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HYDRAZINE MONITORING IN SPACECRAFT

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ABSTRACT

Hydrazine (HZ) and monomethyl hydrazine (MMH) are highly toxic compounds used as fuels in the Orbiter main engines and in its manuvering and reaction control systems. Satellite refueling during a mission may also result in release of hydrazines. During extravehicular activities (EVAs) the potential exists for hydrazines to contaminate the suit and to be brought into the internal atmosphere inadvertently at the conclusion of an EVA. If elevated levels of these compounds are detected in the airlock, countermeasures can be instituted before the airlock is opened to the crew quarters. Because of the high toxicity of hydrazines, a very sensitive, reliable, interference-free, and real-time method of measurement is required.

Current methods for on-board measurement of hydrazine contamination in the airlock include electrochemical sensors and Draeger tubes. These methods may be adequate for measuring hydrazines at relatively high levels (ppm); however, a measurement method capable of accurately measuring concentrations in the low part per billion range (≃10 ppb) is needed. A portable ion mobility spectrometer (IMS) has exhibited a low ppb detection limit for hydrazines, suggesting a promising technology for the detection of hydrazines in spacecraft air.

The Hydrazine Monitor is a modified Airborne Vapor Monitor (AVM) with a custom-built datalogger, manufactured by Graseby Ionics. This off-the-shelf IMS (the military version is known as the Chemical Agent Monitor, or CAM) was developed for the detection of chemical warfare agents on the battlefield. After early evaluations of the AVM for hydrazine measurements showed a serious interference from ammonia, the AVM was modified to measure HZ and MMH in the ppb concentration range without interference from ammonia in the low ppm range.

The Hydrazine Monitor uses a pump to draw a sample over a heated membrane. By dissolution and diffusion, vapors pass through the membrane to the analytical system. Sample molecules are ionized by reactions with a plasma of positive and negative ions, formed by ionization from a radioactive source. Through a series of fast ion-molecular reactions, product ions are formed. Some of these ions enter the drift tube through a pulsed shutter grid. In the drift tube, the product ions drift through the cell under the influence of an electric field and arrive at the collector electrode at different times based on charge, mass, and shape. The current created at the collector electrode is amplified and a signal vs time spectrum is generated. Ammonia, HZ and MMH have characteristic drift times and spectral signatures, which permit identification and quantification of each of these compounds.

INTRODUCTION

Hydrazines are acutely-toxic and carcinogenic compounds used as rocket fuels in the military and in the space program. Monomethyl hydrazine (MMH) is used in the orbital manuvering system and reaction control system of the Space Shuttle, and hydrazine (HZ) has been selected as the fuel for Space Station Freedom. Since both compounds are also used to fuel satellites, the potential exists for hydrazines to contaminate an astronaut's space suit during an extravehicular refuelling operation and thus inadvertently be brought into the airlock at the end of the EVA. Detecting these compounds is necessary before the airlock is opened to the crew quarters. But detection is difficult. The 7-day Spacecraft Maximum Allowable Concentration (SMAC) for both HZ and MMH is 0.04 ppm.[1] Much lower limits have been proposed for new 7-day SMACs and for SMACs for longer exposures (Personal Communication, H. D. Garcia). Furthermore, the American Conference of Governmental and Industrial Hygienists (ACGIH) has recently proposed an 8-hour, time-weighted-average exposure limit of 0.01 ppm for industrial workers. Measuring such low levels quickly and reliably during operations challenges analysts and instrument makers.

The emergence of IMS as a sensitive, reliable, portable, real-time technique for determining chemical warfare agents spurred our interest in applying IMS to the measurement of hydrazines. A preliminary study of a Graseby Ionics AVM by

Dr. Gary A. Eiceman at New Mexico State University[2] was followed by a more detailed study conducted in the Toxic Vapor Detection Laboratory at Kennedy Space Center (KSC) by Ms. Rebecca Young and Dr. Eiceman.[3] They found that the AVM could detect low ppb levels of HZ and MMH, although response and recovery times were longer than desirable and ammonia interfered with the determination.

This positive study encouraged further interest at both KSC and Johnson Space Center (JSC). The interest at KSC arose from the need to monitor very low level exposure during numerous fueling operations. At JSC the issue has been the potential for exposing crews to hydrazines during EVAs. In the past, Draeger tubes and electrochemical measurements were the only viable inflight techniques available; neither method, however, possesses the sensitivity to detect hydrazines at the SMACs. Presently exposure is avoided by purely procedural controls; collecting exposure data is seen as a vital confirmation of the effectiveness of procedural controls. Both NASA centers are funding further development of IMS sensors.

A key step in the further development of IMS for HZ monitoring was removing the interference from ammonia. After Dr. Eiceman and one of us (T.F.L.) demonstrated a promising solution, the JSC Toxicology Group developed a Detailed Test Objective to conduct inflight tests (DTO 640 Hydrazine Monitor). The monitor's first flight was on STS-37 in April 1991. The major objectives were: 1. to assess instrument operation during flight, 2. to evaluate the instrument's ability to remain calibrated during flight, 3. to estimate the effect of ammonia on detecting hydrazines, and 4. to search for the presence of unanticipated compounds in the Shuttle cabin that could interfere with hydrazines' detection. The test plan included calibrations before launch and after landing of STS-37. These calibration tests were designed to collect data on the measurement range, the response times, and the limit of detection for MMH. Other tests were conducted to investigate the resolution of hydrazines from other compounds, especially ammonia, that might interfer.

