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HYPERGOLIC OXIDIZER AND FUEL SCRUBBER EMISSIONS*

by

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ABSTRACT

Hypergolic fuels and oxidizer are emitted to the environment during fueling and deservicing shuttle and other spacecraft. Such emissions are difficult to measure due to the intermittent purge flow and to the presence of suspended scrubber liquor. A new method for emissions monitoring was introduced in a previous paper (JANNAF Interagency Propulsion Comm., Aug., 1994, San Diego). This paper is a summary the results of a one-year study of shuttle launch pads and obiter processing facilities (OPFs) which proved that emissions can be determined from field scrubbers without direct measurement of vent flow rate and hypergol concentration.

This new approach is based on the scrubber efficiency, which was measured during normal operations, and on the accumulated weight of hypergol captured in the scrubber liquor, which is part of the routine monitoring data of scrubber liquors. To validate this concept, three qualification tests were performed, logs were prepared for each of 16 hypergol scrubbers at KSC, the efficiencies of KSC scrubbers were measured during normal operations, and an estimate of the annual emissions was made based on the efficiencies and the propellant buildup data.

The results have confirmed that the emissions from the KSC scrubbers can be monitored by measuring the buildup of hypergol propellant in the liquor, and then using the appropriate efficiency to calculate the emissions. There was good agreement between the calculated emissions based on outlet concentration and flow rate, and the emissions calculated from the propellant buildup and efficiency. The efficiencies of 12 KSC scrubbers, measured under actual servicing operations and special test conditions, were assumed to be valid for all subsequent operations until a significant change in hardware occurred. The efficiencies were: OPFs/fuel--99.924 to 99.926 %, shuttle pads/fuel--99.816 to 99.966 %., OPFs/oxidizer--70.6 to 87.319 %, shuttle pads/oxidizer--99.585 to 99.996 %. An estimate of the total emissions from 16 scrubbers for three years showed that 0.3 kg/yr of fuel and 234 kg/yr of oxidizer were emitted.

INTRODUCTION

This report describes the results of a 1 year study to develop a method which monitored scrubber emissions without having to monitor gas flows. The report includes data collected and analyzed in proof-of-concept field tests performed at Space Shuttle Launch Pads 39A and 39B fuel and oxidizer farm scrubbers. Following successful proof-of-concept (POC) tests efficiencies of 12 KSC scrubbers were measured under normal operating conditions. Long term solution logs from 16 KSC scrubbers were also used to back-calculate propellant emissions based on the new data and concepts discussed below.

A special sample system, made up of a sample cart and sample collection subsystems, was constructed at the Toxic Vapor Detection Laboratory (TVDL) to collect monomethylhydrazine (MMH) and nitrogen tetroxide (N2O4) samples. The sampling system consisted of pumps, valves, switches, and flow meters enclosed in a GN2-purged cart. Sample-collection tubing, valve electrical service leading to the sample ports, and sample valves were positioned at the scrubber sample ports. All of this equipment was designed for use in a hazardous environment.

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The sample system was tested prior to the field tests in the TVDL with MMH and N_2O_4 vapor samples.

Lockheed Space Operations Company (LSOC) personnel connected sample lines to the scrubbers and assisted with the tests. The scrubber sample ports were rinsed prior to the scrubber tests, since the scrubber stacks were wet with scrubber liquor. LSOC Orbital Maneuvering System/Reaction Control System (OMS/RCS) and I-NET TVDL personnel in self-contained atmospheric protective ensemble (SCAPE) performed tests while other personnel from those organizations controlled the tests from the Launch Control Center. This general procedure was used for qualification and monitoring tests.

