

## Total hydrocarbon content (THC) testing in liquid oxygen (LOX) systems

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**Abstract.** The measured Total Hydrocarbon Content (THC) levels in liquid oxygen (LOX) systems at Stennis Space Center (SSC) have shown wide variations. Examples of these variations include the following: 1) differences between vendor-supplied THC values and those obtained using standard SSC analysis procedures; and 2) increasing THC values over time at an active SSC test stand in both storage and run vessels. A detailed analysis of LOX sampling techniques, analytical instrumentation, and sampling procedures will be presented. Additional data obtained on LOX system operations and LOX delivery trailer THC values during the past 12-24 months will also be discussed. Field test results showing THC levels and the distribution of the THC's in the test stand run tank, modified for THC analysis via dip tubes, will be presented.

### 1. Introduction

Stennis Space Center (SSC) routinely tests rocket engines. One of the commodities used during engine testing is Liquid Oxygen (LOX). The procurement of LOX by SSC is driven by MIL Spec 25508 that specifies that the maximum total hydrocarbon (THC) value for the delivered LOX cannot be any higher than 50 ppm. The certified vendor values for THC in LOX delivered to SSC have been erratic over a period of approximately 4 years (Figure 1). More recent follow-up studies show large differences between SSC THC analyses of the purchased LOX and vendor-supplied THC values (Figure 2). The vendor THC values are consistently lower than the SSC analyses. Based on SSC data, the THC values have been trending towards higher values on average and are approaching the 50 ppm procurement limit. In addition to high THC values in LOX deliveries, the THC concentration in LOX tanks has been shown to increase over time due to oxygen boil off<sup>1,2,3</sup>. Data taken from SSC Test Stand LOX storage and run tanks confirm that the THC levels increase over time. Sampling of an SSC LOX run tank has shown THC values as high as 103 ppm<sup>2</sup>. The remainder of this paper will briefly discuss air separation and potential contaminants along with efforts undertaken at SSC to mitigate the rise of THC values in LOX storage/run tanks.



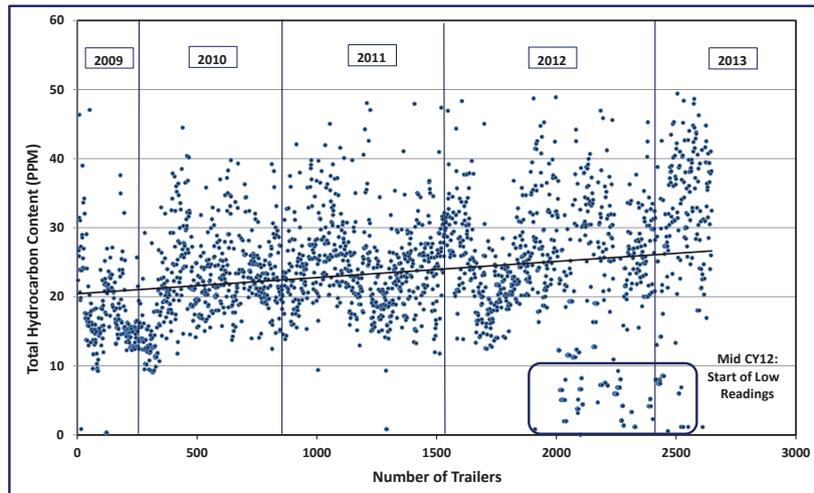


Figure 1. Vendor Certifications: LOX Trailer THC (July 2009) to Mid 2013.