This paper discusses the following results from these tests:

1. Measurement ranges for HZ and MMH
2. HZ and MMH calibration--linearity and stability
3. Response and recovery times
4. Resolution between HZ, MMH and ammonia
5. Flight results--background interferents and other observations

METHODS

HZ and MMH Generation

The apparatus for generating ppb concentrations of hydrazines is installed in the Toxic Vapors Detection Laboratory at KSC. A detailed description of its operation is included in reference 3, but briefly, the hydrazine permeates at a controlled rate through a plastic tube into a humidified air stream. The flow rate of the air stream is increased until the hydrazine concentration drops to the desired level. The most important fact about the generation method is that the final concentration is verified by an independent, reliable analysis. This verification at the point of delivery compensates for losses due to the reactivity and adsorptivity of hydrazines. The air stream temperature was 24-25 ^{o}C, and the relative humidity of the zero and calibration gases was 45±5%. The nominal HZ and MMH concentrations were 40, 100, 300, 600 ppb. The lowest verified concentration available when these calibrations were performed was 9 ppb MMH. Therefore, the limit of detection for the hydrazine monitor was probed using MMH.

Theory of Ion Mobility Spectrometry

Ion mobility spectrometry separates ions by differences in the time it takes them to drift through a gas at atmospheric pressure and an applied electrostatic field[4] (Fig 1). In the instrument described in this paper sample, is introduced across a silicon rubber membrane. Provision is made for a slow airflow (not shown in the figure) to carry the sample to an ionizer, most commonly a nickel-63 radioactive foil. Through a complex process, the beta particles in the ionizer generate a reservoir of positive and negative ions known as reactant ions. The reactant ions undergo complex ion/molecule reactions with the sample molecules in the reaction region. Compounds with high proton affinity such as the hydrazines form positive ions and those with high electron affinity such as halogenated compounds form negative product ions. The reactant ions influence the measurement range of the IMS. Fast, complete reaction of a sample with the reactant ions leads to greater sensitivity (i.e. a lower detection limit). The upper limit to the measurement range is reached at the sample concentration that depletes the reactant ions.

At the end of the reaction region, a fraction of the positive or negative product ions and excess reactant ions (of the same charge) are allowed to enter the drift cell through a pulsed shutter grid. Under a constant electric field, each ion species migrates through the drift gas to the collector at a characteristic velocity. Reversing the polarity of the shutter grid and the electric field allows ions of opposite charge to enter the drift tube. The current generated at the collector plate is converted to a voltage, amplified, measured as a function of time, and a spectrum is generated. Signal averaging increases signal-to-noise ratios. A typical IMS spectrum (bottom of Fig. 1) contains a reactant ion peak (RIP) and product ion peaks, which can number from one to many depending on conditions in the IMS. The IMS conditions are also arranged to produce suitable drift times, between 10 and 20 msec for this work.

A technique used often in IMS to improve selectivity for a particular class of compounds is to alter the ionization

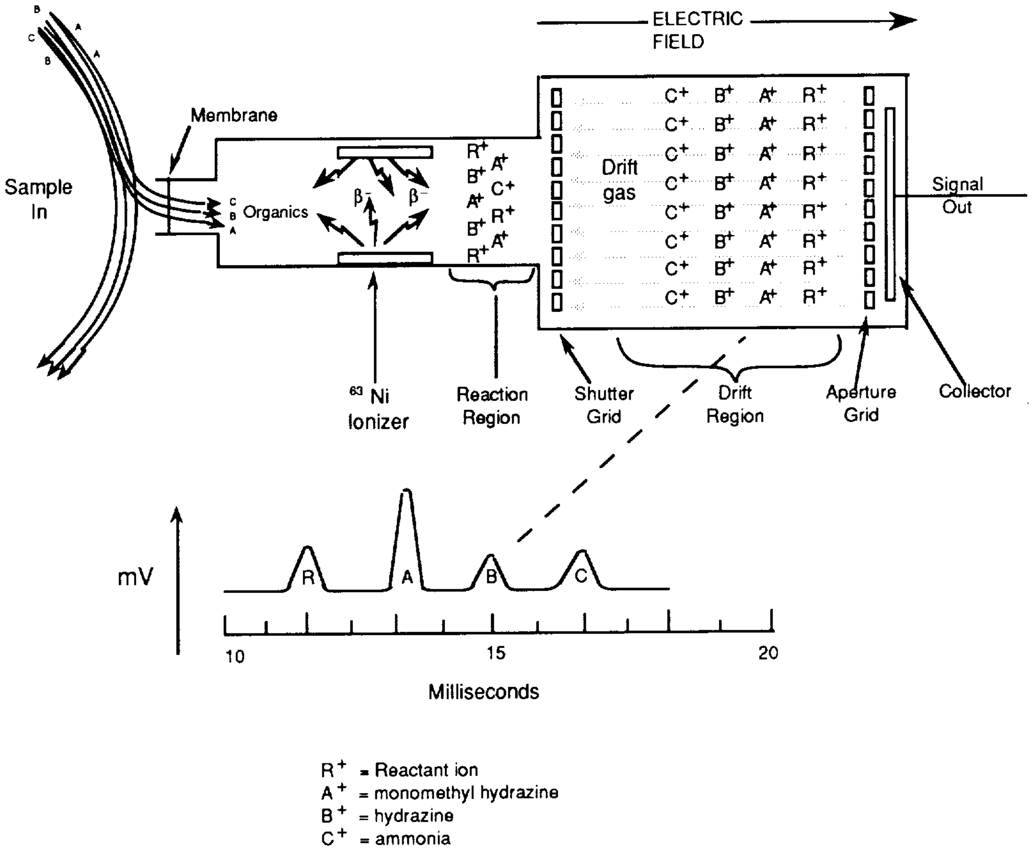


Figure 1: Principles of Ion Mobility Spectrometry

chemistry by adding a dopant chemical to the drift gas. The ions from the dopant become the reactant ions, and their reaction with the sample molecules forms ions that selectively separate from interfering compounds. The constant concentration of dopant necessary is usually maintained with permeation or diffusion tubes in the drift gas stream.