INSTRUMENTATION

Figure 1 is a schematic of the sample cart and sample collection tubes leading to the sample ports on a scrubber. Also, the connections to the storage tank are shown with the rotometer and flow line used to inject fuel or oxidizer into the scrubber. The scrubbers consist of two or four 2.5-foot-diameter, 6-foot-high towers, each packed with 3.5 feet of Tri-Pac 2-inch polypropylene spheres made by Tri-Mer Corp. Hypergol-laden GN2 flows upward in series through the two or four towers. The scrubber liquors are 25-wt-% sodium hydroxide for the oxidizer and 14-wt-% citric acid in water for the fuel. The liquor is pumped from the tank to the towers, sprayed downward onto the packing in parallel 50-gallon-per-minute (gpm) streams, and then drained back to the tank. The liquors are reused until they reach a specified percent of fuel or oxidizer, at which point they is replaced by fresh liquor.

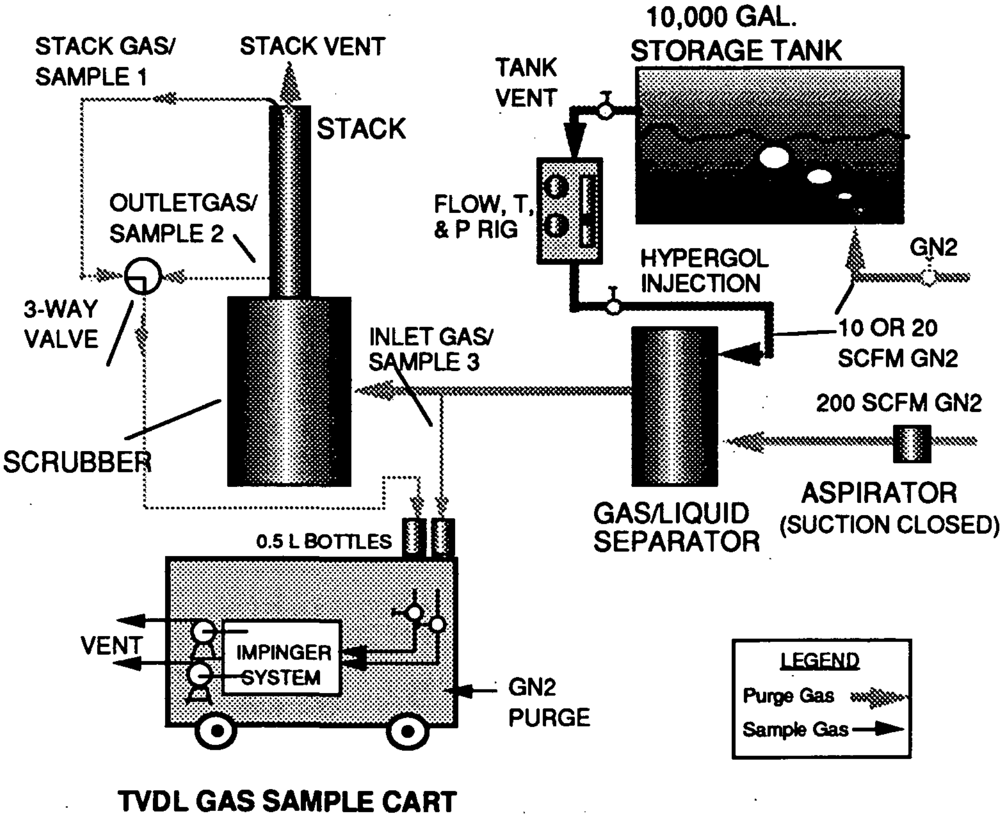

Figure 1. Hypergolic scrubber field test setup

Details of the sample cart and vapor scrub lines are shown in Figure 2. Sample bottles clamped on the cart exterior each contained the scrubber solution, which was pumped by peristaltic pumps to tees at the scrubber sample ports. Scrubber sample gas was also drawn into these tees by vacuum pumps in the purged cart. Liquid from the tubing pumps mixed with the sample gas at the tees, and the two-phase mixture was drawn into the bottles through 40 feet of 1/8-inch ID tubing, thus serving as a gas absorber in route to the sample bottles. This solution was circulated through the sample tubes to the tees and back during the sample period, which was sufficient to collect 1 liter (L) of inlet gas or 10 L of outlet or stack gas, i. e., several minutes.

