

# NASA-STD-6001B Test 7: Impact of Test Methodology and Detection Advancements on the Obsolescence of Historical Offgas Data

Vanessa D. Buchanan<sup>1</sup> and Brenton Woods<sup>2</sup>  
*Jacobs White Sands Group, NASA White Sands Test Facility, Las Cruces, NM, 88012*

Susana A. Harper<sup>3</sup> and Harold D. Beeson<sup>4</sup>  
*NASA White Sands Test Facility, Las Cruces, NM, 88012*

Horacio Perez<sup>5</sup>  
*Lockheed Martin Space Systems, Houston, Texas 77058*

*and*

Valerie Ryder<sup>6</sup>, Alma S. Tapia<sup>7</sup> and Michael D. Pedley<sup>8</sup>  
*NASA Johnson Space Center, Houston, TX, 77058*

**NASA-STD-6001B states “all nonmetals tested in accordance with NASA-STD-6001 should be retested every 10 years or as required by the responsible program/project.” The retesting of materials helps ensure the most accurate data are used in material selection. Manufacturer formulas and processes can change over time, sometimes without an update to product number and material information. Material performance in certain NASA-STD-6001 tests can be particularly vulnerable to these changes, such as material offgas (Test 7). In addition, Test 7 analysis techniques at NASA White Sands Test Facility were dramatically enhanced in the early 1990s, resulting in improved detection capabilities. Low level formaldehyde identification was improved again in 2004. Understanding the limitations in offgas analysis data prior to 1990 puts into question the validity and current applicability of that data. Case studies on Super Koropon<sup>®</sup> and Aeroglaze<sup>®</sup> topcoat highlight the importance of material retesting.**

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<sup>1</sup> Materials Flight Acceptance Testing Scientist and Supervisor, Material and Components Laboratories Office, NASA White Sands Test Facility, 12600 NASA Road, Las Cruces New Mexico 88012.

<sup>2</sup> Materials Flight Acceptance Testing Coordinator, Material and Components Laboratories Office, NASA White Sands Test Facility, 12600 NASA Road, Las Cruces New Mexico 88012.

<sup>3</sup> Materials Flight Acceptance Testing Project Manager, Material and Components Laboratories Office, NASA White Sands Test Facility, 12600 NASA Road, Las Cruces New Mexico 88012.

<sup>4</sup> Materials and Component Testing Laboratories Office Chief, Material and Components Laboratories Office, NASA White Sands Test Facility, 12600 NASA Road, Las Cruces New Mexico 88012.

<sup>5</sup> Orion ECLSS & LRS M&P Lead, Lockheed Martin Space Systems, 2100 Space Park Drive, Houston, Texas 77058.

<sup>6</sup> Toxicology Lead, SK411, NASA Johnson Space Center, 2101 NASA Parkway, Houston, Texas 77058.

<sup>7</sup> Materials and Processes Materials Engineer, ES411, NASA Johnson Space Center, 2101 NASA Parkway, Houston, Texas 77058.

<sup>8</sup> GFE Materials Control Lead, ES411, NASA Johnson Space Center, 2101 NASA Parkway, Houston, Texas 77058.

## Nomenclature

|               |   |                                                      |
|---------------|---|------------------------------------------------------|
| <i>ECLSS</i>  | = | Environmental Control and Life Support System        |
| <i>GC-FID</i> | = | Gas Chromatography Flame Ionization Detection        |
| <i>ISS</i>    | = | International Space Station                          |
| <i>MAPTIS</i> | = | Materials and Processes Technical Information System |
| <i>MLW</i>    | = | Maximum Limit Weight                                 |
| <i>NASA</i>   | = | National Aeronautics and Space Administration        |
| <i>T</i>      | = | Toxic Hazard Index                                   |
| <i>SMAC</i>   | = | Spacecraft Maximum Allowable Concentration           |
| <i>WSTF</i>   | = | White Sands Test Facility                            |

## I. Introduction

Closed loop cabin environments, such as space vehicles or submarines, pose special safety and air quality challenges from offgassing of chemicals from nonmetallic materials. These offgassed chemicals can accumulate due to continuous air recirculation and the minimized opportunity to introduce “fresh” air. Within spacecraft the risk of an accumulation of compounds is managed by a multifaceted approach including an Environmental Control and Life Support System (ECLSS) for onboard cleanup, onboard gas sampling for accumulation monitoring, and material screening prior to flight coupled with quantity use limitations. As part of the material screening leg of this approach, all materials that are slated for use in the cabin’s closed loop environment are required to be tested in order to identify the types and quantities of offgassed compounds as well as assess the crew safety impact of these potentially toxic chemical compounds. This testing is performed per NASA-STD-6001B,<sup>1</sup> *Flammability, Offgassing, and Compatibility Requirements and Test Procedures*, Test 7, “Determination of Offgassed Products,” which NASA White Sands Test Facility (WSTF) has performed for several decades.

