SAMPLE DILUTER FOR DETECTING HYPERGOLIC PROPELLANTS AND OTHER TOXIC OR HAZARDOUS GASES*

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ABSTRACT

Hardware was developed to dilute vapor samples of purged hypergolic propellants (with air) into the range of existing instruments for detection of such toxic vapors. Since these detectors are normally used to monitor at the threshold limit value (TLV), most do not have quantitative capability at percent levels which relate to lower explosion limit (LEL) and fire hazards. For example, the upper limits of Energetic Sciences (ESI) 6000 series detectors used at KSC are 200 parts per million (ppm) for monomethyl hydrazine (MMH) and 500 ppm for nitrogen dioxide (NO_2) arising from decomposition of nitrogen tetroxide (N_2O_4).

Orbiter Processing Facility (OPF) personnel servicing Shuttle thrusters need to measure up to 250 ppm MMH and 7,500 ppm NO_2 with portable, intrinsically safe instruments. Our objective was to quickly fabricate a sample diluter out of existing materials as a temporary measure while other parallel efforts were conducted to provide a commercial or in-house-developed instrument to detect high propellant levels. A 3 to 1 diluter would bring 500 ppm MMH into the range of the existing fuel ESI, and a 30 to 1 diluter would do the same for NO_2. In this way, familiar equipment already available would be used, resulting in minimal paperwork, safety, and training impacts and low cost.

An MMH vapor sample-diluter was constructed from a 1/4-inch Kynar tee, along with specially designed lengths of sample and dilution tubing. The sample line was 3 feet of Bev-A-Line IV, 1/4-inch tube leading to the straight run of the tee. The side run of the tee had a 17-inch length of Bev-A-Line IV, 1/4-inch tube, for nominal 3 to 1 dilution. A gas sample bag was prepared and assayed at 113 ppm MMH, and diluted vapor samples were assayed at 39.5 ppm, or a measured dilution of 2.9 to 1. For NO_2, a 316 stainless steel (SS) 1/8-inch tee with 49.5 inches of coiled, 1/8-inch outside diameter (OD) 316 SS tubing was used as the sampling end of the dilution system. The side run of the tee was open. The measured dilution ratio, based on the input value of 6,480 ppm NO_2 and the average output value of 233 ppm, was 28 to 1. Thus, sample-diluters were successful in diluting concentrated hypergolic propellant vapors, both MMH and N_2O_4, into the ranges of existing TLV detectors.

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INTRODUCTION

In many instances, operations personnel at the OPF have had the vapor detectors used to service the Shuttle reaction control system (RCS) thrusters become saturated so that the concentration of propellant is unknown. As a result, they have had to stop work until the vapor concentrations dropped within the range of the detectors. The request to the Toxic Vapor Detection Laboratory (TVDL) was made for a quick fix to prevent that type of work stoppage associated with servicing thrusters. United Space Alliance (USA) requested assistance in measuring high propellant levels in purge gas exiting Shuttle thruster manifolds before entering the facility vent system leading to vapor scrubbers. This measurement determines whether or not there is liquid in the manifold, which purging would take a long time to remove. Periodic samples of purge gas would indicate whether liquid is present, or whether the manifold is at a sufficiently low vapor concentration such that it could be safely opened for servicing (of course while wearing suitable personnel protection gear). The concern is that if the manifold is wet, there is a significant propellant source which is a safety hazard. Up to this point ESI detectors have been used which measure in the range of 0 to 200 or 500 ppm. In such service operations, the propellant concentration is normally above the instrument range. The requirement is to be able to determine purge levels in order to make a service schedule plan and to know when it is safe to open up the manifold. Without knowledge of the propellant level, there is no knowledge of how much time is needed before being able to start a thruster service operation.

The objective of this work was to produce a simple gas diluter which could be made quickly out of materials on hand in TVDL. Several attempts were made to develop a more rigorous method using in-house instruments and analytical chemistry techniques to quantify the vapors, but no ready solution was found. In the course of development, three versions of MMH diluters were developed: 10 to 1, 3 to 1 and 50 to 1; similarly for oxidizer, 100 to 1, 30 to 1 and 1,000 to 1. The first pair of diluters would allow USA to measure 0 to 250 ppm MMH and 0 to 7,500 ppm NO_2 using ESI 6000 detectors. The latter pair would allow USA to measure 0 to 250 ppm MMH and 0 to 7,500 ppm NO_2 using Interscan 10 ppm peak detectors. These targets are mainly concerned with avoiding fire and explosion hazards.

