

CHEMOCHROMIC INDICATORS FOR THE DETECTION OF HYPERGOLIC FUELS

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ABSTRACT

The toxicity and hazard level associated with the use of hypergolic fuels necessitates the development of technology capable of detecting the presence of such fuels in a variety of different environments and conditions. The most commonly used sensors for the detection of hypergolic fuels are electrochemical in nature, which have serious limitations when used as area monitoring devices. Recent collaborative work between Kennedy Space Center and ASRC Aerospace has led to the development of indicators which exhibit a color change upon exposure to hydrazine under different conditions. The indicators under investigation on this developmental effort are para-dimethylaminobenzaldehyde (PDAB), various formulations of universal pH indicators, and potassium tetrachloroaurate (KAuCl₄). These chemochromic indicators have been tested for the detection of hydrazine under various conditions: pure liquid fuel, aqueous fuel solution, saline aqueous fuel solutions, vapor fuel, and 3-month shelf life study, which included UV protection, thermal extremes, and normal storage conditions. The hypergolic fuel indicator test was conducted with the indicator impregnated into a wipe material to test the applicability of the indicator to be used to capture (absorb) and indicate the presence of hypergolic fuels. Each of the indicators performed well, with the universal pH indicator being the best candidate because of the visible response color change and the indicator stability after the shelf life study.

INTRODUCTION

The use of amine fuels Hydrazine (Hz), Unsymmetrical Di-Methyl Hydrazine (UDMH), and Mono-Methyl Hydrazine (MMH) in hypergolic or mono-propellant systems for aerospace and aeronautical applications is very common these days (in this document hydrazines would be used to describe all three compounds). Hydrazines are highly toxic and reactive. These compounds have Threshold Limit Values (TLV) of 10 parts-per-billion (ppb)¹. Hence, ground operations involving hydrazines are hazardous and require personnel and property protection both during and after operations. At Kennedy Space Center (KSC), there are numerous protection measures that take place during hydrazines operations: various levels of Personal Protective Equipment (PPE), aspirators to remove spills, scrubbers to capture vapor releases, area monitors for gas leaks, and others. These area monitoring gas detectors offer a great option to detect large hydrazine fuel leaks, however, they lack the capability of detecting small localized leaks. There are physical location constraints (located too far from leak source), air movement constraints that dilute the hydrazine, and detection limit constraints at the low 10 ppb personnel threshold level. Small hand-held devices are capable of detecting low level hydrazine vapors, but are maintenance intensive (i.e. calibration cycles), have relatively slow response and recovery, and are sensitive to interference (e.g. humidity).

Chemochromic indicators offer a simplified method to qualitatively determine the presence of the target compound by changing color as a result of interaction between the indicator and the target compound. Chemochromic sensors can be used as area sensors but can also be employed as point sensors when in contact with hardware that has a potential to leak. The use of chemochromic sensors as point sensors offer several advantages, including providing information as to the exact location of a leak source and avoiding the constraints of area sensors that are subject to dilution of the target compound.

Hydrazine fuels are electron donors, making them a Lewis base and reducing agent. In fact, hydrazine fuels are considered strong reducing agents. This property of hydrazines can be exploited to create a chemochromic hydrazine indicators that undergo a color change based upon the specific chemical interaction that occurs. The color change could be the result of (1) the reduction of an indicator by hydrazine, (2) a change in the pH of the fluid (gas or liquid) caused by hydrazine, or (3) a reaction of hydrazine with a compound that results in a product with a different reflectance spectra in the visible wavelength range. This paper summarizes the testing of three indicators representing the three unique processes that cause the color change: potassium tetrachloroaurate (KAuCl_4), universal pH indicator, and para-dimethylaminobenzaldehyde (PDAB).