NASA-STD-6001B recommends all nonmetals be retested every 10 years, or as required by the responsible program/project, with the intent of capturing any changes to manufacturer, manufacturing procedures, solvent, and/or formulation. However, periodic retesting is not a firm requirement, and with the added restriction of continuously strained program budgets, retesting is rarely performed. This retest approach may be acceptable for other test types documented in NASA-STD-6001B, but application to the offgassing should be further examined. The validity of older offgas test data is more susceptible to having changed over the years for two major reasons. First, as was previously shown by Harper, Handley and James,<sup>2</sup> material offgassing data is dependent upon not only the bulk material formulation, but also highly dependent on processing method, processing method parameter changes, blowing agents, minor constituents, solvents, plasticizers, stabilizers, and more. Minor constituents and processing aids frequently change over time yet are not considered formulation changes, and would therefore not be captured via formulation change reports. The second major factor affecting offgassing data validity is developments in analysis technology over the years that allow dramatically more rigorous identification and quantification of compounds compared to historical data. Retesting every 10 years also provides better data as analysis techniques continue to improve. Due to these factors, NASA-STD-6001B Test 7 results are among the most susceptible to changes over the years.

NASA uses the Materials and Processes Technical Information System (MAPTIS) database to compile and archive the Agency’s standard test data. The MAPTIS database is a public tool used to rank materials into different classifications to help narrow down material selection for use in various space applications, as well as for certifying materials used in space applications. Currently there is no requirement to invalidate or remove any test data; therefore, 30 to 50 year old offgas data can be found and applied to current and/or future designs. While MAPTIS rating tables are excellent tools for use in down-selection of materials, final material selection should include a detailed review of the full test report data to assess current applicability. Special testing parameters may limit the application of MAPTIS test results, and age of data should be considered before determining if a material is acceptable for use in current design. Examples of special testing parameters that may limit application of data results include pretest conditioning that was performed, custom conditioning temperatures and durations, and/or simulated use-configuration testing methods. In addition, it is noteworthy that the need to review and update historical data to ensure adequate application to current designs may not just be of value for NASA-STD-6001B data, but may also have analogous validity in other areas such as in the water monitoring community.

## II. NASA-STD-6001 Offgas Test Method

As stated in NASA-STD-6001B, the purpose of Test 7 is “to determine the identity and quantity of volatile offgassed products from materials and assembled articles” that will be located within habitable environments. This is done by testing materials and articles under standardized conditions. Standard thermal conditioning for an offgas test is 72 ( $\pm 1$ ) hr at 50 ( $\pm 4$ ) °C (122 ( $\pm 7$ ) °F).\* The test materials or articles are placed into sealed containers, as shown in Figure 1, and then thermally conditioned. Upon completion of thermal conditioning, the atmosphere inside the test container is analyzed to determine the offgassed compounds. For materials, the standard mass-to-specimen-container-volume ratio is 5.0 ( $\pm 0.25$ ) g/L. There is no standard mass-to-specimen-container-volume ratio for articles; however, the smallest available container that will fit the article is used.

Individual compound toxicity ratings are determined by using the 7-day Spacecraft Maximum Allowable Concentration (SMAC) for each offgassed compound. The total Toxic Hazard Index (T) value is then calculated as a summation of the individual compound toxicity ratings for the offgassed components, as shown in Equation (1). A full explanation of T value calculations is found in NASA-STD-6001B.

$$T = \sum \left( \text{CompoundOffgasQuantity}(\mu\text{g}) \times \frac{1\text{mg}}{1000\mu\text{g}} \times \frac{1}{\text{VehicleVolume}(\text{m}^3)} \times \frac{1}{\text{SMAC}(\text{mg}/\text{m}^3)} \right) \quad (1)$$

The total T value shall be less than 0.5 for the offgas test of materials or assembled articles. A T value of less than 0.5 is required for the total of the amount of material or number of assembled articles to be flown. For example if one article is offgas tested and the resulting T value is 0.09, then only 5 total articles may be flown. These five articles have a combined T value of 0.45 which is less than 0.5.



**Figure 1. Sample loading.** Materials or assembled articles are loaded into sealed, certified-clean containers and thermal conditioning for 72 ( $\pm 1$ ) hr at 50 ( $\pm 4$ ) °C (122 ( $\pm 7$ ) °F) prior to performing analysis of the test atmosphere.

\* Temperature tolerance changed from 50 ( $\pm 3$ ) °C (122 ( $\pm 5$ ) °F) to 50 ( $\pm 4$ ) °C (122 ( $\pm 7$ ) °F) in 2014 per NASA-STD-6001 M&P review board concurrence and will be incorporated in future NASA-STD-6001 revision.