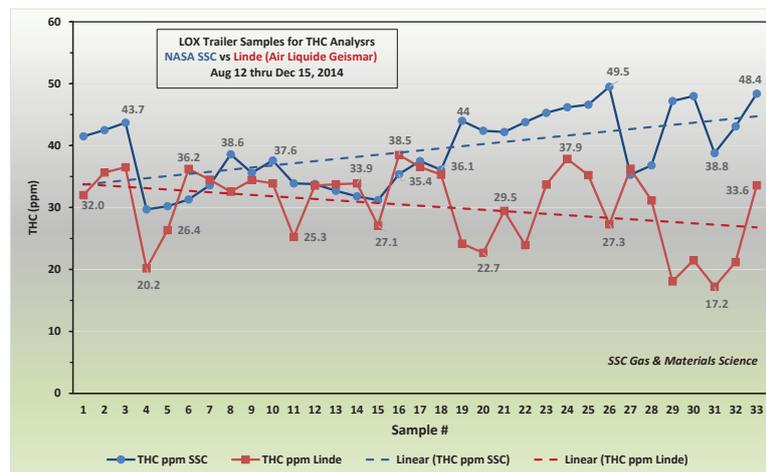


Figure 2. LOX Trailers Random Samples for THC (All trailers not sampled by SSC).

## 2. Background

During processing at an air separation plant, the ultimate source of LOX contamination is the air feed. The effectiveness of the plant in removing contaminants such as acetylene, light hydrocarbons and other combustibles during the separation process will influence the purity of the produced LOX. Acetylene, with a solubility of 8 ppm @ 1.4 bar in LOX, is taken totally out of the LOX stream by the plant in order to mitigate any possibility of solid acetylene accumulation causing explosive problems either at the separation plant or an end-user location. Plant design typically removes propylene and all  $C_4^+$  hydrocarbons to very low levels during processing<sup>4</sup>.

Methane, although it is the major combustible contaminant that may be present in LOX, is the least hazardous. The 50 ppm THC specification limit, as methane, placed on purchased LOX is actually based on solubility and not the flammability limit of this contaminant. The solubility of methane in LOX has been reported at 980,000 ppm<sup>5</sup>. Accounting for LOX vaporization, losses from handling/boil-off and the capabilities of LOX manufacturers, the 50 ppm procurement limit for THC limit was established for LOX initially delivered to a storage tank.

Contaminants with lower vapor pressures, i.e. higher boiling points, than LOX will vaporize less quickly than LOX and will concentrate over time in a given amount of LOX or with handling. These include

methane and acetylene. Conversely, contaminants with higher vapor pressures/lower boiling points than LOX, such as nitrogen, argon, and carbon monoxide, will vaporize more quickly than LOX and will not concentrate over time or with handling. The boiling point data in Table 1 illustrate these points.

Table 1. Component Boiling Point Comparison.

| Component       | B.P. (Deg F) | B.P. (Deg C) | B.P. (K) |
|-----------------|--------------|--------------|----------|
| Nitrogen        | -320.4       | -195.8       | 77.2     |
| Carbon Monoxide | -312.7       | -191.5       | 81.5     |
| Argon           | -302.5       | -185.9       | 87.2     |
| Oxygen          | -297.3       | -183.0       | 90.0     |
| Methane         | -263.2       | -169.0       | 104.0    |
| Krypton         | -244.2       | -153.4       | 119.6    |
| Ethylene        | -154.7       | -103.7       | 169.3    |
| Ethane          | -128.2       | -89.0        | 184.0    |
| Acetylene       | -119.2       | -84.0        | 189.0    |
| Carbon Dioxide  | -70.6        | -57.0        | 216.0    |
| Propylene       | -53.7        | -47.6        | 225.4    |
| Propane         | -43.6        | -42.0        | 231.0    |
| Water           | 212.0        | 100.0        | 373.0    |

Subsequent tracking of the THC values in an SSC LOX Run Tank over a period of 70+ days showed the trend for the THC reported by Kerry<sup>3</sup> and is illustrated in Figure 3. The THC values were obtained from LOX samples taken at the bottom of a LOX run tank. Over the course of this study the volume of LOX decreased by a factor of 10 (100% to 10% liquid level), while the concentration of THC hydrocarbon, measured as methane, increased by a factor of approximately 6. The extrapolation of the THC curve indicates that the methane concentration would not reach dangerous levels<sup>6</sup> by the time all the LOX had evaporated. However, the sharp hydrocarbon increase at end of the curve shows that the rate of methane concentration may increase rapidly toward the end of the evaporation period. In between tests, the level of LOX in the run tank is nominally kept above the 25-30% level. The tank is refilled either after testing and/or when a predetermined liquid level is reached. In rare instances, the tank level has decreased to 20% and levels as low as 6% have been observed during cavitation testing.

