# SPACE SHUTTLE SOLID ROCKET MOTOR EXPOSURE MONITORING

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## ABSTRACT

During the processing of the Space Shuttle Solid Rocket Booster (SRB) segments at the Kennedy Space Center an odor was detected around the solid propellant. An Industrial Hygiene survey was conducted to determine the chemical identity of the SRB offgassing constituents. Air samples were collected inside a forward SRB segment and analyzed to determine chemical composition. Specific chemical analysis for suspected offgassing constituents of the propellant indicated ammonia to be present. A gas chromatograph mass spectroscopy (GC/MS) analysis of the air samples detected numerous high molecular weight hydrocarbons.

## INTRODUCTION

Solid Rocket Boosters (SRB) are processed at the Kennedy Space Center (KSC) as part of the Space Transportation System. Each SRB is made up of four separate segments. The segments are shipped to the KSC by rail car and are received at the Rotation Processing Segment Facility. KSC personnel remove the segments from the shipping containers, remove shipping rings, perform solid propellant grain inspections and prepare the segments for storage in the nearby Surge Buildings. The segments remain in the Surge Buildings for extended periods of time where they are inspected on a weekly basis. After storage, the segments are brought out of the Surge Building and moved to the Vehicle Assembly Building where the segments are stacked and mated to the Space Shuttle Launch Vehicle.

Personnel performing certain SRB operations at KSC have detected odors when working around the solid propellant. Personnel have indicated that the odors are most prevalent when the segment shipping containers are initially removed and during grain inspections. The odors are reportedly stronger in the forward and aft segments where no cross ventilation is available. The chemical identity or source of these odors is unknown. In an effort to determine the identity of the offgassing constituents of the solid

propellant, air sampling was performed inside of a forward segment during storage. The air samples were analyzed for specific chemical compounds as well as being analyzed for the presence of unknowns.

The Material Safety Data Sheet lists the ingredients of the SRB propellant as ammonium perchlorate, aluminum powder, HB polymer, bisphenol A/epichlorohydrin, and iron oxide. The HB polymer contains a polymer identified as polybutadiene acrylic acid acrylonitrile polymer (PBAN) which may contain trace amounts of butadiene, acrylic acid, acrylonitrile, and hydroquinone.

## METHODOLOGY

A MULTI-AIR WM 02-8914 multistation air flow vacuum sampling pump was utilized to pull air through the various sample collection devices. The sampling collection devices were connected to the sampling pump via Tygon tubing. The sampling media were selected based on the possible offgassing constituents of the SRB propellant. The appropriate National Institute for Occupational Safety and Health (NIOSH) sampling methods were utilized for the collection of samples. Table I lists the sampling and analytical methods utilized during the survey.

The sampling collection devices were placed inside the protective Herculite cover at the open end of the forward segment. Continuous sampling was performed beginning May 4, 1992 until May 8, 1992. The same sampling methods were repeated on May 11, 1992 until May 15, 1992. Continuous sampling was performed to obtain large sample volumes. Sampling volumes exceeded the NIOSH recommended sample volumes to insure a sufficient quantity of material for analysis.

Three separate sorbent sampling tubes (one charcoal tube and two Tenax tubes) were also used during the sampling period to test for the presence of unknowns. The sorbent sampling tubes were also connected to the multistage sample pump. An air flow rate through each tube was maintained at 0.4 liters per minute during the sampling period. The sample volume for these tubes ranged from 2521 liters to 2838 liters. Analysis of the sampling tubes was performed using gas chromatography, mass spectroscopy. The major peaks of the gas chromatogram were analyzed by the mass spectrometer to determine the chemical identity of the separated compounds. The GC/MS

analysis results were reported by listing the compounds with the best internal mass spectrometer library match.

A Gastec Passive Dosimeter Tube for ammonia, No. 3D, was also placed inside the Herculite cover and was used to indicate the presence of ammonia. The Passive Dosimeter Tube is cross-sensitive to amines and hydrazine but is not sensitive to aromatic amines. The dosimeter tube is designed to passively measure ambient levels of ammonia and give a visible indication by colorimetric change on the tube. The manufacturer's instructions recommend ten-hour sampling periods to detect a range of 2.5 parts per million (ppm) to 50 ppm. The dosimeter tubes were evaluated for colorimetric indication once each 24-hour period during the survey.