### III. Offgas Data Variability due to Analysis Technique Improvements

Analysis methods for offgas testing at WSTF have improved tremendously over the decades, which is a definite factor in offgas test data variability. In the 1970s the instrument used for identification of compounds was a magnetic sector. The analysis on the magnetic sector required the operator to manually initiate scanning at the time a peak was visible on the gas chromatography flame ionization detector (GC-FID), which could lead to reproducibility errors. At that time, compound concentrations were obtained by manually adding up graphical squares under individual GC-FID chromatography peaks to approximate peak area, as opposed to the current method of automatic integrations using computer software. With respect to offgas compound separation, packed columns that were used had very little resolution when compared to capillary columns in use today. Because of reduced separation with packed columns, multiple compounds co-eluted under a single large peak, making it very difficult or even impossible for the interpreter to individually separate for quantification. Commonly in these cases, the entire peak would be quantified as the most abundant compound within the co-eluted peak because the analysis identification method did not have the sensitivity to detect compounds of lower abundance. As a result, lists of offgassed compounds reported were short, as shown in Figures 2 and 3.

REMARKS: Gas Phase analysis (micrograms per gram): Acetone, 550; iso-Propyl alcohol, 30; Methyl ethyl ketone, 330; n-Butyl alcohol, 310; Toluene, 60; Mesityl oxide, 1,200; Butyl acetate, 1,200; Xylene, 2,600; Cyclohexanone, 2,500; Trimethyl benzene, 100; One unidentified peak, 170; and 7 other peaks, each less than 80.  
Total Condensable Organics - Less than 29.5 micrograms per gram.\*  
\* Minimum detectable limit.

**Figure 2. 1973 offgas report example.** Offgas data at WSTF prior to the use of capillary columns around 1990 commonly had short lists of offgassed compounds. Toxic ratings and maximum limit weight (MLW) were not reported.

|    |                                       | Organic Material (µg/g) |     |
|----|---------------------------------------|-------------------------|-----|
| 1. | Acetone                               | 80                      | 10. |
| 2. | Isopropyl alcohol                     | 10                      | 11. |
| 3. | Methyl ethyl ketone                   | 30                      | 12. |
| 4. | n-Butyl alcohol                       | 50                      | 13. |
| 5. | Toluene                               | 10                      | 14. |
| 6. | Mesityl oxide                         | 30                      | 15. |
| 7. | Butyl acetate                         | 40                      | 16. |
| 8. | Xylene                                | 50                      | 17. |
| 9. | C <sub>10</sub> aromatic hydrocarbons | 6                       | 18. |

**Figure 3. 1978 offgas data report sheet example.** Offgas data at WSTF prior to the use of capillary columns around 1990 commonly had short lists of offgassed compounds.

Historical data in MAPTIS from this period also include offgas tests where identification of specific organic material was not required (Figure 4) and imply that the offgas T value requirements were still in development prior to the 1981 release of NHB 8060.1B.<sup>3</sup> Examining the data packs in the WSTF archives, the offgas test data for report number W75-5356 only included carbon monoxide results and a total quantity for all peaks on the GCFID (total organics). Individual identification and quantification of the organic material was not requested. Total organic quantity of 114 µg/g reported for W75-5356 exceeded the material acceptability criteria in NHB 8060.1A of 100 µg/g, and therefore did not pass the screening test. However, since T value calculations in use today do not include total organics, the total organics quantity is not captured by MAPTIS. MAPTIS lists this material test as allowing nearly 50 lb for Orion. This illustrates the incompleteness of historical data by current standards and invalidates it with respect to applicability to current and future designs. When only carbon monoxide is used for calculating a T value, the T value is artificially low and does not accurately represent the material offgas results. The test results for W75-5356 (Figure 4) are listed in MAPTIS using only the detected carbon monoxide quantity to calculate the T value. A disclaimer is not listed to flag that data as an incomplete offgas test; therefore, the MLW and T values listed may be misleading to a design engineer.

| ANALYTICAL RESULTS (Gas Phase) |              |                         |                                  |
|--------------------------------|--------------|-------------------------|----------------------------------|
| CO                             | 21           | ug/g Co                 | 55 ppm by volume Methods: GC-4   |
| TO                             | 114          | ug/g (as pentane)       | Vol 580 ppm by Volume of methane |
|                                |              | Weight Loss             | 0.0010 g/g                       |
|                                |              | Organic Material (ug/g) | Analytical Methods               |
| 1.                             | Not Reported | 6.                      | a.                               |
| 2.                             |              | 7.                      | b.                               |
| 3.                             |              | 8.                      | c.                               |
| 4.                             |              | 9.                      |                                  |
| 5.                             |              | 10.                     |                                  |

**Figure 4. WSTF #75-5356 offgas data sheet.** Individual identification and quantification of organic material on this 1975 offgas test was not required; therefore, only carbon monoxide and total organics were reported. MAPTIS currently applies the data using the only reported peak (carbon monoxide) to generate a toxic rating. This gives an artificially low toxic rating and a high MLW.