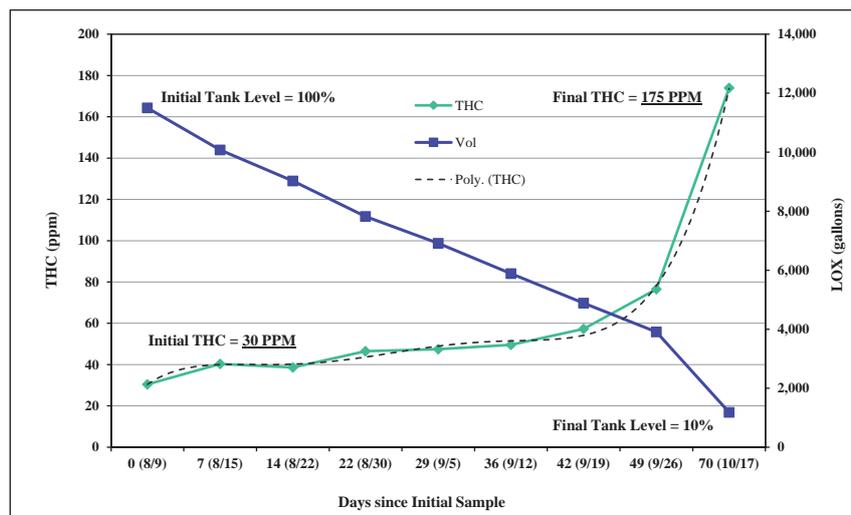


Figure 3. Actual LOX Run Tank Boiloff Test for THC Increase.

The solubility of THC, as methane, would initially suggest that this contaminant would be homogeneously mixed throughout the LOX. Since the LOX is mixed/agitated when transferred from a storage tank to the run tank one can assume uniform solution mixing. Once the LOX has settled in the run tank there may be some stratification of the THC due to temperature gradients within the tank or the presence of tank surface anomalies/hardware. No consistent evidence for the presence of stratification has been recorded although a recent dumping of LOX (10% by volume) from an SSC LOX storage tank decreased the THC level by 10%<sup>1</sup>. In order to test the stratification theory it was decided to monitor the LOX THC levels throughout a large LOX run tank during the time that it evaporated due to boil-off. Agitation of the tank would be minimized by sampling only once a week. The effect of pressurizing the tank in order to force liquid out the dip tubes was minimized by removing as little LOX as possible during the sampling process.

### 3. Test apparatus design and setup

The test apparatus for the LOX Run Tank (nominal 11,500 gallon capacity) study consisted of a flange and accompanying “dip tubes”. These stainless steel dip tubes were made of varying lengths that allowed sampling of vapor/liquid within the tank. A sketch of the dip tube/tank hardware is shown in Figure 4. The flange and associated cryogenic valving for the dip tubes is shown in Figure 5.

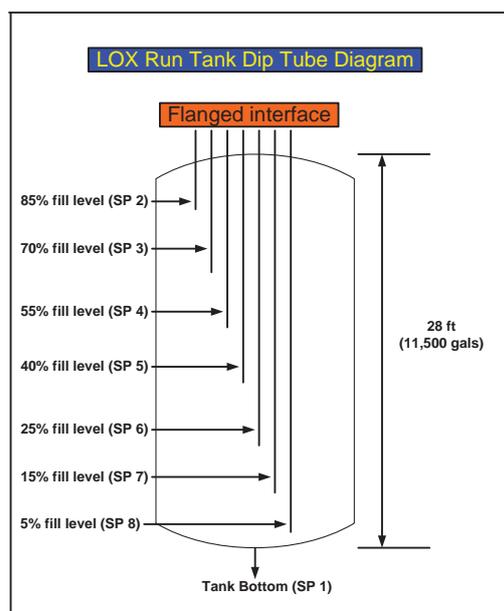


Figure 4. LOX Run Tank Dip Tube Setup.



