

Total Hydrocarbon Content (THC) Testing in Liquid Oxygen (LOX)

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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^{1,2,3}. 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 ppm². A potential issue is the ability to consistently meet the customer's maximum THC limit in Run Tanks. 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.

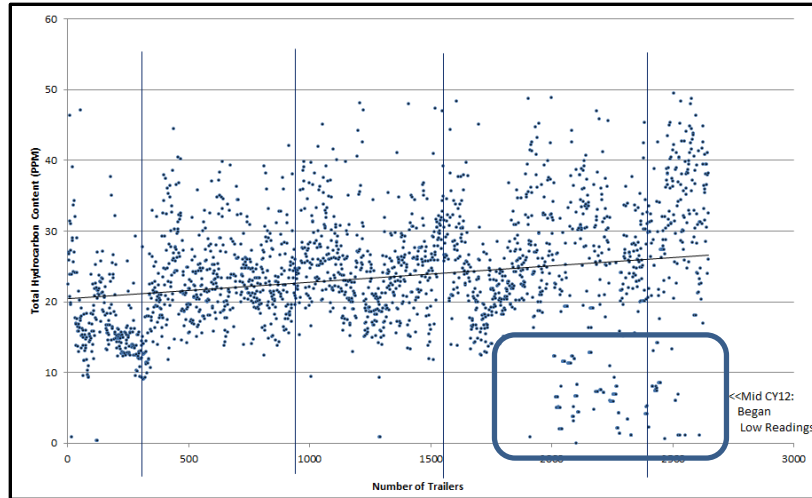


Figure 1. Vendor Certifications: LOX Trailer THC (July 2009) to Mid 2013

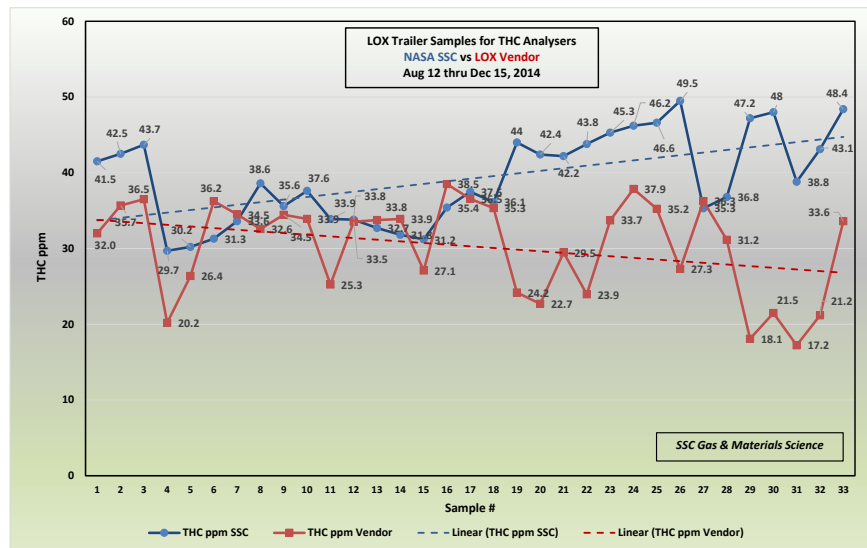


Figure 2 LOX Trailers Random Samples for THC (All trailers not sampled by SSC)

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 C₄⁺ hydrocarbons to very low levels during processing.

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 ppm⁴. Accounting for LOX vaporization, losses from handling/boil-off and the capabilities of LOX manufacturers, the 50 ppm limit for THC limit was established for LOX in 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 Kerry³ 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 levels⁵ by the time all the LOX had evaporated. However, the sharp hydrocarbon increase at end of curve shows that the rate of methane concentration may increase rapidly toward the end of evaporation period. During engine testing, the level of LOX in any run tank is never allowed to go below 25-30%. This would preclude using any LOX with THC levels above the 75 ppm limit.