The use of a wipe product for hydrazine detection is desirable for numerous applications. The vapor pressure of hydrazine above a dilute solution is depressed, making vapor sensors unreliable in certain situations. With an indicating wipe, any unknown liquid can be wiped with and provide qualitative identification of hypergols as well as providing a cleanup means for the spill/leak. Previous work on a hypergolic indicating wipe demonstrated the detection of the hydrazine in an aqueous solution with wipes impregnated with Yamada Universal Indicating solution. In order to use this product in the field on ground support equipment or flight hardware, there are numerous tests that the material needs to pass to ensure it will cause any problems. These initial wipes did not pass all of the required tests, with the first problem being non-volatile residue (NVR) generated by wipes.

In addition to the use of chemochromic hypergol indicating wipes for processing systems, the recovery of a system containing hypergols from a seawater environment is of interest for NASA. One scenario of the recovery of the ORION capsule included a water landing in the ocean. This presented a unique and challenging environment with possible seawater contamination and winds that could make a hydrazine leak difficult to detect. The use of Self-Contained Atmospheric Protective Ensemble (SCAPE) typically used during potentially hazardous operations involving hydrazines is not feasible in the recovery effort for the capsule. The use of a chemochromic leak detector that would allow for the qualitative detection of hydrazines in the presence of seawater was included in the concepts of operation for the recovery effort. To support this need, technology development was initiated to create a chemochromic wipe that could be used in this environment. This paper details the development and testing of a modified indicator wipe, from interferences expected to lifetime testing of the 3 unique wipes developed.

RESULTS AND DISCUSSION

The hypergolic indicators were tested on an absorbent wipe substrate manufactured by 3M (2112-CE 3M High Performance Wipes), especially made for United Space Alliance. These wipes were selected as the substrate for these indicators because they are currently approved to be used during ground processing of the flight hardware. These wipes are impregnated with the indicator solution by submerging the wipe in the indicator solution until the wipe is saturated with the solution. Excess solution is allowed to drip, and the wipes are allowed to dry overnight. Two basic methods of drying wipes were evaluated: (1) Air drying and (2) Vacuum drying in a dessicator. The air drying methodology was further divided into the use of "sorbed" and "non-sorbed" wipes. Wipes that were sorbed were placed on paper towels to absorb the excess liquid from the wipe during the air drying process. Non-sorbed wipes were placed on a non-absorbent surface during the air drying process. "Squeezing" excess solution from the wipe was not done in order to (a) increase amount of indicator that would be deposited on the wipe, thus potentially causing an increase in the final color of the wipe after exposure, and (b) allow a uniform coating of the indicator onto the wipe surface. Once dried, the wipes, originally 8in by 8in, are cut into 1in by 1in coupons. This size was used in order to facilitate testing of a large range of indicator solutions and pH ranges.

Each of the indicator solutions were organic solvent-based (e.g. ethanol, methanol, isopropyl alcohol), in order to dissolve the indicator dyes, which also worked in our favor by

decreasing drying time of the indicator wipes. Several Universal pH indicators were tested including: Yamada, Acros (88365-86 and 88359-76), and Ricca (RC8870-16). Acros and Ricca are commercially available universal pH indicators; whereas, the Yamada was made in-house following published formulations: 0.07mg/g Thymol Blue, 0.17mg/g Methyl Red, 0.67mg/g Bromothymol Blue, and 1.30mg/g of Phenolphthalein in ethanol. When required (as required per the specific testing), the indicator was diluted with DI water and the pH adjusted using 0.1M NaOH or 0.1M HCl. Typically, these universal pH indicators have a color response to a pH range as described in Table I. Hydrazines, with a pH value of 9-11², would result in a color change to blue.

Table I. Typical color chart for universal pH indicators based on universal indicator components.













pH range	Color
0-3	Red
3-6	Orange
7	Green
8-11	Blue
11-14	Purple

The PDAB indicator solutions were prepared by making a 3.2wt% PDAB solution in ethanol. This PDAB solution was then acidified to 0.36M sulfuric acid. The gold salt solution was prepared by dissolving KAuCl₄ salt in ethanol to a molar concentration of 0.01M. As it would be discussed later, the PDAB indicator changes from “clear” to bright orange in the presence of hydrazines, and gold salt changes from yellow to black.