A dopant was used to eliminate the ammonia interference with hydrazines. Under a contract from the JSC Toxicology Group, Dr. Eiceman found that 5-nonanone provided resolution between MMH, HZ and ammonia without loss of sensitivity (G. A. Eiceman and T. F. Limero, manuscript in preparation). Graseby Ionics, Ltd, then built two AVMs using the nonanone dopant. Selectivity for hydrazines was high (ppb levels could be seen in the presence of ppm levels of ammonia), and sensitivity for hydrazines remained in the ppb range.

The Hydrazine Monitor

The Graseby Ionics, Ltd, AVM is a commercial, hand-held IMS (Fig. 2). The nozzle is at the right covered by a filter cap that provides clean air so the RIP can be identified during warmup. Sample drawn through the nozzle by a pump is evenly distributed across the heated membrane behind the white nozzle to speed transfer and thereby reduce response time. The drift tube is immediately behind the membrane. Since it runs parallel with the center line of the instrument, no part of it is visible in the photograph. Behind the drift tube are sieve packs, and around it is a circuit board. The figure shows the display panel, which indicates exposure levels with 0-8 bars. In addition, a three-dot display appears when high sample concentrations deplete the RIP. The handle contains a nickel cadmium battery pack. On the bottom is a datalogger for storing spectra inflight. As shown, the connector at the back of the AVM sends IMS spectra to the datalogger. The spectra can also be sent to a computer for viewing.

RESULTS AND DISCUSSION

Measurement Ranges

The upper measurement limit for MMH was close to 600 ppb, since the bar graph read 8 bars, the maximum, and the three dot display lit.

The lower limit of detection for MMH was probed in an experiment. MMH can be detected at 9 ppb. The MMH peak had a drift time of 15.4 msec (Fig. 3). The height of the peak

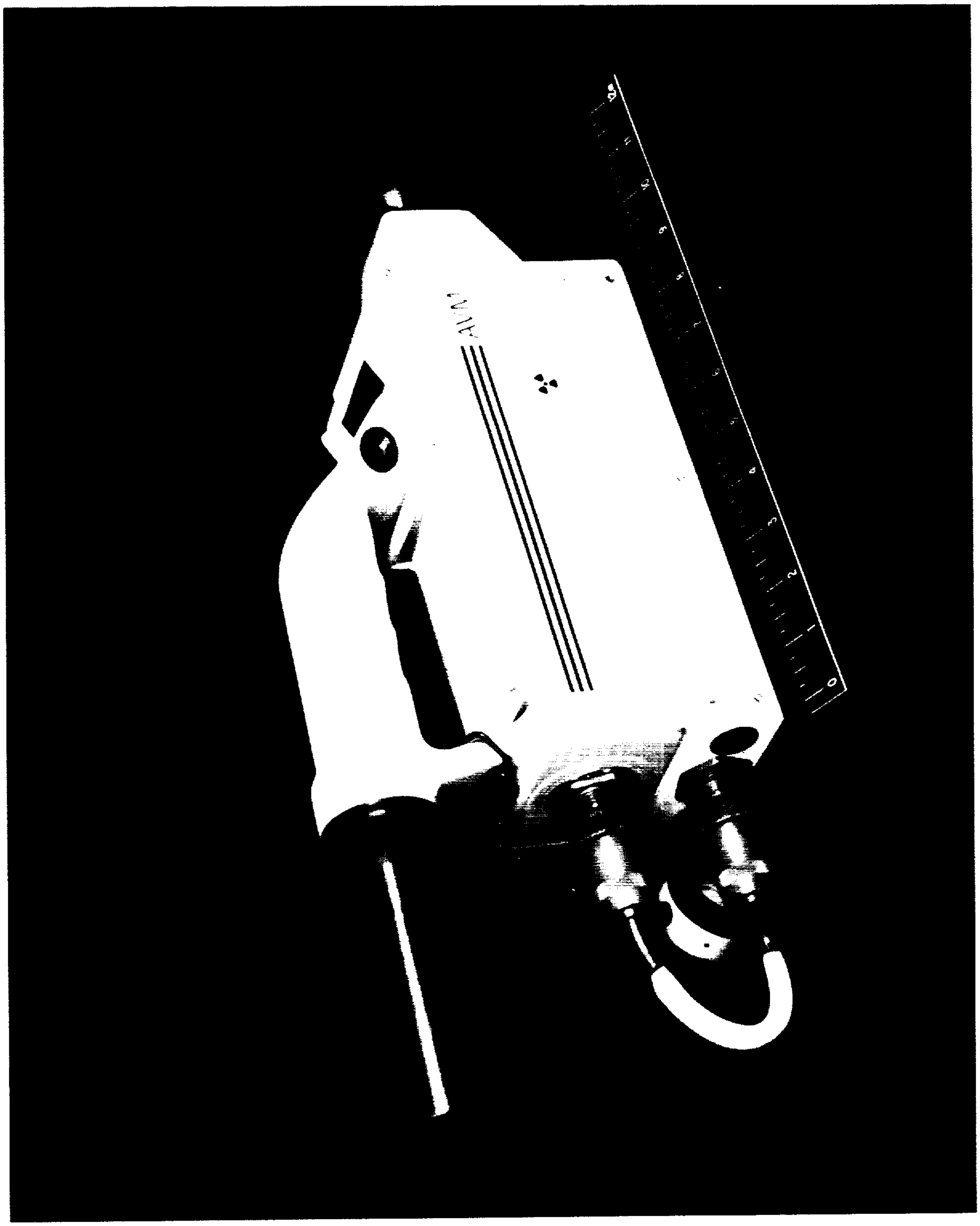


Figure 2: Prototype Hydrazine Monitor with Data Logger

was measured by comparing the voltage reading at the top of the peak with the voltage reading at the same drift time after the MMH was allowed to clear from the AVM. The peak height was 8 mV, small but detectable. Since the MMH peak was clearly discernable, one can speculate that an even smaller concentration could be detected by using more sophisticated signal-to-noise averaging techniques. The peak at 16.3 msec is an impurity in the diluent air; the impurity served as a reference that confirmed the presence of the MMH peak. Note that this experiment shows that at least one of the hydrazines can be detected below the proposed 10 ppb exposure limit.

