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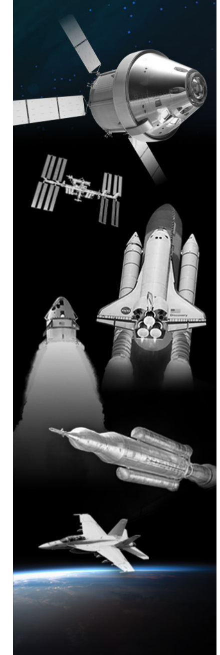

Assessment of Ketazine Derived High Purity Hydrazine for Spacecraft Propellant Systems

Hydrazine and its derivatives have dominated the class of hypergolic liquid propellants for bipropellant propulsion systems in rockets such as the Titan, MX Missile, and Ariane; it has also been widely utilized as a monopropellant in auxiliary power units and in thrusters for altitude and in-orbit control of satellites and spacecraft. With continued use of hydrazine in current and future spacecraft and payloads, it is necessary to understand the historical and current states of synthesis for the commodity and possible implications that may arise from changes in production processes for the United States stock.

Background

A particular concern with newer methodologies for synthesizing high purity hydrazine (HPH) is the presence of extraneous unknown carbonaceous materials. These are organic byproducts from the synthesis processes, which may or may not have serious effects on the long-term storage of the commodity or on propulsion performance of the material. Further, changes in process methods could also alter the residual content levels of other components (e.g., cadmium, tin, or silicon). Traditionally, only iron (Fe) content has a limit in military specification MIL-PRF-26536G HPH; however, with different processes now being utilized for production, not only is a comprehensive analysis of elemental content required to determine what different constituents are present, but the question also remains whether iron should still be the only metal/element monitored on a regular basis.

Arch Chemicals (now Lonza Group) were the pioneers of hydrazine production in the United States using the Olin Raschig Process based on the oxidation of ammonia using alkaline hypochlorite. The development of the Military Specification, MIL-PRF-26536G, for certification of hydrazine, focused on inclusion of contaminants related to this specific production process. While Lonza maintains operation of a blending/purification facility at their plant, they no longer produce hydrazine via the Raschig method. Instead, hydrazine hydrate is purchased from an external, non-U.S., entity and purified to high purity requirements by Lonza. The common newer methods used worldwide for hydrazine synthesis are ketazine-based processes where the oxidation of ammonia occurs in the presence of aliphatic ketones to yield a ketazine intermediate. The intermediate is then subsequently hydrolyzed to form hydrazine. With the introduction of organic species in the synthesis, numerous byproducts can be produced and possibly present in the final product that were not previously a concern and are not identified for monitoring in the procurement specification. Beyond organic impurities, these new processes may also cause other constituents such as metals to be retained in the final product.

Current Results from Hydrazine Sample Testing

Recent testing of HPH samples at Kennedy Space Center (KSC) yielded extraneous, unidentified peaks in the carbonaceous assay when analyzing HPH made from this newer ketazine method. In 2017, Revision G of MIL-PRF-26536 was adapted to include other carbonaceous materials (OCM) - anything that produced a positive FID response – in addition to “other volatile carbonaceous materials, UDMH, MMH, and isopropanol” as part of the total carbonaceous measurement. However, actual identification of these OCM peaks has not been explored until now (See Figure 1). Data for a comprehensive elemental analysis for the HPH material is also lacking for baseline data collection and evaluation. New analytical methods via GC-MS and ICP-OES have been developed to resolve these shortcomings in data for ketazine-derived HPH. With different vendors and processes now being utilized for production, a comprehensive analysis of elemental content is required to determine what different constituents are present. The NESC will soon release a review of synthesis methodologies along with results from current analytical work at KSC for the identification of the aforementioned carbonaceous species and elemental profiling in recent lots of ketazine-derived HPH.

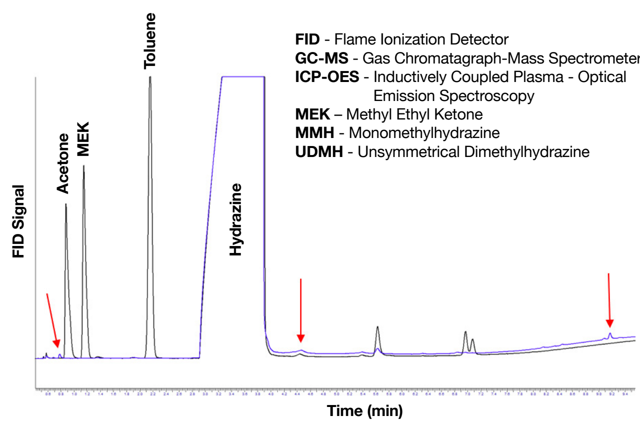

Figure 1. Overlay of 100-ppm Acetone-MEK-Toluene standard (Black) and Ketazine HPH sample (Blue). Red arrows show contaminants not yet elucidated.

Path Forward

NASA programs and other HPH users should evaluate their mission portfolio for hydrazine thruster use to identify potential material incompatibilities based on the results of this on-going work and if appropriate, coordinate any future testing needed by projects. Possible mitigation techniques to remove carbonaceous contamination may be required. Round Robin test results have provided insight into optimal laboratory methodologies for analyzing HPH for elements beyond Fe and recommendations will be made to Air Force owners of MIL-PRF-26536G for possible incorporation into a future revision.

References

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