Figure 5. LOX Run Tank Flange Interface/Valves.

### 4. Testing methodology

All liquid samples were captured using a Cosmodyne TTU-131/E Cryogenic Sampler (Figures 6-7). Standard SSC procedures were used during the capture of LOX samples by the Cosmodyne. During collection of liquid samples the run tank was pressurized with GN<sub>2</sub> in order to force LOX through the dip tubes for capture by the Cosmodyne. As the LOX level in the tank decreased the GN<sub>2</sub> pressure increased from 5-10 psig to approximately 30 psig. Prior to pressurization, the tank vent was closed.

All vapor samples were captured in evacuated 30 liter gas sampling canisters (melons). In comparison to the capture of liquid samples, the LOX run tank vent was closed at least 4-6 hours prior to sampling in order to allow for an increase in the head pressure of the tank. The inlet tubing to a sample gas sampling canister was purged for 5-10 seconds prior to capture of any GOX vapor sample. If required during laboratory analysis, a metered amount of GN<sub>2</sub> was added to the gas sampling canister in order to have adequate sample analysis pressure within the gas sampling canister. The amount of

nitrogen added to the gas sampling canister was later subtracted in order to accurately calculate the concentration of methane or other components within the sample.

The initial sampling of the eight dip tubes used approximately 800 gallons of LOX. Based on this large volume of LOX, the procedure for sample collection was modified to decrease the LOX volume and ensure sampling consistency.



Figure 6. Cosmodyne Cryogenic Sampler.

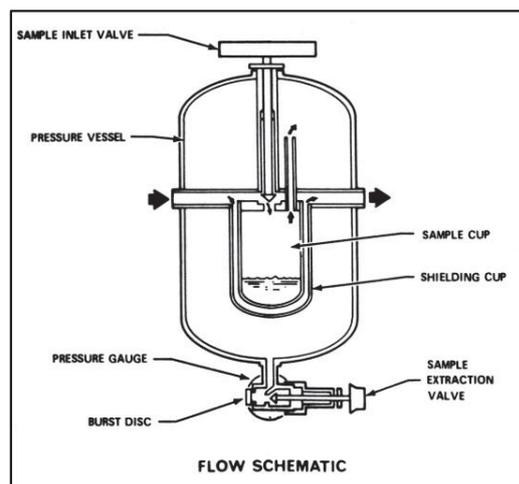


Figure 7. Cosmodyne Flow Schematic.

The amount of time used to flow LOX through the Cosmodyne to ensure the capture of a representative sample, was shortened from 20-25 minutes to 10 minutes. Subsequently, the time between opening and closing the sample valve was set to 1 minute. This timing allowed for 20 – 30 seconds of actual sample collection and mitigated any over-pressurization issues internal to the Cosmodyne that might cause the safety disk to rupture.

Subsequent to sample capture, gas sampling canisters and Cosmodynes were quickly transported to the SSC Gas and Materials Science Laboratory for analysis. All THC analysis were done using a Rosemount 400A THC Analyzer equipped with a Flame Ionization Detector (FID). A 3 component mix (methane, 1% Argon, balance Oxygen) National Institute of Standards and Technology (NIST) traceable standard was used as a calibration gas for all samples. The concentration of methane in the calibration standard was 50 ppm, 100 ppm, 200 ppm, 500 ppm, or 1000 ppm to accommodate a range of THC values. In all cases, the analyzer was pre-calibrated with one of these standards prior to the sample analysis. The analyses of CH<sub>4</sub> and permanent gasses from all samples were completed using a VICI Trace Gas Analyzer equipped with a Helium Ionization Detector (HID) and 5A Mole Sieve drying column. The vendor providing LOX to SSC utilized a proprietary FID for sample analysis and no additional details are available. Samples were taken on a weekly basis, weather permitting.