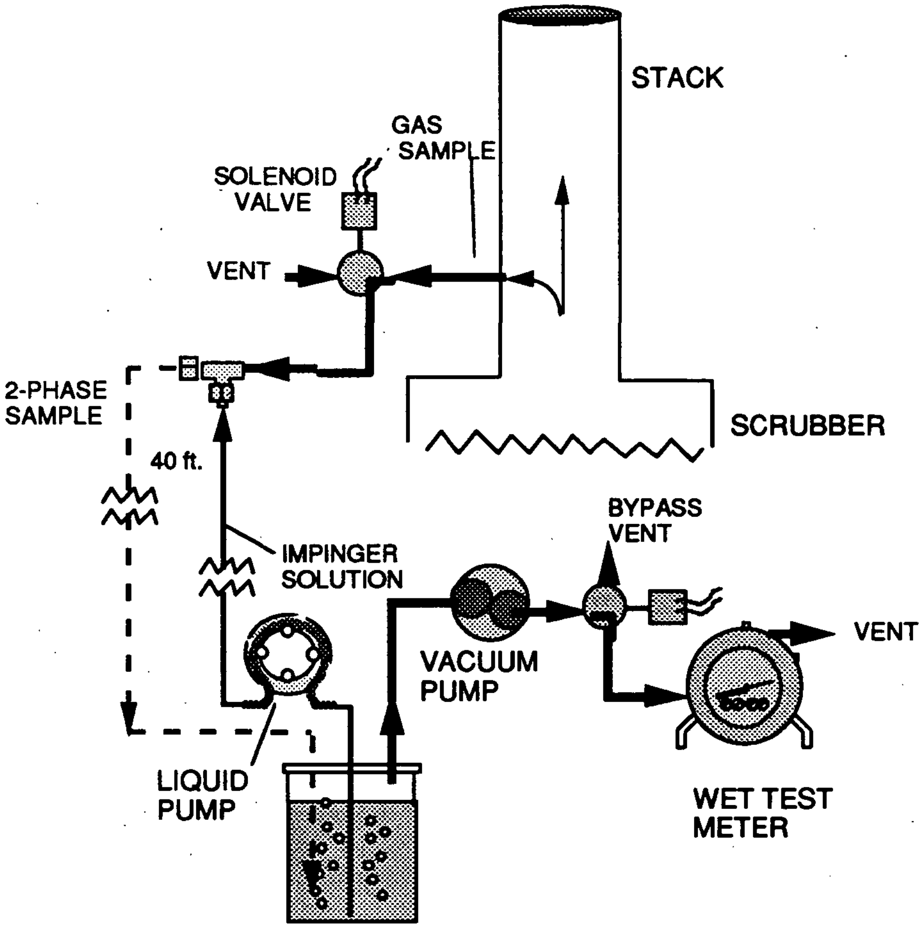

Figure 2. Details of the sampling system for each test point

The main scrubber gas flow under normal operations comes from aspirators, eductors, and tank vents. The normal gases that carry the hypergolic vapors are nitrogen and helium with flow rates to 500 scfm. During the qualification tests, the fuel or oxidizer was injected into the liquid separator by bubbling 10 SCFM or 20 SCFM of GN2 through the storage tank through a valve-purge line at the bottom of the tank. The GN2 from the fuel storage tank was nearly saturated with MMH vapor (72- to 76-percent saturation). The oxidizer tank pressure was sufficient to provide undiluted flow for low concentrations. For higher concentrations GN2 was added to the storage tank. The mixture, GN2 with either fuel or oxidizer, then flowed in succession through a storage tank vent pipe, the rotometer, into the liquid separator where it mixed with GN2 flow, and finally into the scrubber. Three separate sample lines were installed (see Figure 1), one each at the scrubber inlet, scrubber outlet, and stack outlet.