Around 1980, offgas instrumentation computer software applications used at WSTF helped automate the offgas analysis. However, packed columns were still in use; therefore, the same problems with lower resolution and sensitivity remained. WSTF transitioned to capillary columns for offgas testing around 1990, which dramatically increased peak resolution and separation of compounds in the test atmosphere. Soon to follow was the increased capability of data manipulation techniques that allowed for subtractions of ion chromatograms to accurately identify multiple compounds within a co-eluted peak, as well as sift out the smaller compounds buried under larger peaks. Some of these very low concentration compounds that are now able to be detected also have low SMACs; therefore, they can have a significant effect on the T value, which in return restricts the material quantity allowed for use.

In 2004, WSTF was able to further enhance analysis methodology to identify and quantify formaldehyde at SMAC levels. In a recent International Space Station (ISS) payload offgas data analysis, only data after 2004 were used, as it was considered to represent a worst-case and accurate picture of offgassing risks with the inclusion of low level formaldehyde detection. Detection of formaldehyde is important because it is very toxic, is commonly seen in spacecraft environments, and trace gas contaminant removal systems are not very effective at removing it. Historically, formaldehyde has been detected inside the ISS at levels nearer to the SMAC than any other species; however, formaldehyde is currently seen at concentrations roughly 30% of the SMAC.<sup>4</sup>

Advancements in analysis techniques have improved the granularity of offgas test data. Archiving offgas data prior to 1990, when capillary columns enhanced compound resolution and identification, would help direct engineers to valid data by current standards and prevent historical incomplete or obsolete data from being used for material selection for use in new spacecraft. As advancements continue with analytical instrumentation and software, offgassed compound detection capabilities will continue to improve.

#### IV. Case Studies in Offgassing Variability: Super Korocon® and Aeroglaze® A276 White Topcoat

Recent testing at WSTF has exemplified concerns with using older offgas test data and presents two excellent case studies. Various Super Korocon<sup>®†</sup> products and topcoats have been offgas tested through the years and are often used to protect interior structures of the spacecraft from corrosion. Super Korocon 515 x 700 Green with 910 x 704 Catalyst was offgas tested multiple times under various cure and aging conditions. The results are listed in MAPTIS under material code 05015. An ambient temperature and pressure aging of approximately 6 months was performed both in 1975 and in 1997, and the T values varied greatly (see Table 1). The T value for the test in 1975 is 7078.84, allowing up to 0.007 lb to be used for the Orion spacecraft volume. The T value for the test in 1997 is 164.08, allowing up to 0.305 lb to be used for the Orion spacecraft volume. The drastic difference in offgassed data may be due to slight changes to manufacturer procedures, as discussed in a previous ICES paper in 2011.<sup>2</sup>

The variable offgassed data is also affected by test method instrumentation improvements. For example, the 1975 offgas test report in Table 2 lists a large quantity of unidentified compounds which significantly increases the T value. In addition, the large quantities for each compound reported in 1975 is most likely due to the limited separation techniques at that time. Therefore, a large peak was quantified as one single compound instead of the 2 to approximately 15 different compounds that could all be within the peak but are masked by the most abundant compound(s). Table 3 lists the compounds detected on the same primer in 1997, and the list of compounds is significantly longer with only a small quantity of unidentified components.

† Super Korocon® is a registered trademark of Desoto, Inc., Des Plaines, Illinois.

**Table 1. Offgas test data for Super Koropon® Primer.**

| Year Tested | Report Number | Material Name                                      | Orion T value (T100) | Orion Max Limit Weight (lb) |
|-------------|---------------|----------------------------------------------------|----------------------|-----------------------------|
| 1975        | W5213-A       | Super Koropon® 515x700 Green with 910x704 Catalyst | 7078.84              | 0.007                       |
| 1997        | W30536-A      | Super Koropon® 515x700 Green with 910x704 Catalyst | 164.08               | 0.305                       |