Hydrazine produced a larger response from the AVM than did MMH. This observation is consistent with HZ's greater polarity.

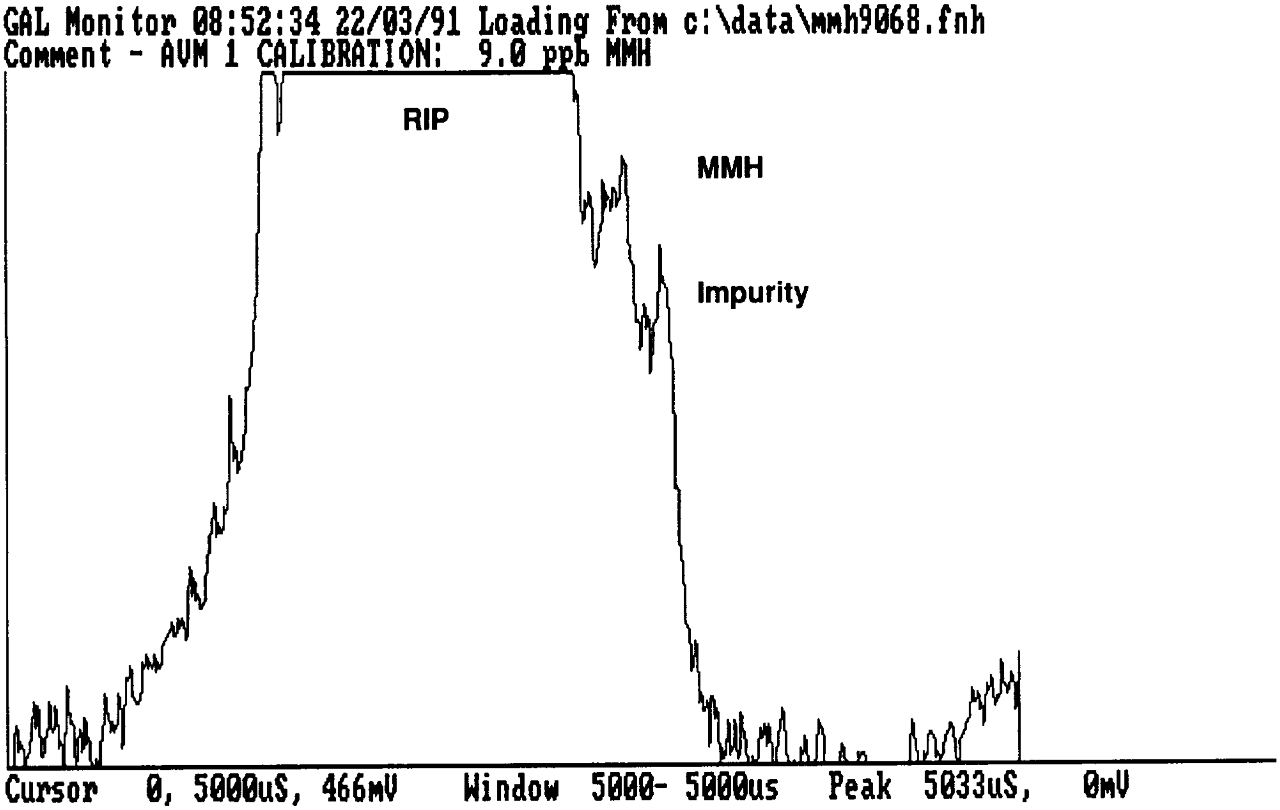
The upper measurement limit for HZ was above 600 ppb (the maximum concentration tested). Although the spectrum for 600 ppb showed a small RIP, the three-dot display indicating RIP depletion was not lit on the display, and therefore the measurement limit was thought to be slightly higher. Considering the size of the RIP at 600 ppb, one can speculate that the upper measurement limit would be about 700 ppb. The bar graph display showed 8 bars (maximum) for 600 ppb.

The lowest HZ concentration we have tested, 40 ppb, gave a strong signal, and therefore the limit of detection is lower. The limit for HZ was inferred from the MMH limit. The peak height for MMH at 9 ppb was 8 mV. For one 40 ppb HZ replicate, the peak height was 80 mV. A HZ peak 8 mV high would thus represent 4 ppb HZ.

Calibration--Linearity and Stability

Calibration was performed over a range of greater than one order of magnitude. Since this was the first time the monitor had been calibrated against known concentrations of HZ and MMH, we focused on examining the relationships between concentration and response. The data were examined several ways; this discussion will emphasize linear relationships across the entire range.

The most nearly linear response to HZ came from the percentage of the HZ peak areas to the total peak areas in the spectrum. As the HZ concentration increased, the RIP



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GAL Monitor 08:52:34 22/03/91 Loading From c:\data\mmh9068.fnh
Comment - AVM 1 CALIBRATION:  9.0 ppb MMH
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Figure 3: IMS Spectrum of 9.0 ppb MMH. The signal from 1024 scans has been averaged.