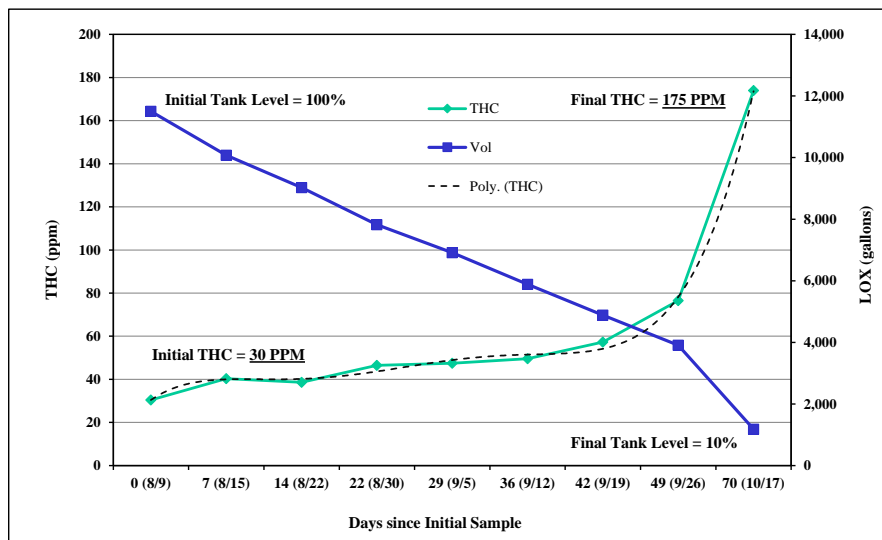
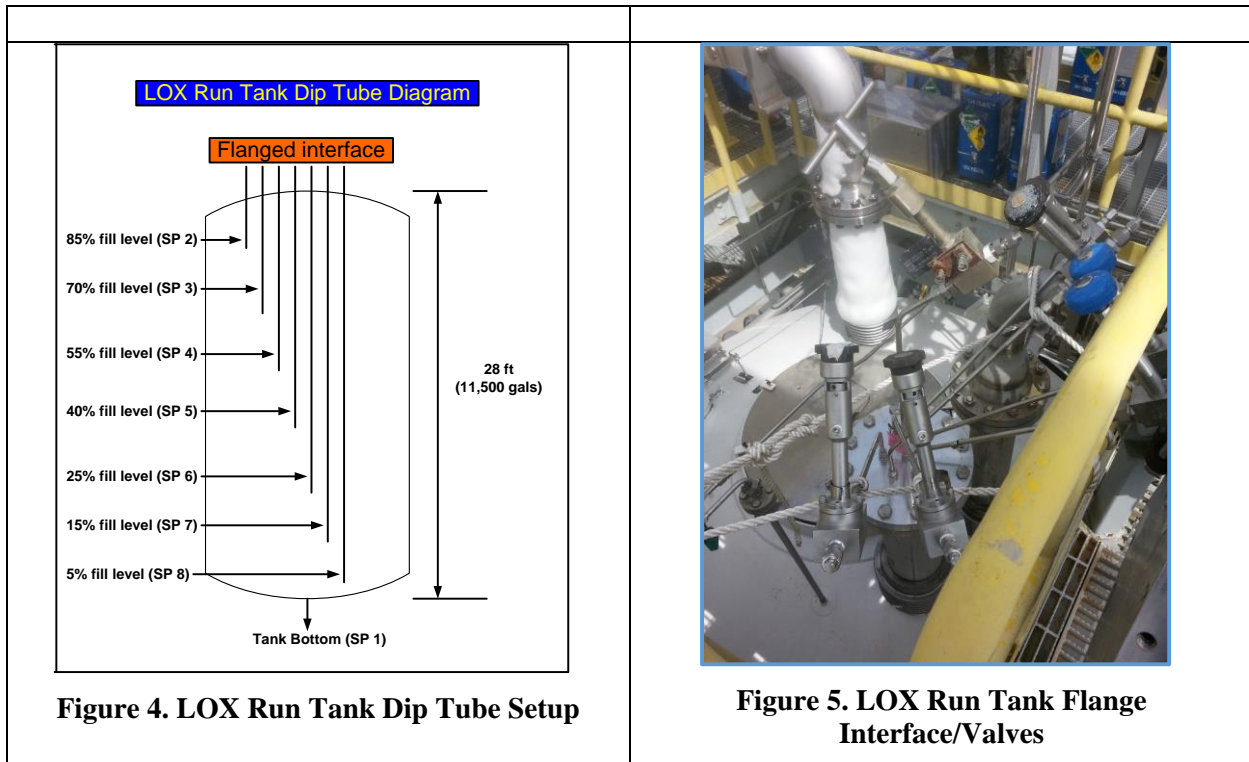


Figure 3 Actual LOX Run Tank Boiloff Test for THC Increase

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%¹. 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 pressurization of the tank in order to force liquid out the dip tubes would definitely stir up the liquid. This effect 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 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**. The flange was etched with sample point numbers for reference during the evaluation phase of the project.



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 5-10 psig GN₂ in order to force LOX through the dip tubes for capture by the Cosmodyne. Prior to pressurization, the tank vent was closed.