PROCEDURE

The test procedure was similar for all tests. First, the liquor volume in the tank reservoir was recorded before the scrubber pump was turned on. A scrubber liquor sample from the liquor storage tank was taken after the scrubber pump was started. Next, the gas-sample fittings were flushed with water to remove any prior contamination. Then, the operation started and samples were collected from the inlet to the scrubber, the outlet of the last scrubber tower, and for the proof-of-concept (POC) test the scrubber exhaust vent. For POC tests GN2 flow through the liquid separator and storage tanks were started and varied according to the test plan.

At the end of the operation, or for the qualification tests when the flow rates were changed, samples were collected from the scrubber liquor storage tank, and the final tank volume was recorded after the scrubber pump was stopped. These data provided efficiencies and concentration changes for all tests and in addition, gas flow rates for the POC tests, and concentration changes in the scrubber liquor.

RESULTS

The key concept demonstrated by this study is that scrubber emissions can be calculated by a one-time measurement of scrubber efficiency and then by periodically measuring the buildup of fuel or oxidizer in the scrubber liquor reservoir. The equation for this calculation is:

$$\text{Emissions (wt.)} = [(1/\text{EFF})-1] \times \Delta\,(\text{wt. of hypergol}) \qquad (1)$$

where the *emissions* is the calculated amount of fuel or oxidizer released during the period between the scrubber liquor samples and the *EFF* is a weighted average of typical operations.

Data from the proof-of-concept tests are used to calculate the emissions two ways. First, flows and outlet concentrations are measured over a representative range of operational conditions. Such a test conforms to the NIOSH Method 3503 for measuring stack emissions. Using these data, the emission value is simply the flow rate times the outlet concentration times the operation time:

$$\text{EPA Emissions (wt.)} = \text{Flow Rate} \times \text{Outlet Conc.} \times \text{Time} \qquad (2)$$

The *EFF* requires an inlet concentration measurement:

$$\text{EFF} = (\text{Inlet Conc.} - \text{Outlet Conc.})/\ \text{Inlet Conc.} \qquad (3)$$

The second or *new* emissions method requires both a knowledge of EFF and samples of scrubber liquor to determine fuel or oxidizer buildup in the liquor. Equation 1 is then used to calculate the second emission value, and this is compared with the NIOSH method using equation 2 for a given time period. The comparison provides a basis for validation of the new emissions method.

Since the gas flow rates through the scrubber, the concentration of the outlet vapor, and the duration of the flow conditions were known for POC tests, it was then possible to calculate the emissions. The results of the emissions estimated by the NIOSH method are compared with the results calculated from the efficiency and weight change in the scrubber liquor in Tables I, II, and III.

Tables I and II show a comparison of the two and four tower fuel scrubbers under the controlled conditions of the POC tests. The test at Pad 39A used flow rates of 10 and 20 scfm of GN2 through the propellant storage tank and the tests at Pad 39B used flow rates of 3.11 and 22.7 scfm through the storage tank. An aspirator was used to generate a GN2 flow rate of 200 scfm to the liquid separator. At Pad 39A the aspirator was used for all tests, while at Pad 39B the aspirator was turned off and on for each flow from the storage tank.

Table I. Summary of Emissions for Two tower Fuel Scrubbers Pad 39A

Time (min)	Total Flow (scfm)	Location	NIOSH Gas Flow Method (gm)	New Method (gm)
198	210	Outlet 39A	6.4	7.9
95	220	Outlet 39A	5.9	8.0
198	210	Stack 39A	4.9	6.1
95	220	Stack 39A	5.3	7.3
		Total, outlet 39A	12.3	15.9
		Total, stack 39A	10.3	13.3

Table II. Summary of Emissions for Four Tower Scrubber (Pad 39B) Tower Fuel Scrubbers

Time (min)	Total Flow (scfm)	Location	NIOSH Gas Flow Method (gm)	New Method (gm)
120	3.11	Outlet 39B	0.05	0.31
110	203	Outlet 39B	1.55	0.60
30	22.7	Outlet 39B	0.29	1.71
30	223	Outlet 39B	2.81	3.33
120	3.11	Stack 39B	0.05	0.28
110	203	Stack 39B	1.54	0.59
30	22.7	Stack 39B	0.25	1.45
30	223	Stack 39B	3.15	3.73
	Tests 1 through 4	Total, outlet 39B	4.70	5.95
	Tests 1 through 4	Total, stack 39B	4.99	6.05