## RESULTS

The sampling results for the compound specific analysis are listed in Table II. The GC/MS analysis of the samples for unknowns are listed in Table III.

## CONCLUSIONS

A number of chemical compounds have been identified to be present in the SRB segment bore. These compounds included ammonia and the high molecular weight hydrocarbons identified by the Gas Chromatography/Mass Spectrophotometry analysis (see table II). Other chemical compounds suspected of being present, based on the chemical composition of the SRB propellant, were not detected or were found to be present at trace amounts. These included, acrylonitrile, bisphenol A, 1,3 butadiene, epichlorohydrin, and hydrogen chloride. The chemical composition of the odor associated with the SRB Propellant is believed to be a mixture of ammonia and the high molecular weight hydrocarbons identified in Table II. The concentration of ammonia detected ranged from 1.8 ppm to 8.2 ppm. The odor threshold of ammonia is listed as 5.2 ppm. It should be noted that odor associated with the SRB propellant does not smell like ammonia. The concentrations of the identified hydrocarbons were unable to be determined due to the analysis method utilized. It is recommended that personnel exposure monitoring be performed during ground processing operations to quantify employee exposure levels to the identified chemical compounds.

**Table I. Sampling and Analytical Methodology**

| Chemical | NIOSH | Collection | Analysis |
|---|---|---|---|
| acrylonitrile | 1604 | Charcoal tube | GC/MS * |
| ammonia | P&CAM S347 | $H_2SO_4$ treated Silica gel | NH3 specific electrode & Ion Chromatography |
| 1,3 butadiene | 1024 | charcoal tube | GC/MS |
| bisphenol A | P&CAM 333 | glass fiber filter | GC/MS |
| epichloro-hydrin | 1010 | charcoal tube | GC/MS |
| hydrogen chloride | P&CAM 310 | silica gel | Ion Chromatography |
| inorganic acid | 7903 | silica gel | Ion Chromatography |

* Gas Chromatography / Mass Spectroscopy

**Table II. Compound Specific Analysis Results**

| Chemical | Sample Analysis | Analysis Method | Sample Results |
|---|---|---|---|
| acrylonitrile | 963 liters | GC/MS * | None detected |
| acrylonitrile | 989 liters | GC/MS | None detected |
| ammonia | 859 liters | Ammonia specific electrode | 1.78 parts per million (ppm) |
| ammonia | 1373 liters | Ammonia specific electrode | 8.24 ppm |
| ammonia | 96 hours passive diffusion | Colorimetric Indicator | 4.7 ppm |
| ammonia | 105 hours passive diffusion | Colorimetric Indicator | 4.8 ppm |
| bisphenol A | 1307 liters | GC/MS | None detected |
| bisphenol A | 1855 liters | GC/MS | None detected |
| 1,3 butadiene | 1698 liters | GC/MS | None detected |
| 1,3 butadiene | 2511 liters | GC/MS | None detected |
| epichlorohydrin | 999 liters | GC/MS | None detected |
| epichlorohydrin | 1392 liters | GC/MS | None detected |
| hydrochloric acid | 1799 liters | IC ** | 0.002 ppm |
| hydrochloric acid | 1210 liters | IC | 0.003 ppm |
| sulfuric acid | 3067 liters | IC | 0.001 ppm |
| sulfuric acid | 3169 liter | IC | 0.001 ppm |
| nitric acid | 3067 liters | IC | 0.002 ppm |
| nitric acid | 3169 liters | IC | 0.001 ppm |
| hydrochloric acid | 3067 liters | IC | 0.002 ppm |
| hydrochloric acid | 3169 liters | IC | 0.001 ppm |