Anhydrous hydrazine (N₂H₄) was used for all testing performed for the hydrazine indicators. The anhydrous hydrazine was obtained from Wiltech Laboratories at Kennedy Space Center. Since one of the objectives of the study was to determine the applicability of using these indicators during a seawater landing scenario of the crew capsule, the anhydrous hydrazine was diluted in ultra-pure water (UPW) and seawater (SW) obtained from the shores at KSC to 10ppm, 500ppm, and 1,000ppm. The ultra-pure water was used as the control during the experiments, due to possible interference from any impurity from the seawater sample.

Hydrazine pH indicators were initially tested with UPW, SW, and basic solutions (pH 9 and 11) to simulate hydrazine. Because hydrazines are basic, the pH indicators were tested starting at a low pH range (acidic). Table II shows the pH indicators exposed to UPW, SW, pH 9, and pH 11 solutions. These exposure tests were performed by dropping a 1-2mL of the solution onto the indicator material. UPW does not have any effect on the pH indicator; hence, the UPW row depicts the initial color of the pH indicator. Also, SW has little effect on the pH indicators. All pH indicators demonstrated a good stability to water and seawater; although, the RICCA indicator had a slight color change to the SW sample, but not to the expected color change response from hydrazine exposure. As it was expected, the indicators changed color when exposed to higher pH solutions. This initial pH indicator test demonstrated that these pH indicators do not have any response to the dilutant used in future hydrazine evaluation, and that each indicator response was very similar under the expected hydrazine pH range.































Table II. Color change of pH indicators to UPW, SW, pH 9, and pH 11 solutions. UPW does not have any effect on the pH indicator; hence, the UPW row depicts the initial color of the pH indicator

	YAMADA- acidic	ACROS- acidic	RICCA- acidic
Ultra-pure water			
Seawater			
pH 9			
pH 11			

Further hydrazine exposure evaluations were conducted on Yamada (acidic), PDAB, and gold salt. Table III shows the response of these indicators to pure hydrazine and to 1000ppm, 500ppm, and 10ppm hydrazine solutions in UPW and SW. Again, these exposure tests were accomplished by dropping 1-2mL of solution onto the wipe material. Pure hydrazine turned the Yamada universal indicator to blue, which correspond to a pH of 8-11. High concentration hydrazine aqueous solutions yielded a color change to green. Green is indicative of a neutral pH solution, which can be attributed to the presence of hydrazine in lower concentrations. Given that the Yamada pH indicator does not have any color change to neither pure water nor seawater, the 3-7 unit change in pH can only be result of the presence of hydrazine. It seems that for the Yamada pH indicator the lower detection limit for an aqueous solution is lower than 500ppm.

PDAB and gold salt indicators changed color to both UPW and SW solutions. Both indicators changed to the expected color upon exposure to hydrazine, being orange and black for PDAB and gold salt, respectively. PDAB changed to light-orange for the 10ppm hydrazine solution in UPW and SW, whereas gold salt had a more distinct response to the 10ppm hydrazine solution in UPW. It seems that for the case SW solution and gold salt, a component in the SW may be interfering with the gold salt reduction. At this point, it is not clear the cause of the lack of gold salt reduction by hydrazine in the presence of seawater. An interesting phenomenon occurs to PDAB indicator when exposed to pure hydrazine where a ring of dark orange forms around the area where the hydrazine drop was placed on the material, leaving a yellow color in the center. This "ring" grows as the liquid hydrazine expands on the substrate, leading to believe that the PDAB-hydrazine reaction product is being displaced on the substrate by the expanding liquid phase.