Figure 6. Cosmodyne Cryogenic Sampler

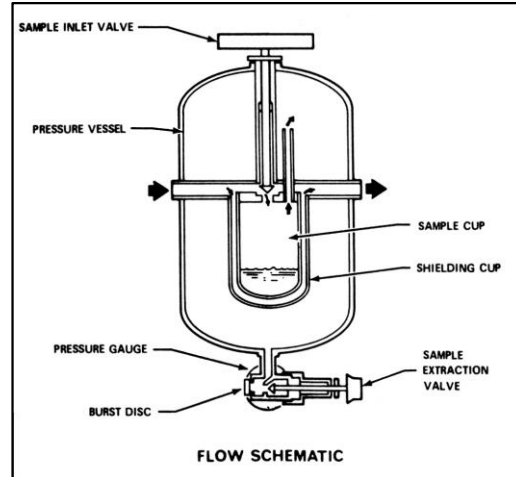


Figure 7. Cosmodyne Flow Schematic

All vapor samples were captured in evacuated 30 liter 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 melon was purged for 5-10 seconds prior to capture of any GOX vapor sample. If required during laboratory analysis, a metered amount of GN₂ was added to the melon in order to have adequate sample analysis pressure within the melon. The amount of nitrogen added to the melon 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. 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, melons and Cosmodynes were quickly transported to the SSC Gas and Materials Science Laboratory for analysis. All THC analysis were accomplished using a Rosemount 400A THC Analyzer equipped with a Flame Ionization Detector. The gas supplies were 40% H₂/60% H₂ fuel gas and Zero Grade Air (< 0.2 ppm THC) oxidizer. A 3 component mix (50 ppm methane, 1% Argon, balance Oxygen) National Institute of Standards and Technology (NIST) traceable standard was used as a calibration gas for samples with a THC value less than 50 ppm. For samples with THC values greater than 50 ppm, 100 ppm, 200 ppm, or 500 ppm calibration standards were used, as required. The analyses of CH₄ 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 also utilized an FID for sample analysis. The analyzer system from the vendor is proprietary in nature and no additional details are available.

Samples were taken on a weekly basis, weather permitting. A model was developed to predict the number of liquid/vapor samples for each test cycle based on the observed boil-off rate for the LOX run tank. Iterations of the model were completed that included small variations in the boil-off rate and consideration for the amount of LOX used during test cycles. The predictions for liquid/vapor samples using this model were compared to predictions based on tank volume data.

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. The sample sequence illustrated in **Figure 4** was always followed for any set of vapor or liquid samples. The sample from the bottom of the

run tank, SP 1, was always taken first in the liquid sample sequence as a direct comparison to previous THC sampling on the same LOX run tank.

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 highlighted in yellow 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 THC values in LOX samples are graphed in **Figure 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.

Table 2. LOX Run Tank THC Values

		THC Values (ppm) - ALL VALUES							
Sample Date	Elapsed Time From Initial Fill (Days)	DT 1 (85% Full)	DT 2 (70% Full)	DT 3 (55% Full)	DT 4 (40% Full)	DT 5 (25% Full)	DT 6 (15% Full)	DT 7 (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	13.9	40.1	43.1	41.3	40.9	41.1	40.3	41.6
03/31/15	19	14.97	33.12	39.3	41.7	40	42.2	40.1	52.4
04/06/15	25	15.9	32.7	44.9	43.1	43.7	43.8	43.7	50.2
04/13/15	32	17	34.1	16.8	52.3	48.7	48.9	50	55.5
04/21/15	40	18.9	27.7	19	52.7	52.8	54.4	52.8	65.5
04/27/15	46	20.8	27.1	20.8	20.6	64.2	66.8	61.7	74.4
05/04/15	53	23.2	26.3	23.4	23.4	69.6	71.2	73.7	88.7
05/11/15	60	28.3	34.3	28.1	28	28.2	95.3	92.3	120
05/18/15	67	36.7	42.6	36.3	35.6	36.3	36.7	132.4	135.1
05/26/15	75	66.9	68.64	65.59	67.46	71.3	72.46		362.3
05/29/15	78							133	699

NOTE: Values in Yellow are from Vapor samples

The THC values obtained from gaseous oxygen (GOX) vapor samples are shown in **Figure 9**. 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**). The measured THC value in the GOX sample was 14 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 separation of dip tube 2 (LOX level 70%) vapor values from 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.

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 in **Figure 10** shows 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 report². 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. No CH₄ values were available for samples taken 32 days after the initial fill since the sample analyzer was off-line. In addition to the requirement for THC values, measured as methane, to be less than 50 ppm, the minimum purity specification for LOX is 99.6%. The measured purity values have all been 99.9%+.