HARDWARE DEVELOPMENT

FUEL VAPOR CONFIGURATIONS

Fuel Configuration 1. A fuel-vapor diluter was constructed from a 1/8-inch-OD stainless steel tee. The sample line was 2 feet long, leading to the straight run of the tee. A 6-inch long section of 1/8-inch tubing completed the straight run to the detecting instrument. The side run of the tee had a 1-inch length of polymer tubing, 1/8-inch OD. This combination gave 9 parts air and 1 part sample gas, resulting in a 10 to 1 dilution. With no side-run tubing or cap fitting, a dilution of 100 to 1 was realized.

Fuel Configuration 2. The above MMH diluter was modified to eliminate the stainless steel tubing to prevent decomposition of the MMH. The dimensions were roughly the same as the first version but used 1/8-inch OD Teflon tubing instead. Flow rates of the sample and dilution streams were checked using an ESI to pump room air through both the sample and dilution legs. With the ESI rotometer at 2+ liters/minute (L/min.), the side leg with a short, small-bore tube gave 1.3 L/min. and the sample tube gave 0.12 L/min., or a flow dilution of about 11 to 1. Removing the small-bore tube resulted in about 60 to 1 flow dilution.

Fuel Configuration 3. A Kynar polymer tee was substituted for the stainless steel tee. Kynar is a plastic material, part number 70-2-K-0, for 1/8-inch OD tubing. Polymer (PFA) sample tubing was 5.5 feet long (straight-run), 1/8-inch OD, 0.030-inch wall; the side run was the same 1/8-inch OD tubing, and 1.5 inches long.

Fuel Configuration 4. The required dilution was changed to 3 to 1. Thus, several changes were made, including a tubing size increase to 1/4 inch, and the device was recalibrated. Configuration 4 is shown in figure 1.