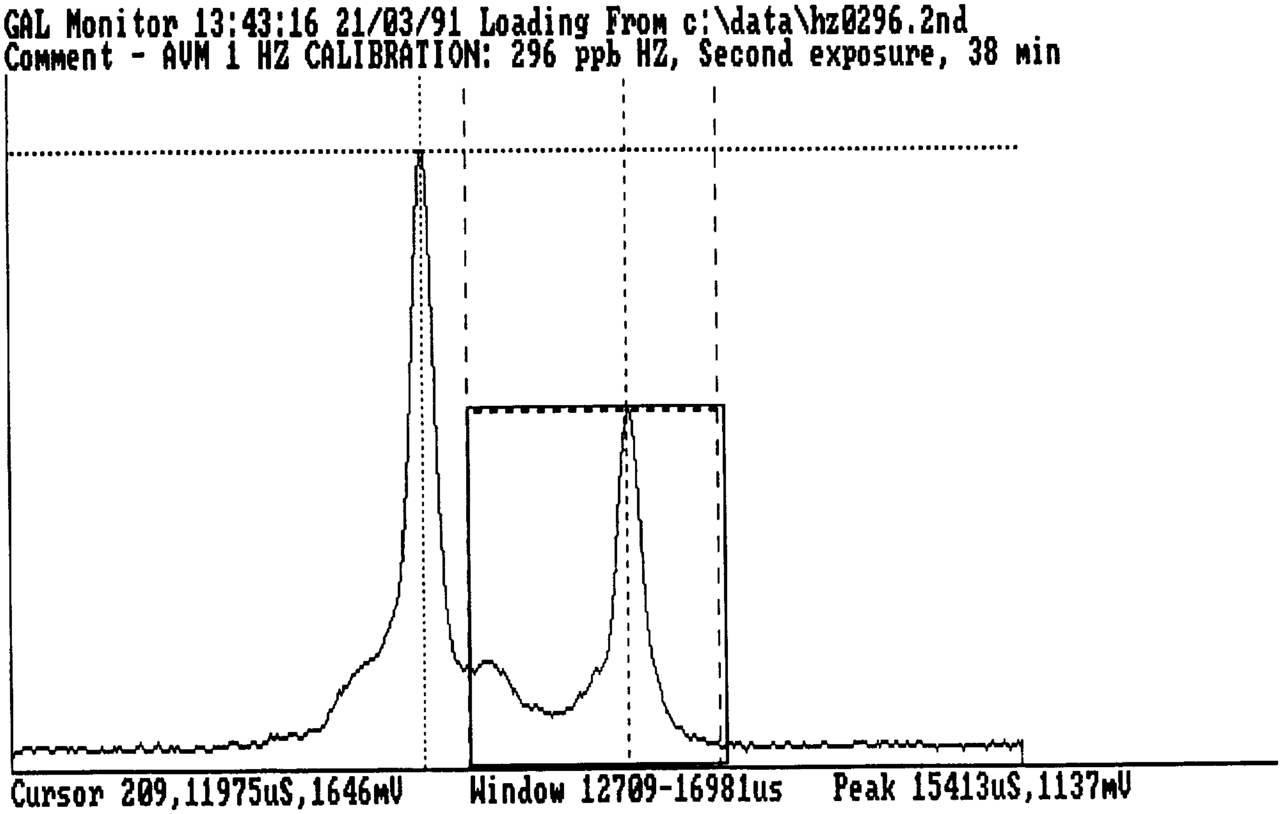


Figure 4: Spectrum of 300 ppb HZ

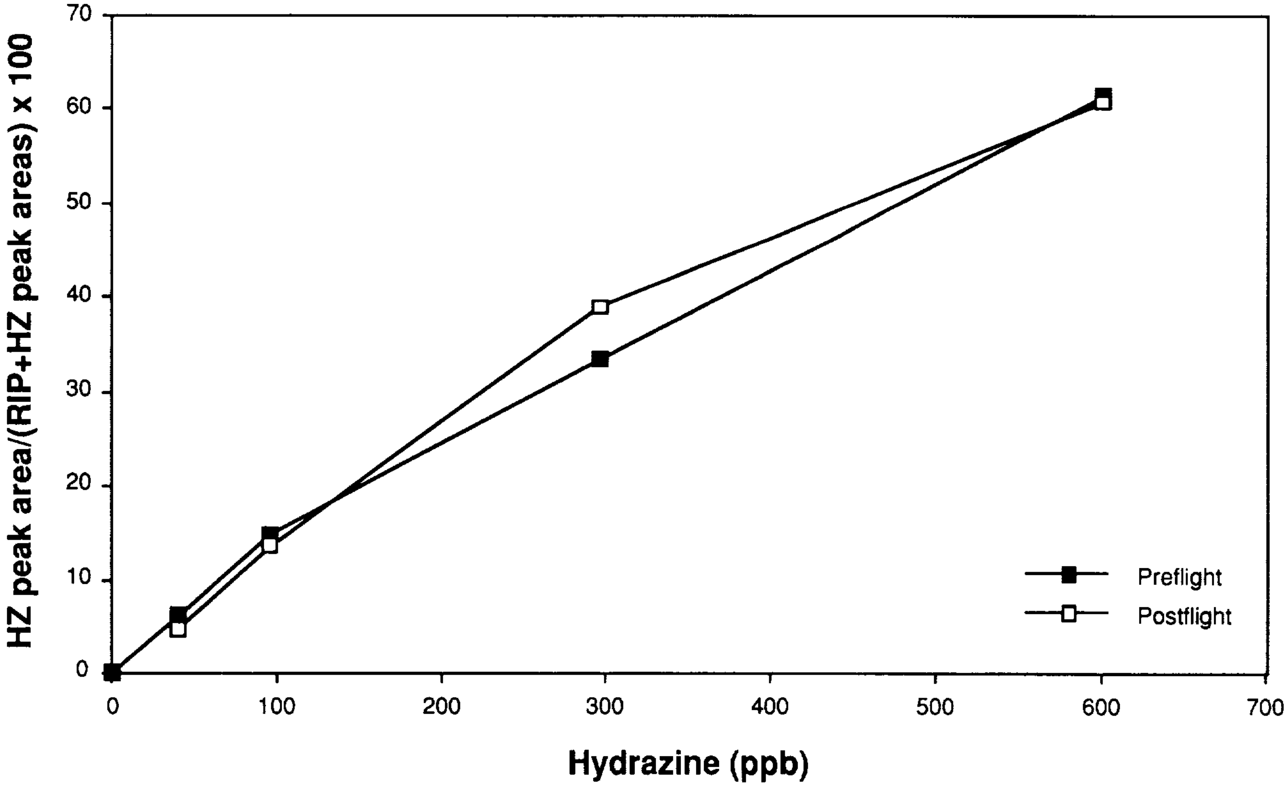
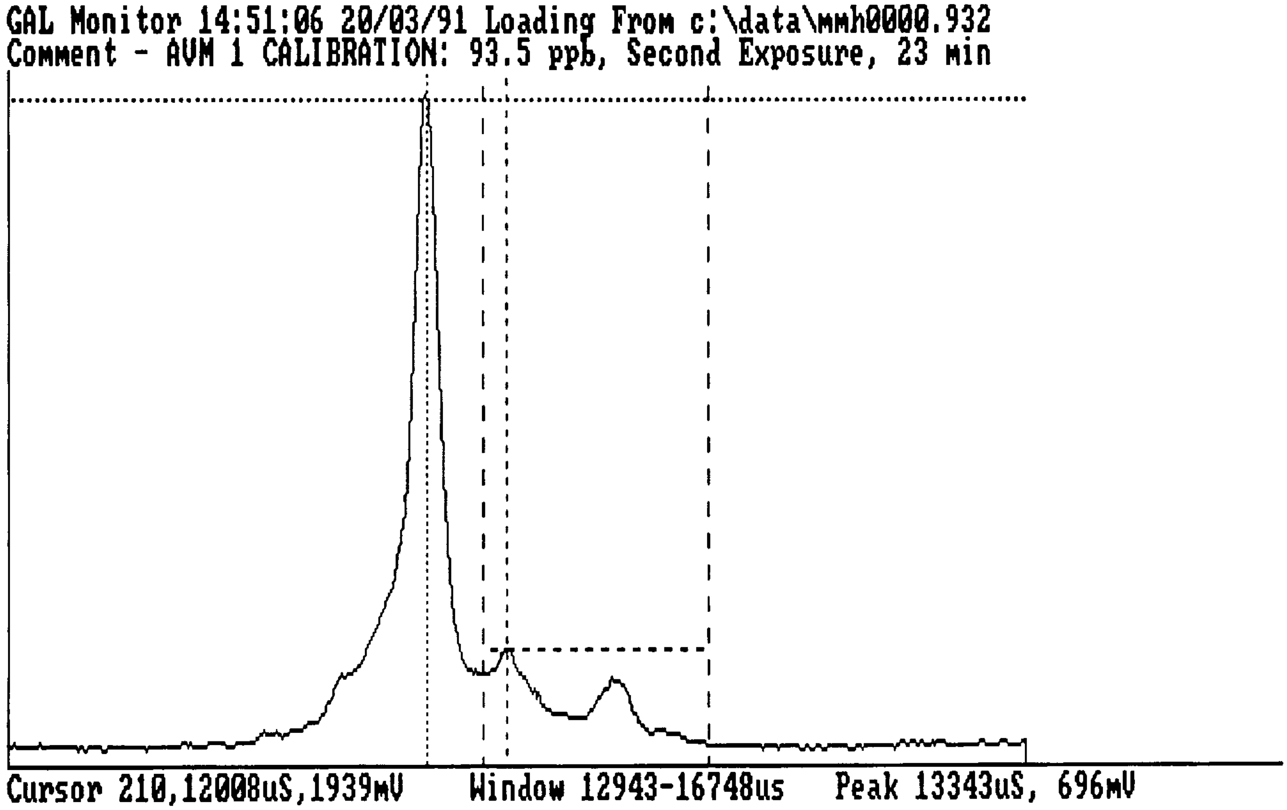


Figure 5: AVM Calibration Curves for HZ Before and After STS-37



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GAL Monitor 14:51:06 20/03/91 Loading From c:\data\mmh0000.932
Comment - AVM 1 CALIBRATION: 93.5 ppb, Second Exposure, 23 min
Cursor 210,12008uS,1939mV    Window 12943-16748us    Peak 13343uS, 696mV
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Figure 6: Spectrum of 100 ppb MMH

decreased and two HZ peaks grew proportionately (Fig 4&5). The total area under the peaks appeared to remain constant up to 600 ppb. The preflight HZ response (as defined above) was linear across the range. In the postflight HZ calibration, the peak area method was also linear (Fig. 5). In this postflight calibration, the linearity of the peak areas was not clearly superior to the linearity determined from the height or the area of the larger HZ peak (the rightmost peak in the spectrum).

Calibrating with peak area worked less well with MMH than with HZ. The total area under the RIP and the two MMH peaks decreased as the concentration of MMH increased, and the curve flattened at higher concentrations.

The most linear response to MMH came from the peak height of the MMH peak at a drift time of 13.3 msec (Fig. 6&7. The vertical dashed line on the smaller peak shows the 13.3 msec peak.). Since at low concentrations, this peak was a shoulder on the RIP, the peak height had to be measured above the "instrument baseline", the baseline at a drift time well away from any peaks, to avoid confusion caused by shifts in the RIP shape. Because the MMH peak at 13.3 msec was a shoulder peak, it was harder to detect at lower concentrations. In contrast, the MMH peak at 15.4 msec became nonlinear at moderate concentrations, but was easier to detect at lower ones.

The correspondence between calibrations before and after flight was remarkably good. Note also that in Fig. 7 the 9 ppb MMH point falls on the curves. For both HZ and MMH, the voltage readings corresponding to particular concentrations were nearly the same for the preflight and postflight calibrations (for MMH, see Fig. 7). This stability indicates that an IMS can undergo the rigors of spaceflight without requirements for on-orbit adjustments. In terms of AVM performance, the calibration stability suggests that the drift tube, the component where the analytical determination takes place, gives stable responses over long times and with active AVM usage.