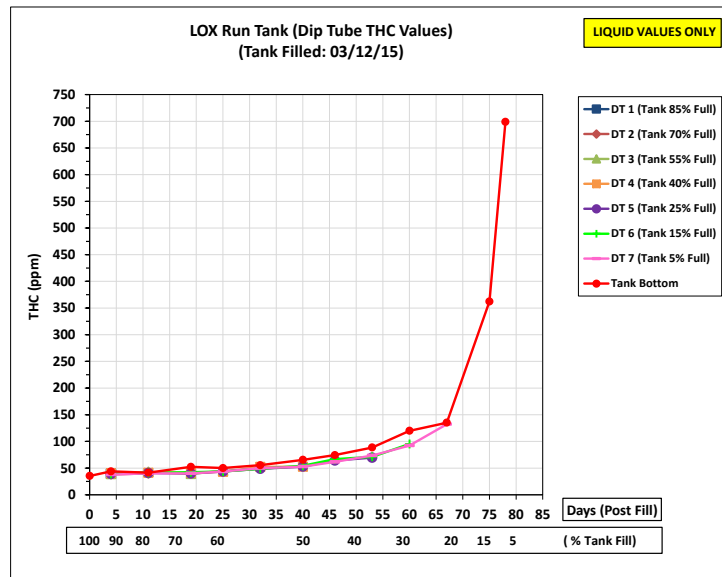


Figure 8. LOX Run Tank THC data (LOX sample)

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:

$$C_1 \times V_1 = C_2 \times V_2 \quad (1)$$

Where: C₁ = Initial concentration or molarity
V₁ = Initial volume
C₂ = Final concentration or molarity
V₂ = final volume

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 value is lower than the initial tank value and very close to the predicted THC value. This dilution methodology has promise for mitigating rising THC values in LOX tanks.

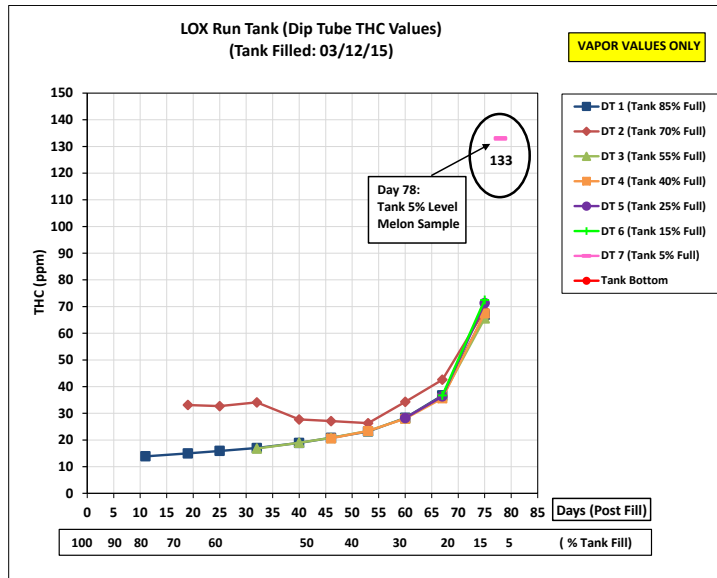


Figure 9. LOX Run Tank THC Data (GOX sample)

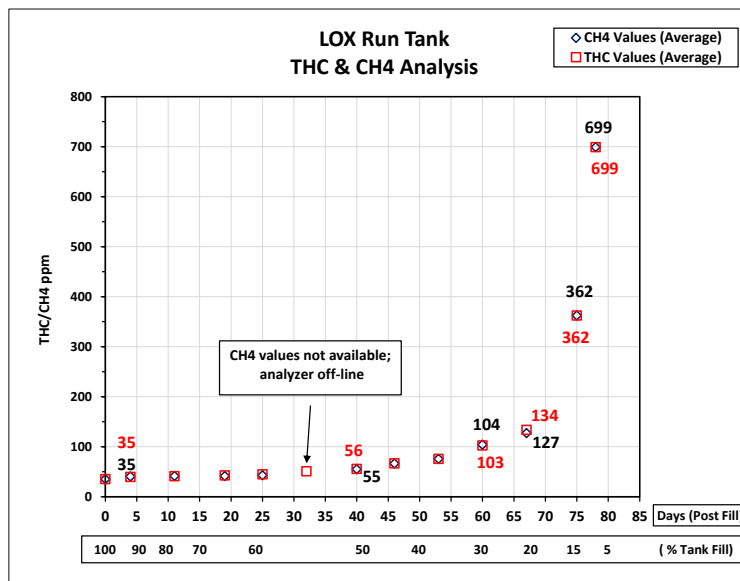


Figure 10. LOX Run Tank (THC & CH₄ Comparison)

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 (Horizontal)	9800	55.6	12300	18	22100	34.1	34.7	1.8
Tank 2 (Horizontal)	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. At present, the vendor is producing LOX with a certified THC level that is less than 30 ppm. This value is more in line with historical THC values. 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.

7. Acknowledgements

The authors wish to thank SSC LOX test stand personnel, the SSC Gas & Materials Science Laboratory, SSC LOX sampling personnel, the SSC Chief Engineer's Office, and all members of the THC Testing in LOX team for their valuable guidance and assistance in making this study possible.

8. References

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