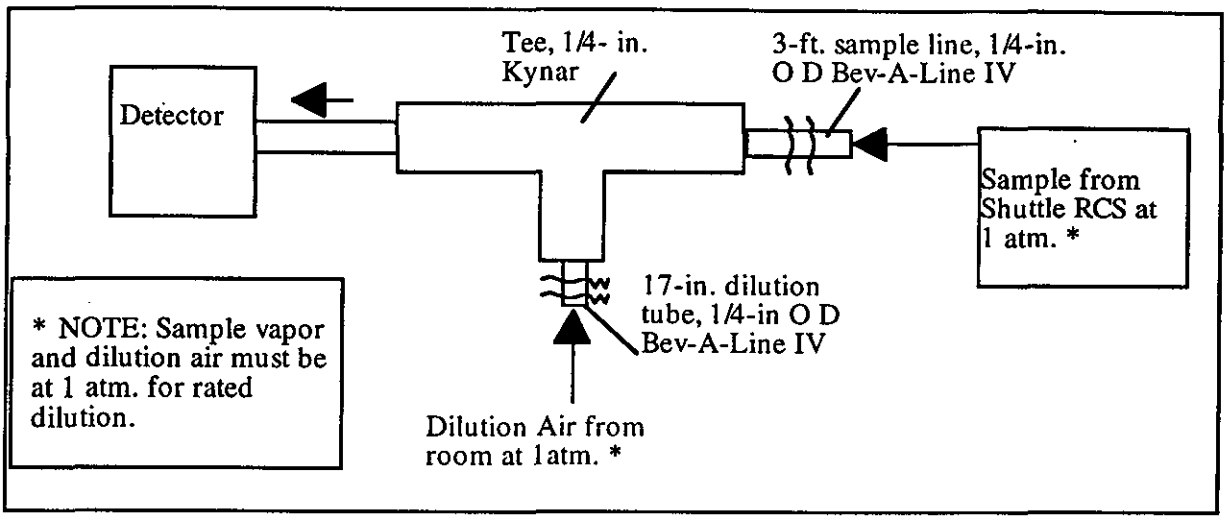

Figure 1. Fuel Configuration 4 for 3 to 1 Dilution of MMH Vapor

Fuel Configuration 5. Other circumstances prompted an instrumentation change to an Interscan 10-ppm peak detector. A requirement to detect 250 ppm MMH with this instrument prompted this last configuration, with a target of 50 to 1 dilution. This detector was more sensitive to flow reduction caused by adding the diluter to the sample line, thus careful recalibration was necessary. A polymer-tee for 1/4-inch OD tubing was fitted with Bev-A-Line IV tubing to create the diluter. This unit is being tested at this writing.

OXIDIZER VAPOR CONFIGURATIONS

Oxidizer Configuration 1. The initial requested dilution ratio for oxidizer was 100 to 1. The basic design is reflected in Configuration 2 below, except Configuration 1 had a longer sample line to reduce sample flow.

Oxidizer Configuration 2. After a visit to the TVDL facility by USA orbital maneuvering system/reaction control system (OMS/RCS) personnel, the dilution requirement was lowered to 30 to 1. The initial stainless steel dilution apparatus was modified and tested under controlled conditions for verification of the requested dilution ratio. This modified dilution system consists of the following pieces: (1) 4.75 inch of 1/8-inch OD 316 SS tube used as the connection between the dilution tee and the detector inlet tube; (2) a 316 SS Swagelok run tee; and (3) 49.5 inch of coiled 1/8-inch OD 316 SS tube used as the sampling end of the dilution system. Figure 2 illustrates the hookup and use of the oxidizer dilution system.

Oxidizer Configuration 3. A change to Interscan detectors for NO_2 prompted another redesign. The latter had an upper detection limit of 10 ppm. The request was to be able to measure at 7,500 ppm NO_2, thus a nominal dilution of 1,000 to 1 was needed. An 0.01-inch gas orifice was connected to a 1/8-inch Swagelok SS tee using only fittings and no tubing. The orifice is on the side run, which is the sample line. The air dilution line is 4 feet of 1/4-inch-inside-diameter (ID) Tygon tubing, and the detector line is 2 feet of 1/4-inch-OD Bev-A-Line IV tubing, both on the straight run. The dilution leg was made longer than usual to ensure that the dilution air was not contaminated with vented oxidizer. The sample line was made as short as possible to ensure a small transit time in the orifice sample line.