Table III. Color change of Yamada pH indicator, PDAB and gold salt to pure hydrazine and 1,000ppm, 500ppm, and 10ppm hydrazine solution in UPW, and SW

Seawater				Ultra-pure water			
	Yamada	PDAB	KAuCl ₄		Yamada	PDAB	KAuCl ₄
Before Exposure				Before Exposure			
Hydrazine				Hydrazine			
1000ppm				1000ppm			
500ppm				500ppm			
10ppm				10ppm			

The intensity of the color change on PDAB and gold salt indicators is proportional to the concentration of hydrazine in solution. A Minolta Chromameter was used to measure lightness (L^*), redness (a^*) and yellowness (b^*) of each of the indicator material to quantify the color change of each indicator. These parameters (L^* , a^* , b^*) are used to determine the linear change in light reflectance (ΔE^*) off the surface of the indicator by the following equation:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2},$$

where ΔL^* , Δa^* , and Δb^* are the change in the L^* , a^* , and b^* measurement from the initial reference material, respectively. Larger ΔE^* values are easier to discern the color change, with a minimum detection limit of 1 for most people to be able to see a color difference. Figure 1 and 2 depict the ΔE^* values for each indicator (Yamada, PDAB, and gold salt) for both UPW (labeled DI) and SW, respectively. Each plot includes ΔE^* values for dry and wet material as reference.

Most of the pH indicator samples had a ΔE at least of 20 for the tests where the reference was the dry material. The PDAB and gold salt samples had ΔE 's ranging from 50-100. Lower ΔE 's were seen for the tests using the wet wipes as the reference sample, due to small increase in absorption from the wet indicator material. The PDAB and gold salt indicator had extremely high values for most of the samples, from ~45 – 85. Replicate tests of indicators were also conducted. The 10 ppm solutions of both UPW and SW were more difficult to discern after application to the wipe material. The most obvious color changes were to the PDAB and gold salt wipes. These color changes were very similar to previous results. As it is seen from the pictures in Table III, Yamada and gold salt had a very small color change in response to the 10 ppm hydrazine solution in seawater. This can be seen quantitatively in Fig. 2, where the ΔE value for these indicators was 1 and 8 for Yamada and gold salt (wet substrate referenced), respectively.

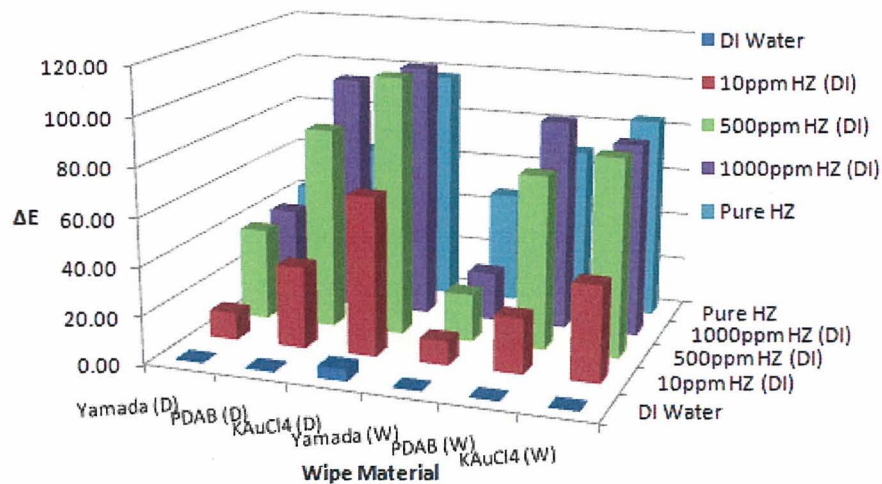


Figure 1. ΔE^* response value for each indicator to UPW (labeled DI) hydrazine solutions for dry and wet material as reference