Response and Recovery Times

Although the AVM detected 40 ppb concentrations of HZ and MMH in 2 min, stable response times for both HZ and MMH were lengthy, from 15 to 20 minutes. The long response time for hydrazine was partially mitigated by the great sensitivity of the AVM; after 2 minutes, the hydrazine peak was measurable and its size could be extrapolated to predict the final concentration. While 9 ppb MMH was identifiable at 10

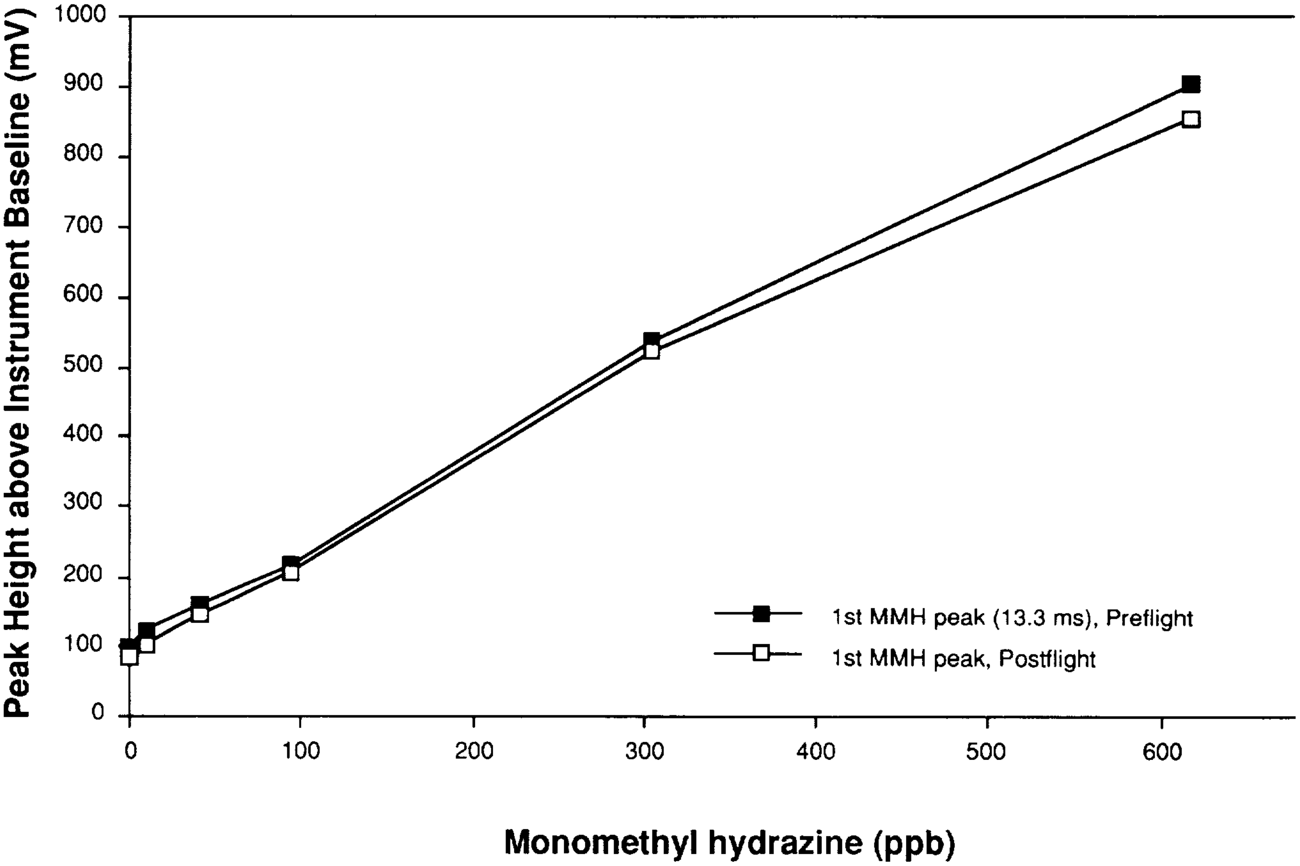

Figure 7: AVM Calibration Curves for MMH Before and After STS-37

min, quantification of 9 ppb required a 60 min exposure of the AVM.

At lower concentrations, 40-100 ppb, the recovery times for HZ and MMH were 10-15 min. At higher concentration, the recovery times for HZ (>40 min) were longer than for MMH (≈30min), which was consistent with HZ's greater polarity. While long recovery times are undesirable, they do indicate that decomposition of these very reactive rocket fuels was not the primary cause of long response times. Decomposition of the sample is regarded as a problem in the analysis of hydrazines, and this indication that its importance is low encourages further development.

Considering the excellent drift tube performance discussed above, one can speculate that the long response and recovery times arise from another component of the AVM. The high polarity of hydrazines suggests that they may be adsorbing strongly in the nozzle or the membrane.

Resolution

The results described above were obtained with unmixed hydrazines. Identification and quantification were straightforward based on the drift times of the two peaks for each. We have also found that ammonia was well separated; its drift time, 16.4 msec, was longer than either HZ or MMH. Ammonia could be present at perhaps 8 ppm before its peak would broaden to obscure hydrazine. Figure 8 shows a spectrum of all three compounds. The ammonia concentration was roughly 4 ppm, and the peak heights of HZ and MMH show them to be roughly 100 ppb. Distinguishing between HZ and MMH would be relatively easy, because each has two peaks. Quantification and identification of mixtures of low concentrations of both HZ and MMH may require be more difficult, since the one peak in the spectrum of HZ and MMH have the same drift time.