Table III summarizes the results from the POC tests for the oxidizer scrubber at Pad 39A. In this case the flow rates through the oxidizer storage tank were 1.94 and 14.8 scfm and the aspirator flow rate was 200 scfm. The 1.94 scfm was produced from the vapor pressure of N_2O_4 in the tank and no GN2 was added, while the 14.8 scfm flow from the oxidizer storage tank represents a mixture of nitrogen tetroxide and nitrogen. One characteristic of scrubbers like the ones used at KSC is that the efficiency decreases as the gas flow rate increases for the same scrubber liquor flow rate, see Figure 3. A major component that accounts for part of this decrease is the decreased residence time in the scrubber. These factors contribute to the differences between the the emissions with and without the aspirator GN2 flow. All of the oxidizer scrubbers have four towers; therefore, only the scrubber at Pad 39A was used for the POC tests.

Table III. Summary of Emissions, Oxidizer Scrubber, Pad 39A

Time (min)	Total Flow (scfm)	NIOSH Gas Flow Method (gm)	New Method (gm)
109	1.94	0	0
125	202	2836	703
55	14.8	3.66	1.85
41	215	2744	2765
	Total All Flows	5584	3470

The emissions as measured by gas samples and gas flow rate, Tables I, II, and III (NIOSH Method 3503), agree reasonably well with the emissions calculated by equation 1 using scrubber liquor sample assays. The agreement between the NIOSH method and the new method is much better than the data collected by continuously sampling at a constant rate, which is the current method used at KSC. There are experimental errors in each method. For example, scrubber gas and liquor ports could become contaminated if not flushed properly between each sample. Also, the primary gas flow value was based on standard orifice tables and was not verified by field measurement.

Figure 3 illustrates the effects of an increase in the total gas flow rate on the efficiency of the scrubber. The L/G ratio is the ratio of the mass flow rate of the scrubber liquor divided by the mass flow rate of the gases that flow through the scrubber. Since the pumping rate of the scrubber pumps are constant at 200 gpm, the change in the L/G ratio is the result of changes in the gas Flow rate. The data illustrated in Figure 3 resulted from a study where the aspirator used to generate the data in Tables I -III was supplemented with a GN2 manifold that was capable of providing flows of 100, 200, 300, 400, and 500 scfm.

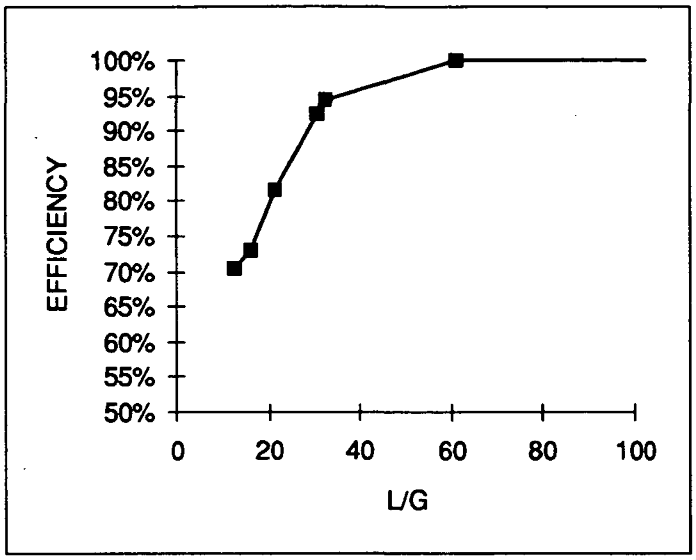

Figure 3. Efficiency versus L/G for the oxidizer farm scrubber Pad 39

The efficiency data provided in Table IV represents the inlet concentration weighted average efficiencies for each scrubber measured during their normal operations. The inlet weighted average adjusts the efficiency for those operations that contribute high concentrations of hypergol to the scrubber. The efficiency values provided in Table IV are recommended efficiencies that should be used with the scrubber waste logs to calculate the emissions.