Due to the time required to achieve equilibrium head pressure in the ullage space of the LOX run tank, vapor samples were always obtained prior to liquid samples. When taking liquid samples, dip tubes close to being uncovered according to measured tank LOX levels were sampled first followed by the bottom of the run tank (Figure 4, SP 1). This protocol mitigated dip tubes from being uncovered by the sampling process rather than the LOX boil-off. Overall, the sample sequence illustrated in Figure 4 was followed for any set of vapor or liquid samples.

## 5. Example test results and discussion

The THC values obtained during the testing of the LOX run tank are shown in Table 2. The dramatic rise near the end of the test in the THC value for the tank bottom is consistent with the data trend shown in Figure 3. The vapor sample THC values shown as bold, underlined text in Table 2 also show an

upward trend as the volume of LOX in the run tank decreases. This is consistent with an equilibrium being established in the bulk vapor space based on the evaporation of the remaining THC, as methane, from the remaining LOX in the tank. Methane, as the higher boiling component, increases in concentration as the LOX evaporates. Subsequently, the vapor phase will contain a larger mole fraction of methane as the volume of LOX decreases.

The entire set of THC values obtained during testing is listed in Table 2. In looking at the graph of THC values from LOX liquid samples (Graph 8) it should be noted that the general shape of this curve is very similar to that of Figure 3. This bears out the relationship between the rate of boil off for LOX and methane based on their boiling points (Table 1). Between 50 and 65 days (post fill) [40 and 22 % Tank Fill] the concentration of THC in the sample from the bottom of the tank shows the greatest difference compared to values for the remainder of the tank. At this point, a potential mitigation to the rising THC value would be to offload a calculated percentage of the LOX based on possible stratification of the THCs. One test was completed on a LOX storage tank where dumping 10% of the tank volume caused a 6% drop in the measured THC value. Further evaluation of this method is proposed. Dilution of the LOX in the tank with material having a lower THC value may also mitigate the high THC. This method is discussed in more detail later in this section.

The THC values obtained from gaseous oxygen (GOX) vapor samples show that the shortest dip tube, positioned at approximately the 85% liquid level in the run tank, became exposed due to LOX boil off 11 days after filling of the tank (Table 2) and had a measured THC value of 13.9 ppm. In a manner similar to the rise of the THC values in LOX, the GOX vapor values show a steady rise as the volume of LOX in the run tank decreases. The higher vapor values for dip tube 2 (LOX level 70%) compared to other dip tubes is not due to baffles or other obstructions on the inner tank walls since the tank wall is a smooth surface. At this time, the dip tube assembly is still in-place. At the end of testing the dip tube assembly will be removed from the run tank and examined for potential physical defects that may explain the THC vapor value differences at the 70% tank fill level.

Table 2. LOX Run Tank THC Values.