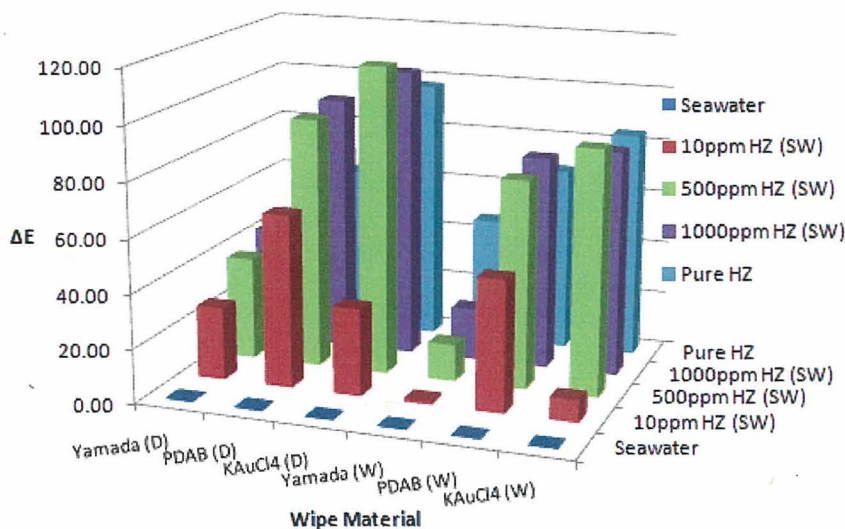


Figure 2. ΔE^* response value for each indicator to SW hydrazine solutions for dry and wet material as reference

A large portion of the hypergol indicator testing involved an evaluation of the approximate shelf-life for the indicators. This evaluation, approximately 3 months in duration, was set up to test the ability of the indicator wipe to respond to hydrazine after exposure to different environmental and storage conditions, as described in Table IV. Each location (representing a specific storage extreme) included indicator wipes inside UV-resistance zip-lock bag, vacuum sealed bag, or just open to the environmental condition.

Table IV. Long Term Study Conditions

Condition	Location Description
Heat	Indicator material was placed in an oven set to 120°F simulating the inside of a parked car under a typical summer day in

	Florida.
Cold	Extreme for best storage for chemicals. Current dosimeter badges utilizing PDAB as the indicator are stored in the refrigerator during long-term storage
No light	Indicator materials were stored inside a drawer.
Ambient Light	Indicator material was set on a table under normal fluorescent lighting
Direct Sunlight	Indicator material was placed on an area inside the office building under direct sunlight for more than 4-5 hrs per day
Outside	Indicator material was placed at the KSC Corrosion Test Facility on the shores of the Atlantic Ocean

Samples were scheduled to be retrieved at time = 0 days, 1 day, 7 days, 14 days, 1 month, 2 month, and at 3 months. Once retrieved, these samples were to be exposed to HZ to determine the effect, if any, environmental conditions had on the effectiveness of the wipes to detect the presence of hypergolic fuels.

The samples at 0 days and 1 day were taken to be considered control for this experiment. After 7 days of exposure to the environmental conditions, visual inspection of the wipes set outside showed much more variability in wipe color, due to the exposure to various environmental conditions found at the beach site (including several rain storms). Some of the color variation also was likely due to differences in the folding of the wipes (different exposures to direct sunlight). As it was expected, these indicator wipes showed some variability as compared to wipes which were not exposed to more extreme conditions. The indicator wipes under the outside environment were deemed un-usable after 30 days under these conditions. These results were expected given the extreme environmental condition.

In comparison, the wipes under direct sunlight (indoor) were much more uniform in color, and appeared to be identical to the original material. The wipes contained within the UV-resistant bags seemed to be afforded the most protection from the environmental conditions; although; even in those materials, some color darkening was seen in the PDAB indicator. The performance of these wipes upon exposure to hydrazine solutions was as expected, but the overall change for many of the wipes were less than from previous tests (due to the storage conditions of the indicator before exposure). Many of the gold salt samples had already turned a faint purple (false positive), but upon exposure to hydrazine went to a much darker purple. Additionally, the pH indicator material showed a much more slight color change than expected (except for the UV-resistant wipes). The indicator wipes from the ambient/cooled/dark environments showed no visible change in appearance. The indicator wipes in the heated environment did show some changes, most noticeably in the PDAB wipes (darkening of the indicator color).