Table IV. Efficiencies of KSC Scrubbers for Calculation of Emissions
by the New Method

Scrubber	Efficiency (%)
Pad 39A fuel farm	99.816
Pad 39A oxidizer farm	99.925
Pad 39A Fixed Service Structure fuel scrubber	99.922
Pad 39A Fixed Service Structure oxidizer scrubber	99.765
Pad 39B fuel farm	99.966
Pad 39B oxidizer farm	99.585
Pad 39B Fixed Service Structure fuel scrubber	99.966
Pad 39B Fixed Service Structure oxidizer scrubber	99.585
OPF Bays 1 and 2 fuel scrubber	99.924
OPF Bays 1 and 2 oxidizer scrubber	83.810
OPF Bay 3 fuel scrubber	99.926
OPF Bay 3 oxidizer scrubber	87.319
HMF Building 961 fuel scrubber *	99.925
HMF Building 961 oxidizer scrubber *	85.565
HMF Building 1212 fuel scrubber *	99.925
HMF Building 1212 oxidizer scrubber *	85.565

* Values shown were not measured, but calculated as the average efficiency of the OPFs.

In addition to the primary comparison of the new method with the NIOSH method and the scrubber efficiencies, there were many factors considered to ensure the new procedure could be used to correctly calculate the scrubber emissions from the efficiency and the change in the scrubber liquor concentration. For example:

a. Is there a loss of the fuel or oxidizer from the scrubber liquor tanks due to storage?

b. Will the combinations of the flushed line and impinger capture the gas sample?
c. Is misting a significant contributor to the outlet gas stream?
d. Will citric acid affect the MMH analysis?
e. How stable are the MMH samples in contact with stainless steel?

Answers to these questions, as well as safety concerns due to the emissions of MMH caused by misting and neutralization, were examined.

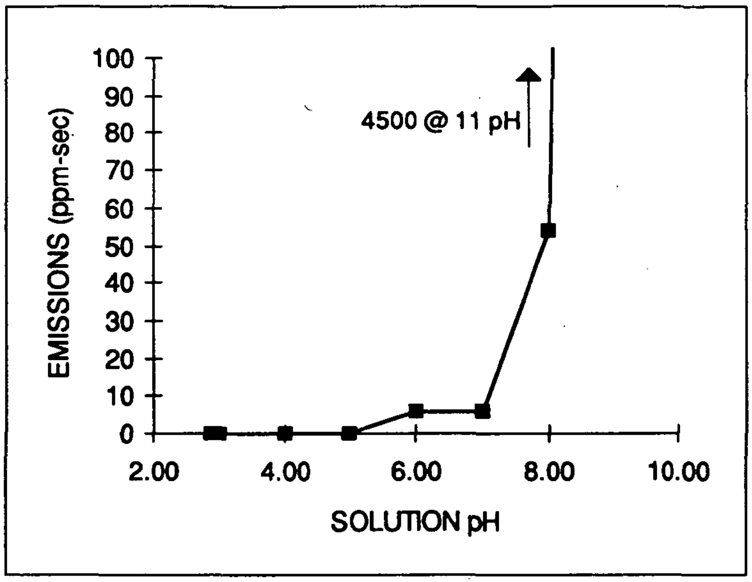

Figure 4. MMH emissions from used fuel scrubber

A major concern was the effect of misting of fuel scrubber, since a change in pH can release the hydrazine from the scrubber liquor solution. To illustrate this point, used scrubber liquor that contained 4.05 mg/mL of MMH, was neutralized with 5-N sodium hydroxide and the emissions monitored with an Energetics Science, Inc.

