



Contaminant Reduction in High Purity Hydrazine

Hydrazine and its derivatives are used ubiquitously in liquid propulsion systems. In smaller thruster systems, contaminant build up has historically caused flow decay and consequently performance losses. Many of these contaminants are not controlled by the current revision of MIL-PRF-26536^[1], the High Purity Hydrazine (HPH) procurement specification, yet have been observed to be present in HPH at variable concentration and, often exceed potentially problematic levels for small thrusters. This technical bulletin outlines recent work aimed at identifying appropriate separation processes to remove specific target elemental and carbonaceous contamination in HPH.

Background

Following a change in the HPH production process used for US spaceflight application, efforts were undertaken to characterize impurities in the HPH produced by the new method. Results focused on probable identification of extraneous carbonaceous contamination and extended elemental characterization to assess risk to programs and payloads compared to legacy HPH^[2-5]. Elemental contaminants, other than iron, are not currently regulated by MIL-PRF-26536 and are not currently required to meet a specific level for HPH procurement. Certain HPH users and missions have required specific low elemental levels that have been largely controlled through testing of cylinders to identify acceptable stocks. Recent discussions throughout the HPH user community have focused on the addition of limits for such contaminants to be added in the next full revision of MIL-PRF-26536. The NESC initiated a study to investigate methods to reduce specific problematic elements should new limitations be implemented and HPH stocks require purification to meet programmatic needs. Additionally, the purification methods were assessed for capacity to simultaneously remove extraneous carbonaceous content in the new HPH. Several lab-scale separation techniques including alumino-silicate-based molecular sieves, ion exchange resins, crystallization, sublimation, and vacuum-assisted distillation were screened for compatibility with HPH, target elemental removal performance, and carbonaceous content reduction.

Testing Conclusions

Alumino-silicate molecular sieves proved to be non-viable as a purification process due to modest removal of the target element and leaching of other problematic elements into the HPH. A selected ion exchange resin was determined to provide excellent target element removal; however, it introduced unacceptable levels of nonvolatile residue (NVR) to the HPH. While the cause of this NVR was not conclusively determined, the ion exchange resin cannot be considered viable without resolving this issue.

The advantage of thermodynamic separation techniques tested in this context is that HPH is not exposed to foreign material, other than the process vessels themselves. Crystallization, sublimation, and vacuum-assisted distillation all displayed the ability to reduce the target element concentration in HPH in non-optimized lab scale testing. Vacuum-assisted distillation also reduced other elemental contaminants and significantly reduced extraneous carbonaceous content. Preliminary data suggested crystallization and sublimation may also achieve carbonaceous content reduction. However, additional work is required to quantify the removal. For use, vessel material considerations are required to avoid using process stabilizers (which become contaminants) on an industrial scale. It is worth noting that crystallization was previously used to purify Viking grade hydrazine^[6]. Crystallization and sublimation carry the advantage of being less hazardous than distillation when purifying HPH.

Table 1: Summary of Lab Scale Findings

Method	Target Element Removal*	Carbonaceous Removal	Considerations
Crystallization	28%	Possible Reduction**	Supercooling
Sublimation	97%	Possible Reduction**	Supercooling
Vacuum-Assisted Distillation	99.7%	35%	Stabilizer Potentially Necessary for Upscale
Ion Exchange Resin	97%	Additional Contamination	Increase in NVR and Exchange Ion Concentration
Alumino-Silicate Molecular Sieves	N/A***	N/A***	Dissolution into HPH

*Target Element Removal Rates for Non-Optimized Lab-Scale Demonstration

**Further Study Needed to Quantify Reduction

***Study Halted Prior to Full Evaluation Due to Non-Compatibility

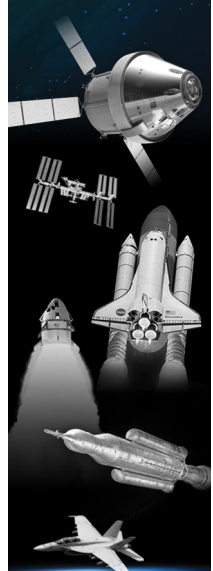
Path Forward

NASA programs and thruster manufacturers should continue to assess elements of concern not currently controlled in MIL-PRF-26536 that could impact their HPH thruster systems. Molecular sieves and ion exchange resins should not be considered viable purification methods for HPH without testing the specific material for NVR and carbonaceous material introduction into HPH. In order to build a large-scale purification capability, it is recommended that the thermodynamic separation solutions shown to be successful in this work^[2] on a non-optimized bench scale, be further investigated for optimization and upscaling.

References

1. Performance specification - Propellant, Hydrazine, MIL-PRF-26536G w/Amendment 1. Department of Defense. (July 13, 2021).
2. Parker, D., Dorney, D., Coutts, J., Maynard, A., & McClure, M. (2020). State of Hydrazine Synthesis and Its Potential Impact on Spaceflight Applications. NESC Technical Assessment Report NESC-RP-20-01504. Available from the NESC.
3. NESC Technical Bulletin No. 20-08, Assessment of Ketazine Derived High Purity Hydrazine for Spacecraft Propellant Systems, Sept. 2020, <https://www.nasa.gov/nesc/technicalbulletins>.
4. Lesson Learned 29801, Best Practices for the Elemental Profiling of High-Purity Hydrazine, Dec. 2020, <https://lis.nasa.gov/lesson/29801>.
5. NESC Technical Bulletin No. 21-03-1, Best Practices for the Elemental Profiling of High-Purity Hydrazine, March 2022, <https://www.nasa.gov/nesc/technicalbulletins>.
6. Schuler, W.; Pharo, T.; and Hall, C., "The Removal of Impurities from Hydrazine for Control of Contamination Caused by Rocket Engine Exhaust," AIAA/SAE 8th Joint Propulsion Specialist Conference, AIAA Paper No. 72-1046, New Orleans, LA, April 1972, (p. 1046).

For information, contact Donald Parker donald.s.parker@nasa.gov
and Janelle Coutts janelle.coutts@nasa.gov.



NESC tech bulletin