After 105 days, the wipes exposed to sunlight (indoor) showed a marked bleaching effect, as well as several false positive color (darkening) change in the gold salt wipes (except for the UV-resistant wipes). Additionally, the darkening of the PDAB wipes was seen in all samples except those protected by the UV-resistant bags. These bags have proven to be the best protection against color degradation for wipes exposed to excessive sunlight. The wipes exposed to the ambient light environment continue to show the bleaching effect seen in previous samples. The other types of protection show marked bleaching of the gold salt indicator wipes. The indicator wipes in the dark environment did have some color variation after 105 days. The PDAB and gold salt indicator wipes seemed to darken, even in the UV-resistant bags. The indicator wipes kept within a cooled environment had the least color change. The indicator wipes exposed to the heated environment continued to show color degradation of the indicator. This is most prevalent in the darkening of the PDAB; although, there was some darkening of the open gold

salt wipes. All the indicators changed color as expected upon addition of the hydrazine solution, even if the indicator had slightly faded or darken.

The indicator wipes were also evaluated for the main concern during exposure to hydrazine: hydrazine compatibility, flammability, and electrostatic discharge. These tests are standard tests performed to understand material properties: hydrazine compatibility per NASA-STD-6001A A.7, flammability per NASA-STD-6001A Test 1, and electrostatic discharge per ASTM D 257. The acceptance criteria for these tests are as follow: (a) hydrazine compatibility: temperature rise criteria of 2.8°C during a 10min period after exposure to hydrazine, (b) flammability: the material is determined non-combustible or self-extinguishing if 6in or less of the sample are consumed and flaming particles from the test sample does not ignite K-10 paper, (c) electrostatic discharge: material having a resistivity less than 10^{12} ohms per square. The substrate wipe material failed the hydrazine compatibility test, as well as the PDAB and gold salt, with temperature rise in average of 6°C. Surprisingly, the Yamada indicator wipe passed this compatibility test with a temperature increase of 2.6°C. ~~NEED EXPLANATION FOR THIS~~. All indicators passed flammability test, with burning lengths less than 4 inches; however, all the indicator wipes, including the substrate wipe, failed the electrostatic discharge test, with surface resistivity greater than 1.7×10^{14} ohms per square. Future collaboration with operational personnel will identify the best use of these sensors and will determine the required testing for the product.

SUMMARY AND CONCLUSIONS

Several hydrazine chemochromic indicators have been identified and evaluated to be used as a quick and inexpensive qualitative determination of the presence of hydrazine. The leading candidates for the chemochromic hydrazine indicators are Yamada universal pH indicator, gold salt, and PDAB, each providing a distinctive color change after exposure to various concentrations of liquid hydrazine. These hydrazine indicators are capable of detecting hydrazine at concentration as low as 10ppm in the liquid phase. Laboratory testing has shown the chemochromic sensors to successfully detect hydrazine in both water and seawater without interference. This is critical in operational environments as the vapor pressure of hydrazine is severely depressed when it is in solution with water or seawater. The depression of the vapor pressure precludes the use of the typical hydrazine vapor sensors. In addition to the qualitative determination of hydrazine, these sensors (specifically the Yamada universal pH indicator) can be used to discern fuel from oxidizer. This is especially useful when identifying and unknown liquid in a system with hypergolic fuels.

These chemochromic hydrazine indicators have been incorporated into a wipe substrate and tested for color change when exposed to solutions of hydrazine as well as exposed to environmental effects such as heat and UV exposure. The data provide positive results for their applicability to be used as a hydrazine indicating wipe in operational and laboratory settings, as well as acceptable storage conditions for a 3 month shelf life. These wipes can be used during ground processing of spacecrafts as well as during the water recovery of the Orion crew capsule. The chemochromic wipes are easy and inexpensive to fabricate and have a shelf-life of at least three months if stored under controlled temperature protected from UV exposure (i.e. using UV-resistant bags). Chemochromic hydrazine detecting wipes provide a valuable tool for personnel working around hypergolic systems.,

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