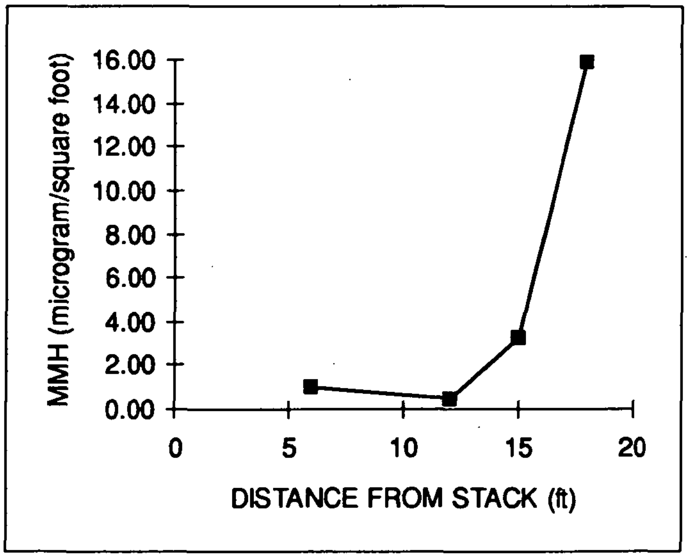

Figure 5. MMH emissions from scrubber stack Pad 39B fuel farm

instrument. The duration and rate of the emissions as the pH was increased using sodium hydroxide was plotted vs. pH in Figure 4. As can be seen, there is a significant increase in the emissions as the pH increases to 11. Since scrubber solutions are neutralized with 25 percent sodium hydroxide after some operations, the potential for rerelease of captured hydrazines is a safety and environmental concern.

The presence of misting was confirmed by capturing citric acid, the fuel liquor, down wind. In this example, clean glass plates were positioned downwind from the scrubber stack. After a POC test the glass plateswere analyzed in the TVDL for the presence of citric acid, which is the scrubber liquor used to capture hydrazines. The results of those tests are illustrated above in Figure 5. As can be seen, there is a significant amount of citric acid emitted from the scrubber stack.

The scrubbers can emit mist, which upon neutralization will release hydrazine. Figure 5 illustrates the emissions from a fuel scrubber captured on 0.25 ft^2 glass plates placed down wind from the scrubber stack.

Stability tests were performed on fuel and oxidizer scrubber liquors by purging samples (spiked and unspiked with fuel or oxidizer). Neither the fuel or oxidizer concentration change significantly after storage for more than 50 days in stainless steel cylinders with an air purge. Preliminary tests with dilute hydrazine solutions (100 ppb) in contact with stainless steel showed a 4-percent loss after 18 hours. Scrubber liquor solutions are much more stable than hydrazine solutions, since they are solutions of salts of the hydrazines and citric acid.

CONCLUSIONS

The new method demonstrated in this project appears to be valid for fuel and oxidizer emissions based on the data in Tables I, II, and III. That is, emissions based on the NIOSH method and those based on scrubber liquor buildup agree within experimental error.

Comparisons of outlet vapor versus stack concentrations indicate an average lower amount of fuel in the stack outlet gas versus the scrubber outlet gas (Table I). However, the data were scattered enough such that the differences in outlet versus stack concentrations were not significant.

The data needed to calculate the emissions are routinely collected for all of the scrubbers as part of the safety program to maintain to provide adequate capacity in the scrubber liquor. A log of the spent scrubber liquor was compiled and used to provide an estimate of the total emissions from the scrubbers by using the efficiencies generated by this study.

ACKNOWLEDGMENTS

The concept of the new method is credited to Clyde Parrish. Dr. Parrish wrote the proposal and Dale Lueck and Rebecca Young of NASA found funding for the project within KSC environmental activities. Besides the authors, a team of TVDL personnel contributed to the success of this work: Tim Hodge built the rotometer system; Jeff Rees, Dave Counts, and Terry Hammond wired the electrical service; and David LeMay helped with setup and did pre- and post-assays in the lab. LSOC personnel did the test arrangements, set up sampling valves on the scrubber, and participated in hands-on work during the field test. Jeff Litton and Dale Flemming worked particularly hard assisting us; and their supervisors, Greg Kamp and Mike Stefanovic, were fully supportive of our tests on the busy launch pad.