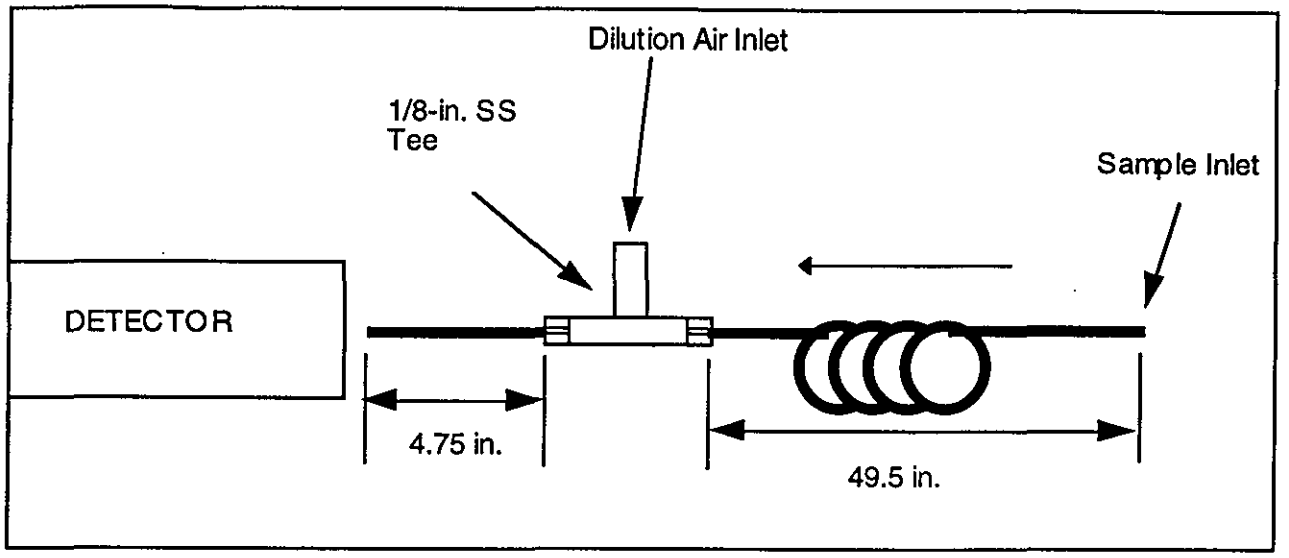

Figure 2. Configuration 2 of Oxidizer Dilution Device

FUEL AND OXIDIZER EXPERIMENTAL RESULTS

FUEL VAPOR RESULTS

Preliminary Experiments With Configuration 1. A Kin-Tec Span Pac produced a nominal 850 parts per billion (ppb) hydrazine vapor stream, as measured by an Interscan with the side run of the tee capped, i.e., an undiluted sample. Removal of the side cap resulted in readings of 5 to 15 ppb or roughly 85 to 1 dilution. Addition of a fitting and 1-inch of small-bore polymer tubing to the side run resulted in a reading of about 80 ppb, for a dilution of roughly 11 to 1. These results were repeated and verified several times. The response time was two to five minutes

The above combination of stainless steel tee and tubing was able to give approximate dilution factors of 10 to 1 and 100 to 1. Note that any change in tubing lengths, diameters, or fittings would have changed the dilution factors. Alterations in dilution could be made with tube length changes, since longer length reduces the flow in a specific tube. Similarly, the flow is reduced when smaller-bore tubing is employed. Also, an orifice could be substituted for a portion of the tubing to further restrict the vapor flow.

Fuel Configuration 2. The unit with polymer (FEP) tubing was tested by Wiltech, the contractor responsible for detector calibrations, with an inlet flow of 2+ L/min. at 20 ppm MMH flowing out of a large plastic bag. The apparatus in the above configuration for 10 to 1 gave 2.5 ppm MMH. Thus, the approximate 10 to 1 dilution was verified with MMH at 8 to 1 for low fuel level.

Fuel Configuration 3. An ESI was used with a total flow of 1 L/min. MMH was mixed in GN2 inside a 40-L sample bag. With the side leg closed and the straight run open, 115 ppm was measured. The side leg fitted with a 1-inch-long small-bore tube gave 16-ppm average, for a 7 to 1 dilution. With the side leg open (no tube), 2.6 ppm average, or 46 to 1, was observed

Fuel Configuration 4. A brief test was performed to prove the dilution ratio at an appropriately high concentration of MMH, close to that anticipated in the application, as opposed to the nominal 0.3-ppm MMH concentration, which is used to calibrate the portable ESI detectors. Because no portable detector was available for this test, an ESI 7000 MMH detector (not portable) was used instead. The latter had a range of 0 to 200 ppm MMH.

A 4.7-L Teflon sample bag was filled with 3 L of GN2 and several microliters of liquid MMH. A nominal MMH concentration in the bag was calculated from the GN2 volume, and the liquid MMH

was injected with a syringe. With the dilution device connected to the ESI, readings of undiluted sample and diluted sample were recorded. Table 1 shows typical results of a single sample preparation. (After showing successful performance in TVDL, the diluter was turned over to Wiltech for official calibration, in which procedure the nominal dilution ratio of 3 to 1 was verified.)

Table 1 - Fuel Dilution

Nominal Bag Conc., ppm MMH	ESI Reading, Undiluted, ppm MMH	ESI Reading, Diluted, ppm MMH	Observed Dilution Ratio
50	110	35	3.1
50	116	44	2.6

Thus, the dilution device gives roughly 3 to 1 as desired. It will give an acceptably accurate dilution if all of the precautions listed at the end of the paper are followed.

Fuel Configuration 5. No test results are available.

OXIDIZER VAPOR RESULTS

Oxidizer Configuration 1. No test results are available.

Oxidizer Configuration 2. Measurements were taken of the flows at both the dilution air and sample inlets using an SKC Inc. ACCUFLOW Digital Calibrator, as shown in table 2.