**Table 2. Offgas test results for 1975 W5213-A Super Koropon® Primer.**

| Gas Code | Gas Name                   | CAS Number | Offgassed Amount (µg/gm) | 7-day SMAC (mg/m <sup>3</sup> ) |
|----------|----------------------------|------------|--------------------------|---------------------------------|
| 035200   | TOLUENE                    | 108-88-3   | 27                       | 15                              |
| 039100   | XYLENE                     | 1330-20-7  | 760                      | 73                              |
| 098800   | C8 UNSATURATED HYDROCARBON |            | 140                      | 115                             |
| 110500   | ACETONE                    | 67-64-1    | 100                      | 52                              |
| 112000   | CYCLOHEXANONE              | 108-94-1   | 400                      | 60.01                           |
| 114000   | 3-PENTEN-2-ONE, 4-METHYL-  | 141-79-7   | 160                      | 25                              |
| 115000   | 2-BUTANONE                 | 78-93-3    | 45                       | 30                              |
| 119550   | C9 UNSATURATED KETONES     |            | 100                      | 0.1                             |
| 161000   | CARBON MONOXIDE            | 630-08-0   | 61                       | 63                              |
| 999999   | UNIDENTIFIED COMPONENT     |            | 131                      | 0.1                             |

**Table 3. Offgas test results for 1997 W30536-A Super Koropon® Primer.**

| Gas Code | Gas Name                                              | CAS Number | Offgassed Amount (µg/gm) | 7-day SMAC (mg/m <sup>3</sup> ) |
|----------|-------------------------------------------------------|------------|--------------------------|---------------------------------|
| 011600   | 1-BUTANOL                                             | 71-36-3    | 470                      | 80                              |
| 012000   | 2-BUTANOL                                             | 78-92-2    | 0.16                     | 120.73                          |
| 012400   | TERT-BUTYL ALCOHOL                                    | 75-65-0    | 0.16                     | 150                             |
| 013600   | ETHANOL                                               | 64-17-5    | 0.12                     | 2000                            |
| 014800   | METHYL ALCOHOL                                        | 67-56-1    | 0.12                     | 90                              |
| 016000   | 1-PROPANOL                                            | 71-23-8    | 0.07                     | 97.7                            |
| 016400   | ISOPROPYL ALCOHOL                                     | 67-63-0    | 32                       | 150                             |
| 020300   | ACETALDEHYDE                                          | 75-07-0    | 0.29                     | 4                               |
| 021500   | BUTANAL                                               | 123-72-8   | 1.1                      | 14.72                           |
| 031600   | ETHYLBENZENE                                          | 100-41-4   | 34                       | 130                             |
| 035200   | TOLUENE                                               | 108-88-3   | 44                       | 15                              |
| 038210   | C9-C10 AROMATIC HYDROCARBONS                          |            | 4.8                      | 15                              |
| 039100   | XYLENE                                                | 1330-20-7  | 180                      | 73                              |
| 041200   | ACETIC ACID, BUTYL ESTER                              | 123-86-4   | 180                      | 189.11                          |
| 041600   | FORMIC ACID, BUTYL ESTER                              | 592-84-7   | 3.8                      | 83.5                            |
| 043600   | ISOBUTYL ACETATE                                      | 110-19-0   | 0.06                     | 190                             |
| 043700   | ACETIC ACID,1-METHYL ETHYL ESTER                      | 108-21-4   | 9.3                      | 208.65                          |
| 045630   | 1-METHOXY-2-PROPYL ACETATE                            | 108-65-6   | 0.14                     | 54                              |
| 069000   | 1,2-DICHLOROETHENES                                   | 540-59-0   | 0.03                     | 0.4                             |
| 097601   | BUTENE                                                | 9003-28-5  | 0.06                     | 57                              |
| 098850   | C8-C10 SATURATED ALIPHATIC (NON-ALIPHATE) HYDROCARBON |            | 10                       | 5                               |
| 099680   | C11-C12 SAT/UNSAT ALIPHATIC HYDROCARBONS              |            | 0.68                     | 47                              |
| 110500   | ACETONE                                               | 67-64-1    | 0.43                     | 52                              |
| 112000   | CYCLOHEXANONE                                         | 108-94-1   | 13                       | 60.01                           |
| 115000   | 2-BUTANONE                                            | 78-93-3    | 71                       | 30                              |
| 116000   | METHYL ISOBUTYL KETONE                                | 108-10-1   | 0.54                     | 140                             |
| 117000   | 2-HEPTANONE                                           | 110-43-0   | 49                       | 23.35                           |
| 117350   | 4-HEPTEN-3-ONE, 5-METHYL-                             | 1447-26-3  | 20                       | 0.8                             |
| 118750   | C8 KETONES                                            |            | 7.2                      | 13.12                           |
| 156610   | NITROMETHANE                                          | 75-52-5    | 0.66                     | 18                              |
| 161000   | CARBON MONOXIDE                                       | 630-08-0   | 1.5                      | 63                              |
| 999999   | UNIDENTIFIED COMPONENT                                |            | 0.86                     | 0.1                             |

An Aeroglaze<sup>®</sup>‡ A276 white topcoat was offgas tested in 1981 with a resulting T value of 9.21, allowing 5.43 lb to be used on the Orion spacecraft. This topcoat was retested in 2016 and results varied significantly, allowing only 1/5 of the previously allowed material from the 1981 test (Tables 4 through 6).

