Distillation Process of Hydrazine

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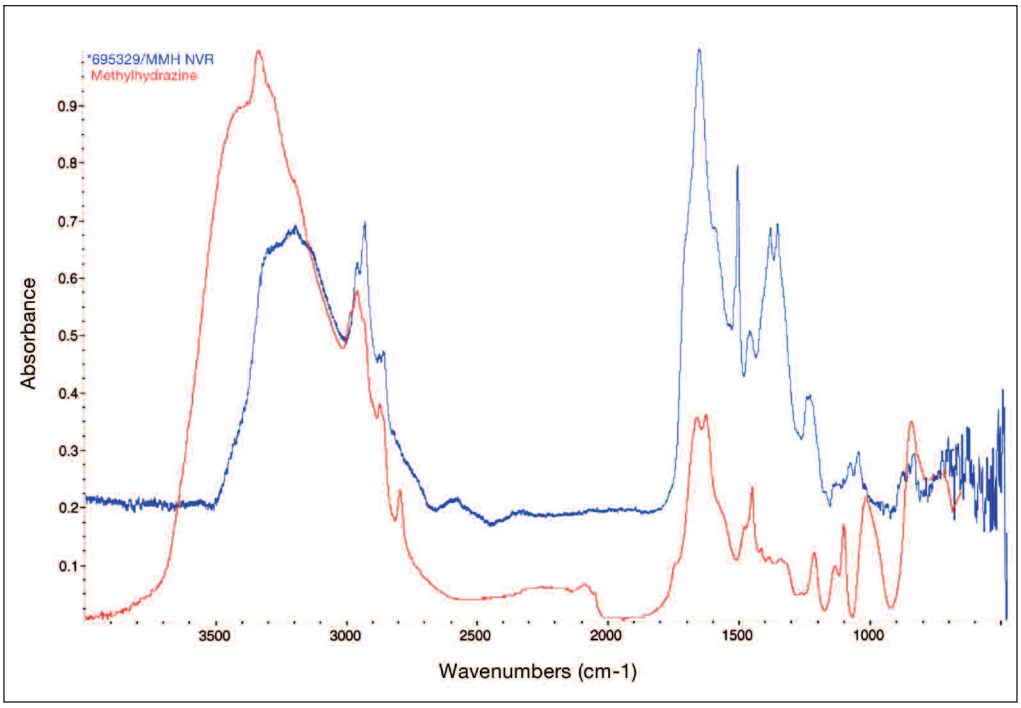
White Sands Test Facility (WSTF) routinely operates hypergolic propulsion systems. Some of the on-site activities include long-duration studies on the operational life of these systems, a few of which have been in use for over 20 years. During this span of time, contamination has built up in the propellant and some of the distribution infrastructure. This study investigated the nature of this contamination and the pathology of its generation, and developed a process for removal of the contamination.



To begin, a survey was performed on all hypergolic propellants at WSTF to determine which were contaminated and what quantities of contamination were present. Monomethylhydrazine (MMH) was the material determined to have the greatest quantity of contamination. A nonvolatile residue (NVR) level greater than 10 mg/L is unacceptable for use per SE-S-0073, *NASA Specification Fluid Procurement and Use Control*. Quantities of MMH were analyzed and found to have NVR levels as high as 30 mg/L.

Analysis of the contamination was performed to investigate its nature and to assist in developing a treatment process. NVR in hydrazine-based fuels is difficult to label because it is composed of organic derivatives of hydrazine. Analysis by Fourier transform infrared spectroscopy (see figure) indicates that fuel NVR is a hydrazine-based compound with nitrogen-hydrogen and carbon-hydrogen bonds. WSTF scientists and technicians hypothesize that fuel contaminants result from interaction between hydrazine-based fuels and atmospheric components during handling of and transferring the propellants. Long-term stored propellants do not show the decomposition that is shown on site. In an experiment performed by the WSTF Chemistry Lab, artificial aging of MMH was accomplished by injecting air into a test container filled with a sample of the fluid, causing NVR to form. A control sample did not have a detectable NVR signature.

A site survey determined that WSTF currently has more than 3,000 gal of MMH with an NVR concentration in excess of the specification limit. The MMH has been collected in tanks for several years for future disposition. Rather than dispose of unusable MMH, the feasibility of decontaminating the propellant was proposed as a cost-effective and environmentally friendly alternative.

To ensure the development of an appropriate and safe process, the chemical characteristics of the propellant were considered during a separation technique assessment. MMH is corrosive and toxic; it is also highly flammable, toxic by contact or inhalation, and causes severe burns.

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continued

This propellant requires personal protection equipment and limited human exposure. In addition, limited materials can be exposed to MMH. Acceptable materials include 300-series stainless steel, Teflon, and perfluorinated greases.

With the proper controls, distillation is used as the industry-standard analytical process for determining NVR content. This technique is based on the volatilities of substances being separated, and consists of the addition and removal of heat. Any evaporable compound can be separated from nonvolatile substances using this technique, and extra waste is not generated. The process materials are nonselective and can be used with any propellant as long as the boiling point range and autoignition temperature are known. The still, constructed with compatible materials, can be easily stored, cleaned, and operated. If distillation is conducted under reduced pressure, it decreases the required temperature for evaporation while increasing safety.

A pilot plant project was performed to determine whether the analytical technique could be scaled up to handle processing larger quantities. A bench-top processing apparatus was assembled in the WSTF Chemistry Lab. Propellant sampling locations were assessed based on the level of contamination and volume of the container. Two propellant storage tanks were chosen for sampling, and two samples were taken from each tank. Samples were 1 L each, and were processed individually through the apparatus. The pilot plant was able to reduce contamination levels of 12 to 25 mg/L to a level of 0.1 or 0.2 mg/L. The complete results were reported. The final analytical assessment validated the process for larger quantities.

Requirements were developed for the procurement of a distillation unit. Fire, explosion, and safety hazards were considered in the design of this MMH system. MMH is a strong reducing agent, weakly alkaline, and very hygroscopic. It reacts readily with a variety of organic and inorganic compounds and is thermodynamically unstable. Introducing heat to MMH needs to be under very specific and well-controlled parameters. Also considered was the ability of the unit to process the NVR from approximately 30 mg/L to less than 1 mg/L. The unit will be fabricated per the latest revision of ASME B31.3 *Process Piping*, "Normal Fluid Service," to take advantage of industry experience and provide an appropriately robust processing unit.

All of the specifications and requirements were documented in a statement of work titled "Propellant Analysis and Distillation Statement of Work." The next phases of this project will submit the document to the procurement process for acquisition of a distillation unit. At that point, implementation of an operational envelope and standard work procedures will be developed. The unit is planned to be in operation for an extended period and will alleviate the need for costly material disposal. It will also provide reclaimed propellant for use in future testing.