Table 2. NO_2 Dilution System Flow Measurements

Flow at Dilution Air Inlet (sccm)	Flow at Sample Inlet (sccm)
745	26.6
740	27.9
732	27.4
735	27.1
738 average	27.3 average

The calculated *flow* ratio for the dilution system using the averages from table 2 is 738/27.3 = 27. The dilution apparatus was subsequently attached to the detector and set up to pull in a sample of NO_2 in air. The NO_2/air mixture was obtained from Air Products as a certified gas mixture whose concentration was 6,480 ppm. The data in table 3 show the observed detector readings for a series of sampling tests.

Table 3. Detector Readings

Test Number	Detector, ppm NO_2
1	230
2	240
3	228
4	235
average	233

The calculated dilution ratio based on the input value of 6,480 ppm NO_2 and the average output value of 233 ppm NO_2 is 28. Thus, any reading observed on the detector should be multiplied by 28 to obtain the true reading. The agreement between flow rates and concentration-dilution results indicate that the results are consistent. The NO_2 dilution device dilutes roughly 30 to 1 as requested (also verified by Wiltech).

Oxidizer Configuration 3. One preliminary measurement was made. Concentrated N_2O_4 vapor was injected via syringe into a sample bag, which was then filled with GN2. The bag content was assayed using an ion chromatograph. A 10-mL gas sample was drawn from the bag and absorbed by 10 mL of 0.001 M sulfuric acid with 0.3 percent hydrogen peroxide in deionized water. The ion chromatograph indicated a nitrate ion concentration which represents 16,940 ppm NO_2 volume-to-volume (v/v) in the vapor. A 7000 ESI indicated the diluted vapor sample at 55-ppm NO_2. This is a dilution ratio of 308. Future increase of tubing length and/or decrease of orifice diameter would bring the ratio to a nominal 1000 to 1.

SUMMARY AND CONCLUSIONS

Both MMH and NO_2 diluters work within acceptable accuracy and serve the requirement to measure high propellant levels using a TLV or low-level detector. Dilution ratios from 3 to 1 to over 300 to 1 are attainable. The diluter concept is flexible in that dilution ratios may be changed easily by substituting different tubing diameters or lengths, as well as gas orifices. The MMH and NO_2 dilution systems will give an acceptably accurate dilution if all the precautions listed below are followed:

1. The sample must be at 1 atmosphere pressure. A flexible sample bag is recommended.
2. The sample and dilution tubes must not be not blocked with particulates.
3. The dilution tube must be at 1 atmosphere, and must not draw propellant-contaminated air.
4. After calibration of the diluter, the sample and dilution tubes should neither be lengthened nor shortened, and not fitted with other elements or fittings which would alter the flow resistances.
5. Both sample and dilution streams must be drawn under suction by the detector suction pump.
6. The detector, diluter, and sample tube must be calibrated together and kept as a unit. Total sample flow to the detector should not be changed after calibration. The dilution ratio may change if total flow to the detector is varied appreciably from the calibration value.

Another precaution relates to the detectors having finite response times. A measurement requires at least two or three times the instrument response time constant to be reasonably accurate. The OPF technique at present is to compress the manifold with purge gas and then vent the manifold through a small valve to the atmosphere. Basically, this produces a puff of sample to be assayed by the detector. This technique is a problem for small sample volumes because time required for accurate readings is on the order of a few minutes for existing detectors. Also, the sample vented to the atmosphere is not protected from dilution by surrounding air. The latter case would result in a low estimate of the propellant concentration, perhaps leading to a premature and hazardous manifold opening. Further, if sample volume is low, a dilution device gives an advantage, i.e., it only requires a total sample volume of the detector flow rate times the sample time divided by the dilution ratio. In all of the above, a primary consideration is that the actual sample-transit-time through the diluter must be one-third or less than the total sample time.

It should be noted that extreme accuracy in these measurements is not warranted, nor will the dilution devices necessarily give such accuracy. The desired dilution ratios are set using safety factors to restrict servicing operations to vapor levels well below hazardous limits. USA will now pursue a purchase of portable, intrinsically safe detectors with greater ranges but will also use the diluters in the interim and as backups to the new instruments.