**Table 4. Offgas test data for Aeroglaze<sup>®</sup> A276 White.**

| Year Tested | Report Number | Material Name                     | Orion T value (T100) | Orion Max Limit Weight (lb) |
|-------------|---------------|-----------------------------------|----------------------|-----------------------------|
| 1981        | W14488-D      | Aeroglaze <sup>®</sup> A276 White | 9.21                 | 5.432                       |
| 2016        | W46814-A      | Aeroglaze <sup>®</sup> A276 White | 47.35                | 1.056                       |

**Table 5. Offgas test results for 1981 W14488-D Aeroglaze<sup>®</sup> A276 White.**

| Gas Code | Gas Name                                | CAS Number | Offgassed Amount (µg/gm) | 7-day SMAC (mg/m <sup>3</sup> ) |
|----------|-----------------------------------------|------------|--------------------------|---------------------------------|
| 038200   | C9 AROMATIC HYDROCARBONS                |            | 4                        | 15                              |
| 039100   | XYLENE                                  | 1330-20-7  | 87                       | 73                              |
| 090750   | 1-BUTENE                                | 106-98-9   | 0.05                     | 456.39                          |
| 099150   | C9-C12 SAT/UNSAT ALIPHATIC HYDROCARBONS |            | 3.1                      | 5                               |
| 110500   | ACETONE                                 | 67-64-1    | 0.4                      | 52                              |
| 115000   | 2-BUTANONE                              | 78-93-3    | 0.9                      | 30                              |
| 116000   | METHYL ISOBUTYL KETONE                  | 108-10-1   | 59                       | 140                             |
| 161000   | CARBON MONOXIDE                         | 630-08-0   | 0.4                      | 63                              |
| 999999   | UNIDENTIFIED COMPONENT                  |            | 0.05                     | 0.1                             |

‡ Aeroglaze<sup>®</sup> is a registered trademark of Lord Corporation, Erie, Pennsylvania.



**Table 6. Offgas test results for 2016 W46814-A Aeroglaze® A276 White.**

| Gas Code | Gas Name                                    | CAS Number | Offgassed Amount (µg/gm) | 7-day SMAC (mg/m <sup>3</sup> ) |
|----------|---------------------------------------------|------------|--------------------------|---------------------------------|
| 014950   | PROPAN-2-OL, 1-METHOXY-                     | 107-98-2   | 0.08                     | 73.5                            |
| 045630   | 1-METHOXY-2-PROPYL ACETATE                  | 108-65-6   | 73                       | 54                              |
| 117000   | 2-HEPTANONE                                 | 110-43-0   | 0.009                    | 23.35                           |
| 114500   | 2-HEXANONE                                  | 591-78-6   | 0.007                    | 40.89                           |
| 117500   | 2-PENTANONE                                 | 107-87-9   | 0.09                     | 70.2                            |
| 053600   | FURAN, 2-PENTYL-                            | 3777-69-3  | 0.03                     | 0.1                             |
| 020300   | ACETALDEHYDE                                | 75-07-0    | 0.16                     | 4                               |
| 110500   | ACETONE                                     | 67-64-1    | 0.1                      | 52                              |
| 030400   | BENZENE                                     | 71-43-2    | 0.005                    | 1.5                             |
| 097600   | BUTENES                                     | 25167-67-3 | 0.35                     | 5                               |
| 021500   | BUTANAL                                     | 123-72-8   | 0.008                    | 14.72                           |
| 175500   | C10-C11 ALIPHATIC AND AROMATIC HYDROCARBONS |            | 1                        | 0.1                             |
| 018900   | C6 ALCOHOL                                  |            | 0.06                     | 20.87                           |
| 047601   | C6 ESTER                                    |            | 0.05                     | 0.1                             |
| 057001   | C6 ETHER                                    |            | 0.02                     | 8.3                             |
| 048000   | C7 ESTERS                                   |            | 0.04                     | 0.1                             |
| 057501   | C7 ETHER                                    |            | 0.02                     | 0.25                            |
| 118711   | C7 KETONE                                   |            | 0.01                     | 23.5                            |
| 048601   | C8 SATURATED ESTERS                         |            | 37                       | 116                             |
| 119051   | C8 UNSATURATED KETONES                      |            | 0.03                     | 0.77                            |
| 038210   | C9-C10 AROMATIC HYDROCARBONS                |            | 0.47                     | 15                              |
| 099170   | C9-C10 SATURATED ALIPHATIC HYDROCARBONS     |            | 0.05                     | 5                               |
| 161000   | CARBON MONOXIDE                             | 630-08-0   | 0.58                     | 63                              |
| 112000   | CYCLOHEXANONE                               | 108-94-1   | 0.006                    | 60.01                           |
| 092400   | DECANE                                      | 124-18-5   | 0.03                     | 232.38                          |
| 093000   | N-DODECANE                                  | 112-40-3   | 0.04                     | 278.26                          |
| 042400   | ETHYL ACETATE                               | 141-78-6   | 0.03                     | 179.34                          |
| 013600   | ETHANOL                                     | 64-17-5    | 0.02                     | 2000                            |
| 031600   | ETHYLBENZENE                                | 100-41-4   | 5.5                      | 130                             |
| 027010   | HEPTANAL                                    | 111-71-7   | 0.005                    | 28                              |
| 093750   | HEPTANE                                     | 142-82-5   | 0.04                     | 204.47                          |
| 164500   | HEXAMETHYLCYCLOTRISILOXANE                  | 541-05-9   | 0.04                     | 90                              |
| 094200   | HEXANE                                      | 110-54-3   | 0.01                     | 176                             |
| 016400   | ISOPROPYL ALCOHOL                           | 67-63-0    | 0.08                     | 150                             |
| 044000   | ACETIC ACID, METHYL ESTER                   | 79-20-9    | 0.5                      | 120.73                          |