| Sample Date | Days from initial fill | DT 1 (Tank 85% Full)    | DT 2 (Tank 70% Full) | DT 3 (Tank 55% Full) | DT 4 (Tank 40% Full) | DT 5 (Tank 25% Full) | DT 6 (Tank 15% Full) | DT 7 (Tank 5% Full) | Tank Bottom |
|-------------|------------------------|-------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|---------------------|-------------|
| 03/12/15    | 0                      |                         |                      |                      |                      |                      |                      |                     | 35.4        |
| 03/16/15    | 4                      | 39.3                    | 38.5                 | 39                   | 40.6                 | 39.1                 | 39.2                 | 37.9                | 43.9        |
| 03/23/15    | 11                     | <b>13.9<sup>1</sup></b> | 40.1                 | 43.1                 | 41.3                 | 40.9                 | 41.1                 | 40.3                | 41.6        |
| 03/31/15    | 19                     | <b>15</b>               | <b>33.1</b>          | 39.3                 | 41.7                 | 40                   | 42.2                 | 40.1                | 52.4        |
| 04/06/15    | 25                     | <b>15.9</b>             | <b>32.7</b>          | 44.9                 | 43.1                 | 43.7                 | 43.8                 | 43.7                | 50.2        |
| 04/13/15    | 32                     | <b>17</b>               | <b>34.1</b>          | <b>16.8</b>          | 52.3                 | 48.7                 | 48.9                 | 50                  | 55.5        |
| 04/21/15    | 40                     | <b>18.9</b>             | <b>27.7</b>          | <b>19</b>            | 52.7                 | 52.8                 | 54.4                 | 52.8                | 65.5        |
| 04/27/15    | 46                     | <b>20.8</b>             | <b>27.1</b>          | <b>20.8</b>          | <b>20.6</b>          | 64.2                 | 66.8                 | 61.7                | 74.4        |
| 05/04/15    | 53                     | <b>23.2</b>             | <b>26.3</b>          | <b>23.4</b>          | <b>23.4</b>          | 69.6                 | 71.2                 | 73.7                | 88.7        |
| 05/11/15    | 60                     | <b>28.3</b>             | <b>34.3</b>          | <b>28.1</b>          | <b>28</b>            | <b>28.2</b>          | 95.3                 | 92.3                | 120         |
| 05/18/15    | 67                     | <b>36.7</b>             | <b>42.6</b>          | <b>36.3</b>          | <b>35.6</b>          | <b>36.3</b>          | <b>36.7</b>          | 132.4               | 135.1       |
| 05/26/15    | 75                     | <b>66.9</b>             | <b>68.6</b>          | <b>65.6</b>          | <b>67.5</b>          | <b>71.3</b>          | <b>72.5</b>          |                     | 362.3       |
| 05/29/15    | 78                     |                         |                      |                      |                      |                      |                      | 133                 | 699         |

<sup>1</sup> BOLD, underlined values are THC vapor values. All other values are THC liquid values.

As a check to ensure that the reported THC values were only methane, all Cosmodyne liquid samples were run on both the Rosemount THC Analyzer and the VICI HID Analyzer. The data showed agreement between the THC and methane values and confirms that the measured THC is, in fact, only methane. There is no data indicating the presence of any hydrocarbon heavier than methane in the samples run on the HID analyzer. Similar results were reported in the Air Products report<sup>2</sup>. The test

results for each analytical method are within the bounds of experimental error. Out of the 13 sample sets taken only 3 showed small differences between the reported THC and methane.

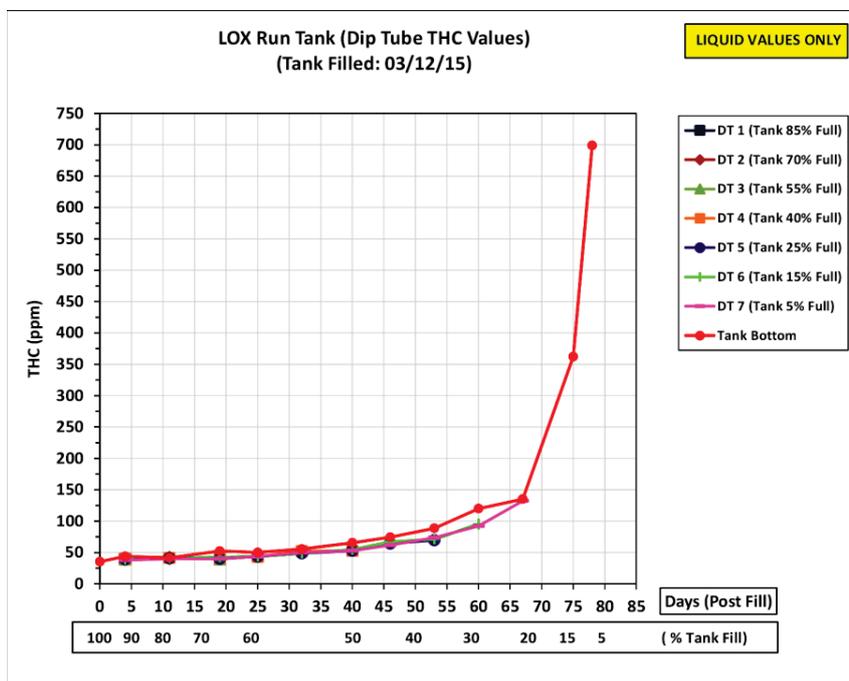


Figure 8. LOX Run Tank THC data (LOX sample).