* Gas Chromatography Mass Spectroscopy ** Ion Chromatography

**Table III. Gas Chromatography/Mass Spectroscopy Analysis Results**

| Sample # | Sample Media | Desorption Agent |
|---|---|---|
| 92-05-085 | Charcoal tube | Carbon Disulfide |
| **Retention Time** | **MS Library Match** | |
| 401 seconds | 4-ethnyl cyclohexene | |
| 653 seconds | 2,6,7-trimethyl decane | |
| 732 seconds | 2,5,6-trimethyl decane | |
| **Sample #** | **Sample Media** | **Desorption Agent** |
| 92-05-085-02 | Tenax | methylene chloride |
| **Retention Time** | **MS Library Match** | |
| | No peaks detected | |
| **Sample #** | **Sample Media** | **Desorption Agent** |
| 92-05-085-03 | Tenax | methylene chloride |
| **Retention Time** | **MS Library Match** | |
| 642 seconds | trans-4-chlorocyclohexanol | |
| **Sample #** | **Sample Media** | **Desorption Agent** |
| 92-05-086-01 | Charcoal | carbon disulfide |
| **Retention Time** | **MS Library Match** | |
| 393 seconds | 4-ethenyl-cyclohexene | |
| | (E,Z) 1,5-cyclooctadiene | |
| 731 seconds | 2,5,6-trimethyldecane | |
| **Sample #** | **Sample Media** | **Desorption Agent** |
| 92-05-087-01 | Charcoal | carbon disulfide |
| **Retention Time** | **MS Library Match** | |
| 418 seconds | 4-ethenyl-cyclohexene | |

| Sample # | Sample Media | Desorption Agent |
|---|---|---|
| 92-05-090-01 | Charcoal | carbon disulfide |
| **Retention Time** | **MS Library Match** | |
| 398 seconds | 4-ethenyl-cyclohexene | |
| 651 seconds | 2,6-dimethylnonane | |
| 656 seconds | 4-ethenyl-cyclohexene | |
| 732 seconds | 2,5,6-trimethyldecane | |

| Sample # | Sample Media | Desorption Agent |
|---|---|---|
| 92-06-186-01 | Charcoal | carbon disulfide |
| **Retention Time** | **MS Library Match** | |
| 321 seconds | 4-ethenyl-cyclohexene | |
| | 1,5-cyclooctadiene | |
| 581 seconds | decane | |
| | 2,5,6-trimethyldecane | |
| 611 seconds | 4-methyldecane | |
| 702 seconds | 2,5,6-trimethyldecane | |

| Sample # | Sample Media | Desorption Agent |
|---|---|---|
| 92-06-181-01 | Charcoal | carbon disulfide |
| **Retention Time** | **MS Library Match** | |
| 378 seconds | 4-ethenyl-cyclohexene | |
| | 1,5-cyclooctadiene | |
| 603 seconds | decane | |
| | 2,5,6-trimethyldecane | |
| 629 seconds | 4-methyldecane | |
| 712 seconds | 2,5,6-trimethyl decane | |

| Sample # | Sample Media | Desorption Agent |
|---|---|---|
| 92-06-184-01 | Charcoal | carbon disulfide |
| **Retention Time** | **MS Library Match** | |
| 291 seconds | 4-ethenyl-cyclohexene | |
| 396 seconds | 2,5,6-trimethyldecane | |
| 564 seconds | decane | |
| | 2,5,6-trimethyldecane | |
| 596 seconds | 2,3-dimethylnonane | |
| 693 seconds | 2,5,6-trimethyldecane | |

| Sample # | Sample Media | Desorption Agent |
|---|---|---|
| 92-06-198-01 | Charcoal | carbon disulfide |
| **Retention Time** | **MS Library Match** | |
| 382 seconds | 4-ethenyl-cyclohexene | |
| | 1,5-cyclooctadiene | |
| 606 seconds | decane | |
| | 2,5,6-trimethyldecane | |
| 633 seconds | 2,6-dimethylnonane | |
| 714 seconds | 2,5,6-trimethyldecane | |

| Sample # | Sample Media | Desorption Agent |
|---|---|---|
| 92-06-198-03 | Tenax | methylene chloride |
| **Retention Time** | **MS Library Match** | |
| 616 seconds | 4-ethyl-pyridine | |

| Sample # | Sample Media | Desorption Agent |
|---|---|---|
| 92-06-198-05 | Tenax | methylene chloride |
| **Retention Time** | **MS Library Match** | |
| 564 seconds | 4-ethyl-pyridine | |