**Table 6. Offgas test results for 2016 W46814-A Aeroglaze® A276 White (continued).**

| Gas Code | Gas Name                        | CAS Number | Offgassed Amount (µg/gm) | 7-day SMAC (mg/m <sup>3</sup> ) |
|----------|---------------------------------|------------|--------------------------|---------------------------------|
| 014800   | METHYL ALCOHOL                  | 67-56-1    | 0.15                     | 90                              |
| 115000   | 2-BUTANONE                      | 78-93-3    | 0.46                     | 30                              |
| 044800   | METHYL FORMATE                  | 107-31-3   | 0.05                     | 12.3                            |
| 116000   | METHYL ISOBUTYL KETONE          | 108-10-1   | 3                        | 140                             |
| 117700   | METHYL VINYL KETONE             | 78-94-4    | 0.005                    | 5.69                            |
| 090600   | BUTANE                          | 106-97-8   | 0.07                     | 236.57                          |
| 041200   | ACETIC ACID, BUTYL ESTER        | 123-86-4   | 0.04                     | 189.11                          |
| 011600   | 1-BUTANOL                       | 71-36-3    | 0.03                     | 80                              |
| 023400   | HEXANAL                         | 66-25-1    | 0.1                      | 20                              |
| 156610   | NITROMETHANE                    | 75-52-5    | 0.07                     | 18                              |
| 095550   | NONANE                          | 111-84-2   | 0.009                    | 314.03                          |
| 165100   | CYCLOTETRASILOXANE, OCTAMETHYL- | 556-67-2   | 0.05                     | 280                             |
| 095850   | OCTANE                          | 111-65-9   | 0.04                     | 348.92                          |
| 024000   | PENTANAL                        | 110-62-3   | 0.01                     | 21.1                            |
| 096300   | PENTANE                         | 109-66-0   | 0.05                     | 588.28                          |
| 023600   | PROPANAL                        | 123-38-6   | 0.007                    | 14.3                            |
| 035200   | TOLUENE                         | 108-88-3   | 0.43                     | 15                              |
| 168500   | SILANOL, TRIMETHYL              | 1066-40-6  | 0.11                     | 4                               |
| 999999   | UNIDENTIFIED COMPONENT          |            | 0.21                     | 0.1                             |
| 039100   | XYLENE                          | 1330-20-7  | 17                       | 73                              |

Despite all the variability seen across the years with respect to Super Koropon offgas testing, we begin to see comparability to recently generated data in Table 7, starting after 1990 when capillary columns were implemented. Though analysis techniques continue to improve, this 1990-to-recent data comparison serves as an excellent example demonstrating how the implementation of capillary columns in the 1990s is a key milestone in marking the current era in offgassing techniques and a valuable marker in identifying what data can be considered applicable by current standards.

**Table 7. Offgas test data for Super Koropon® Primer.**

| Year Tested | Report Number | Material Name                                                                                            | Orion T value (T100) | Orion Max Limit Weight (lbs) |
|-------------|---------------|----------------------------------------------------------------------------------------------------------|----------------------|------------------------------|
| 1996        | W30261-A      | Super Koropon® 515x700 Green with 910x704 Catalyst                                                       | 309.31               | 0.162                        |
| 2015        | W46678-B      | Super Koropon® 515x700 Green with 910x704 Catalyst                                                       | 346.24               | 0.144                        |
| 1997        | W31376-B      | Super Koropon® 515x700 Green with 910x704 Catalyst                                                       | 56.95                | 0.878                        |
| 2016        | W46761-A      | Super Koropon® 515x700 Green with 910x704 Catalyst<br>(Ambient Temperature and Pressure 12-month Aging)  | 54.91                | 0.911                        |
|             |               | Super Koropon® 515x700 Green with 910x704 Catalyst<br>(Ambient Temperature and Pressure ~16-month Aging) |                      |                              |