Flight Results

Data were collected at three locations at five times for a total of 15 data sets. The sampling locations were the airlock, the galley and the waste control system (WCS) at the following times:

Before prebreathe (Cabin pressure=14.7 psia, nominal)
Before contingency EVA (10.2 psia)
After contingency EVA (10.2 psia)
Before scheduled EVA (10.2 psia)
After scheduled EVA (10.2 psia)

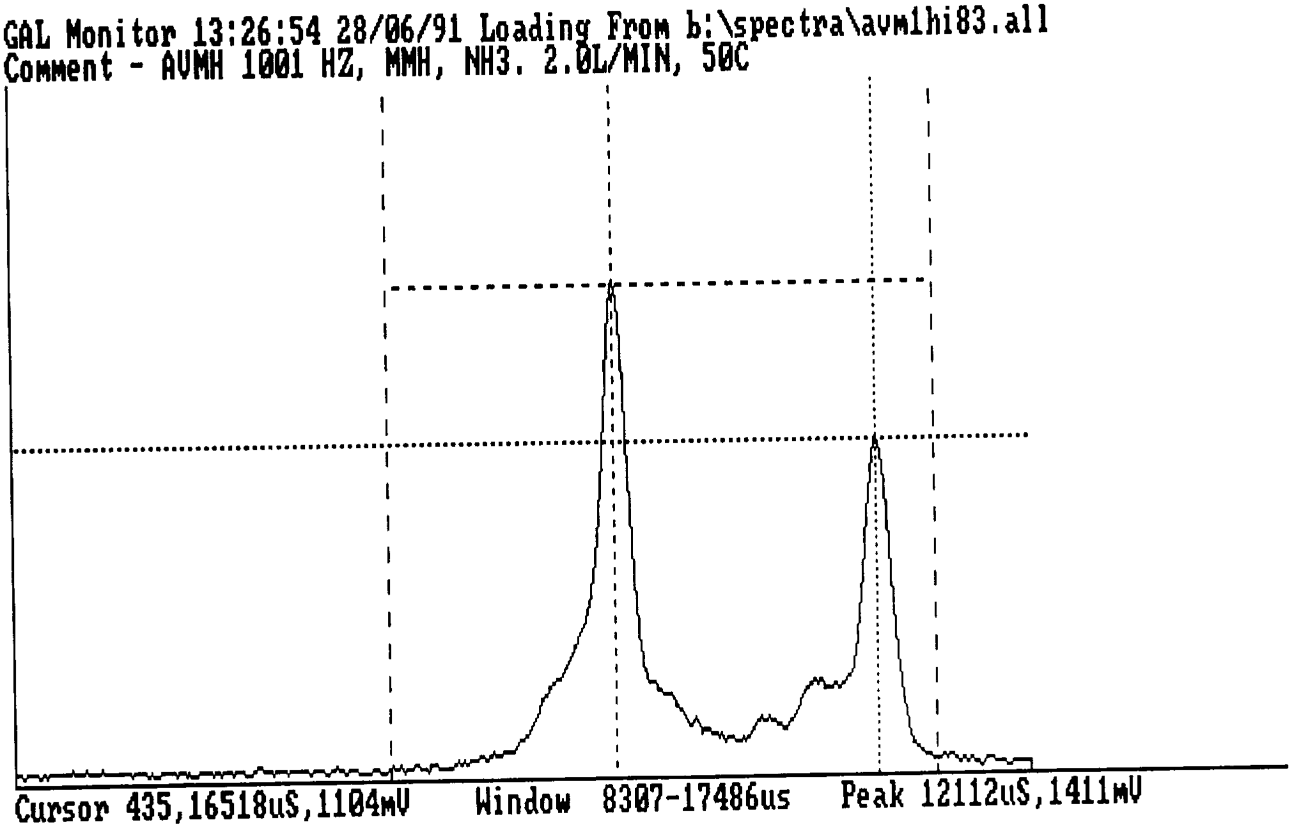

Figure 8: Spectrum of Approx. 100 ppb each HZ and MMH and Approx. 4 ppm of Ammonia

No interfering compounds were detected at any location. Small peaks did appear before the RIP in two data sets, and ammonia peaks just above the noise level were tentatively identified in several data sets, but no significant peaks appeared for hydrazines or any other compound.

Cabin pressure changes caused the RIP to shift position. In a postflight experiment, drift time was linear and directly proportional to the pressure; a pressure change of one psia changed the RIP drift time by 0.8 msec. Pressure changes affect all ions equally[4]. Thus, the resolution between ions is unaffected. In other words, the proportional separation between ions remains the same during pressure changes. The AVM uses proportional counting to locate the hydrazines relative to the RIP, which it identifies as the largest peak in the spectrum during warmup.

Summary and Conclusions

The hydrazine monitor was stable and sensitive with HZ producing a large response at 40 ppb and MMH detectable at 9 ppb. The instrument maintained linear calibration from <10 ppb to >600 ppb for over a month and throughout a spaceflight. Replication between calibrations before and after flight was excellent. Resolution between ammonia at >4 ppm and HZ and MMH was at least 20 to 1. Although response times were longer than desired, probably because the polar hydrazines adsorbed in the inlet, both compounds could be detected in about two minutes. The instrument worked well during flight and at reduced pressures. Compounds in the Shuttle cabin atmosphere that might interfere with the determination of hydrazines are either absent or present in low concentrations. Finally, the performance of the AVM on STS-37 suggests that IMS technology is suitable for hydrazine detection in spaceflight.

Future Work

The JSC Toxicology Group is currently identifying the most important instrument modifications to be made before the STS-49 mission in April 1992, which is the next mission with a scheduled EVA. Modifications to the nozzle and membrane are likely to reduce the response and recovery times. Data reduction algorithms specfic for detecting and quantifying hydrazines will be developed. After these improvements are incorporated into the AVM and the datalogger, another flight test will be conducted to insure the absence of interfering compounds in the spacecraft environment.

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