One simple mitigation strategy to counteract rising THC levels in LOX is dilution. In theory, one should be able to decrease the concentration of the THC (solute) by simply mixing in more LOX (solvent). Mathematically this relationship can be shown in the Equation 1:

$$[(C_{1a} \times V_{1a}) + (C_{1b} \times V_{1b})] = C_2 \times (V_{1a} + V_{1b}) \tag{1}$$

- Where:
- $C_{1a}$  = Initial concentration or molarity (tank 1)
  - $V_{1a}$  = Initial volume (tank)
  - $C_{1b}$  = Added concentration or molarity (tank 2)
  - $V_{1b}$  = Added volume (tank 2)
  - $C_2$  = Final concentration or molarity (tank 1)

Table 3 shows the results when a known volume of LOX (low THC) is added to a LOX tank with a higher THC value. In both cases, the final THC tank value is lower than the initial THC tank value and very close to the predicted THC value. This dilution methodology has promise for mitigating rising THC values in LOX tanks. Both tanks in Table 3 are horizontal in design.

Table 3. THC Dilution mitigation results.

|        | Initial Volume (gallons) | Initial Volume THC (ppm) | Added Volume (gallons) | Added Volume THC (ppm) | Final Volume (gallons) | Final Volume THC (ppm) | Final Volume THC (ppm) [predicted] | % Diff (Predicted vs Measured) |
|--------|--------------------------|--------------------------|------------------------|------------------------|------------------------|------------------------|------------------------------------|--------------------------------|
| Tank 1 | 9800                     | 55.6                     | 12300                  | 18                     | 22100                  | 34.1                   | 34.7                               | 1.8                            |
| Tank 2 | 35400                    | 112.4                    | 12200                  | 57.1                   | 47600                  | 101.7                  | 99                                 | -2.7                           |

## 6. Conclusions

Several mitigations have the potential to lower the THC levels in LOX storage/run tanks to ensure that SSC customers obtain LOX whose THC levels are consistently below the 50 ppm allowable level.

SSC is currently working with the LOX vendor to ensure that the LOX delivered to SSC is well below the allowable level of 50 ppm and that the vendor THC analysis is not only accurate but close to the SSC analytical value. Starting with LOX that has a lower certified THC value will decrease SSC analysis time and provide an increased confidence level in the incoming LOX THC value.

Some of the data presented in this paper indicated that stratification may occur in LOX tanks. A lowering of the THC level by 6% in a LOX storage tank was observed when 10% of the LOX volume was dumped. Data from a LOX run tank (Figure 8) shows that when the tank volume is 20-40% full the THC level at the bottom of the tank is significantly higher than the remainder of the tank. This may also indicate stratification and imply that dumping a portion of the run tank may decrease the overall THC level. If there is stratification in a storage tank, an alternative to dumping the LOX may be to use some of the material at the bottom of the tank to chill run lines prior to the transfer of LOX to a run tank.

The method that seems to hold the most promise for mitigating high THC values in LOX tanks is dilution. It is clear that dilution of high THC LOX with LOX of a lower value will decrease the THC value in the final volume (Table 3). Further studies of this method in both horizontal (storage) and vertical (run) LOX tanks is needed to validate the dilution model. As an assist to engine test programs additional models are being tested that would take known THC data and project THC levels over time as LOX resides in either storage or run tanks. This modeling could indicate to test programs how long LOX could remain in storage/run tanks before the THC value exceeded allowable levels.

It should be noted that replicate testing of a LOX run tank is currently in progress to compare with the data presented in this paper.

## Acknowledgements

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