## V. NASA-STD-6001B Ten Year Retest Recommendation

NASA-STD-6001B recommends all nonmetals have testing performed if the data are 10 or more years old. NASA-STD-6001 Test 7 is one of the more critical tests for which this recommendation is of value. With offgas testing, even slight formulation changes can cause large changes to toxicity ratings. SMACs used for calculating toxicity ratings are continually evolving as more is learned about various compounds through toxicity testing. The UK Royal Navy

abides by a strict 3-year requirement for all toxicity data because of formulation and processing changes that are commonly marketed under the same product name and number. The Royal Navy removes all data from its material-use database once it reaches 3 years from the initial data review, to help ensure outdated data are not used. With the 10-year retest recommendation in NASA-STD-6001B, NASA is making steps toward a similar policy.

Data prior to 1990 has known inaccuracies stemming from two sources: application of screening level requirements, and limited compound separation from packed column testing capabilities. Initial test methods prior to the 1981 NHB 8060.1B required only material “screening” level resolution of carbon monoxide (CO) and total organics (TO) quantification; therefore, individual offgassed compounds were not always determined and reported. Inaccurate data are generated when attempting to translate historical TO/CO screening data to current T value rating methodology through the MAPTIS database. Total Organics data and its relevance to historical acceptance criteria of 100 µg/g is not entered in MAPTIS, and therefore its value is lost. The TO/CO screening test data are applied using only CO quantity to generate a T value for the material, making it inaccurate as well as not conservative from a toxicological perspective. The same applies when individual offgassed compounds were determined and reported using analog magnetic sector mass spectrometers prior to approximately 1980. The ability to identify the individual compounds was very poor; therefore, T values are inaccurate.

Later refinements to the test method, prior to capillary column use in 1990, still utilized techniques that limited separation and identification of compounds. Limited compound separation yielded large groupings of compounds under a single identification, which is inaccurate when compared to current test methods. Inaccuracies could lead to extra conservatism if the co-eluted peak is labeled as an unidentified component, or less conservatism if identified as a compound with a high SMAC value.

The case studies presented here highlight inconsistent patterns between historical and recent data. Older results may be more or less conservative from toxicological perspective than those obtained using the current analytical techniques. It should be noted that, despite the lower sensitivity of packed column data compared with capillary columns, the successful use of packed column data for Orbiter, Spacelab, ISS, and commercial cargo vehicles means that the lower sensitivity was still adequate to ensure an acceptable crew breathing environment in these vehicles. Nonetheless, data collected after 1990 when capillary columns were implemented, and/or after 2004 when formaldehyde detection was improved, are considered far superior to historical data and should be required for future programs.

MAPTIS flags data older than 10 years (Figure 5), so the next step is to evaluate flagged test data. For current programs where retesting is not within scope, a structured plan to evaluate margin on the T value should be implemented. Specific compounds that contributed to the T value, analytical methods used to identify those compounds, as well as ECLSS capabilities for the vehicles in question should all be reviewed to determine if retesting would be expected to have an impact, therefore justifying the expense of reanalysis.

**Data exceeds 10 years. All nonmetals should be retested every 10 years or as required by the responsible program/project (Ref.: NASA-STD-6001B, paragraph 5.b).**

**Figure 5. MAPTIS retest flag.** Data in MAPTIS that exceed 10 years are flagged with this note.

## **VII. Conclusion**

Though the 10-year retest recommendation may not always be appropriate for all test methods under NASA-STD-6001B, offgas testing (Test 7) is more sensitive to minor material constituent and process variations. The need to review and update historical data to ensure adequate application to current designs may not just be of value for NASA-STD-6001 data but may also have analogous validity in other areas such as in the water monitoring community. Offgas testing analysis techniques, specifically, have dramatically improved detection capabilities over the years, providing far superior analysis methods and reporting since the 1990s while adding reliable formaldehyde identification in 2004. Understanding the limitations in offgas analysis data prior to 1990 puts into question the validity and current applicability of that data, despite the successful use of those data for Orbiter, Spacelab, ISS, and commercial cargo vehicles. Furthermore, the applicability of data collected prior to 1990 when improved compound resolution was obtained via capillary columns, or 2004 when formaldehyde monitoring was optimized, should be scrutinized. As new programs develop, it is increasingly important to continue to ensure air quality is maintained by reviewing the quality and applicability of historical materials screening data and assigning expiration dates to inadequate or obsolete materials offgas data where appropriate.

## **Acknowledgments**

The authors acknowledge Mark Drexler and George Aldrich for providing the history of offgas instrumentation used at the NASA White Sands Test Facility over the last 40 years.

## References

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