCLUSIONS AND RECOMMENDATIONS

NASA's crowdsourcing effort brought forth innovative ideas and concepts worthy of further evaluation for their potential enhancement of the CDK for hydrazine, MMH, and UDMH detection and related applications. Participant input was accordingly focused because the effort was geared around the CDK and color detection using $KAuCl_4$, although color detection schemes including PDAB and $KAuCl_4$ coupled with 3,3',5,5'-tetramethylbenzidine (TMB) were also proposed. Pretreatment of sensing pads with sodium metasilicate or cetyltrimethylammonium bromide to enhance gold nanoparticle formation and promote aggregation were notable innovations that may be explored further in the WSTF laboratory. Innovations were suggestive of literature work coupled with considerable efforts in research and development. While some proposals have limitations for actual space operations, the applications may be suitable as low-cost options for monitoring during MMH and hydrazine ground operations.

Participants designed their own sampling systems and prepared their own color detection substrates using off-the-shelf hardware or designing and 3D printing parts on their own. Overall, participants expressed appreciation for the exciting opportunity to work on a NASA project and should be congratulated for their contributions toward hydrazine in space and human health and safety.

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