
DRI STANDARD OPERATING PROCEDURE

Trace Oxygen Level Measurement in Helium Atmospheres of DRI Model 2015 Thermal/Optical Carbon Analyzers by LD8000 Trace Impurity Analyzer

DRI SOP #4-119r0

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1. GENERAL DISCUSSION

1.1 Purpose of procedure

Thermal/optical carbon analyses are first performed under an inert helium atmosphere to evolve organic carbon (OC) then switched into oxidative atmosphere (98% helium/2% oxygen) to evolve elemental carbon (EC). The presence of oxygen in a helium atmosphere can interfere with carbon analysis. Oxygen levels >100 ppm can evolve carbon at lower temperatures and potentially evolve EC in helium atmospheres, causing underestimation of EC measurement.

This document describes Standard Operating Procedures (SOPs) for the measurement of trace oxygen levels. Trace oxygen are measured on DRI Model 2015 thermal/optical carbon analyzers every 12 months to monitor for system leaks, contamination in helium supply, faulty valves and fittings, and desorption from analyzer components. The procedures described here serves as an evaluation of the reliability of the analyses performed on the carbon analyzers.

1.2 Measurement principle

Trace oxygen measurements are performed using the LD8000 Multigas Trace Impurity Analyzer (LDetek, Thetford Mines, Qc, Canada). This analyzer uses a NTRON SENZTX-200 electrochemical sensor for O_2 measurement based on a potentiometric method. The key elements of the electrochemical sensors are a membrane, cathode, anode, electrolyte, and measurement circuit. The sensing membrane (covering the cathode) is made of PTFE and is mounted over a metal perforated electrode. The space between the membrane and the electrode is filled either with an aqueous alkaline or an acid electrolyte. In normal operation, all portions of the anode and cathode are immersed in the electrolyte. As oxygen diffuses through the membrane into the electrolyte, it causes a reaction between the cathode and anode generating an electromotive force. This current is proportional to the amount of oxygen present in the sample gas. In the absence of oxygen, there is no output from the electrochemical sensor, meaning only one calibration is required.

1.3 Measurement interferences and their minimization

Oxygen in air is the potential interference to O_2 measurement. To minimize this interference, the analyzer should be purged with ultra-high-purity (UHP) helium for at least 24 hours.

1.4 Ranges and typical values of measurements

The NTRON SENZTX-200 sensor has a measurement range of 0-1000 ppm. The O_2 concentration in the carbon analyzers should be ≤100 ppm.

1.5 Typical minimum detection limits, precision, and accuracy

The NTRON SENZTX-200 sensor has a minimum detection limit (MDL) of 0.1 ppm and its accuracy is specified at within ±1% of the full scale.

1.6 Responsibilities of personnel for carrying out portions of this procedure

All managers, technicians, and analysts involved in trace oxygen measurements should read and comprehend the entire SOP. The procedures are outlined in the latest version of this SOP.

The technician or analyst is responsible for: 1) properly operating and calibrate the analyzer; 2) measuring O_2 concentrations in carbon analyzers; and 3) documenting measurement results.

The laboratory manager is responsible for: 1) ensuring understanding and compliance of SOP by laboratory personnel; 2) ensuring O_2 measurement is done within required time frame; 3) verifying recorded values; and 4) ensuring the QA records have been backed up to the server.

The EAF quality assurance (QA) officer is responsible for: 1) ensuring that proper O_2 calibration gases are available for analyzer calibration, 2) evaluating and validating the data acquired, 3) evaluating potential impacts to data if O_2 exceeded the specified limit, 4) ensuring corrective actions are taken to maintain carbon analyzer O_2 concentration < 100 ppm; and 5) maintaining a calibration record for each carbon analyzer.

1.7 Definitions

The following definitions are used throughout this SOP:

- MDL=Minimum Detectable Limit, the lowest value at which a valid response can be detected by the procedure.
- Precision=The repeatability of measurements for the same sample, as determined from replicate analysis and propagation of errors.
- Accuracy=Deviations from independent quality auditing standards or standard reference materials.
- Calibration standard=mix gas containing trace oxygen of known concentrations

2. APPARATUS, INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus and instrumentation

Trace oxygen measurements are conducted using the LDetek LD8000 Trace Impurity Analyzer. A NTRON SENZTX-200 electrochemical sensor is used for O_2 measurement. This sensor was calibrated by the manufacturer for measuring oxygen in helium. The electrochemical sensor has a nominal shelf life of one year according to the manufacturer. To lengthen the sensor life, the sample inlet and detector vent of the analyzer should be capped. The sensors should be calibrated before use to ensure that it is still accurate.

2.2 Spare/replacement parts list

The following parts are used in O_2 measurement with the LDetek LD8000:

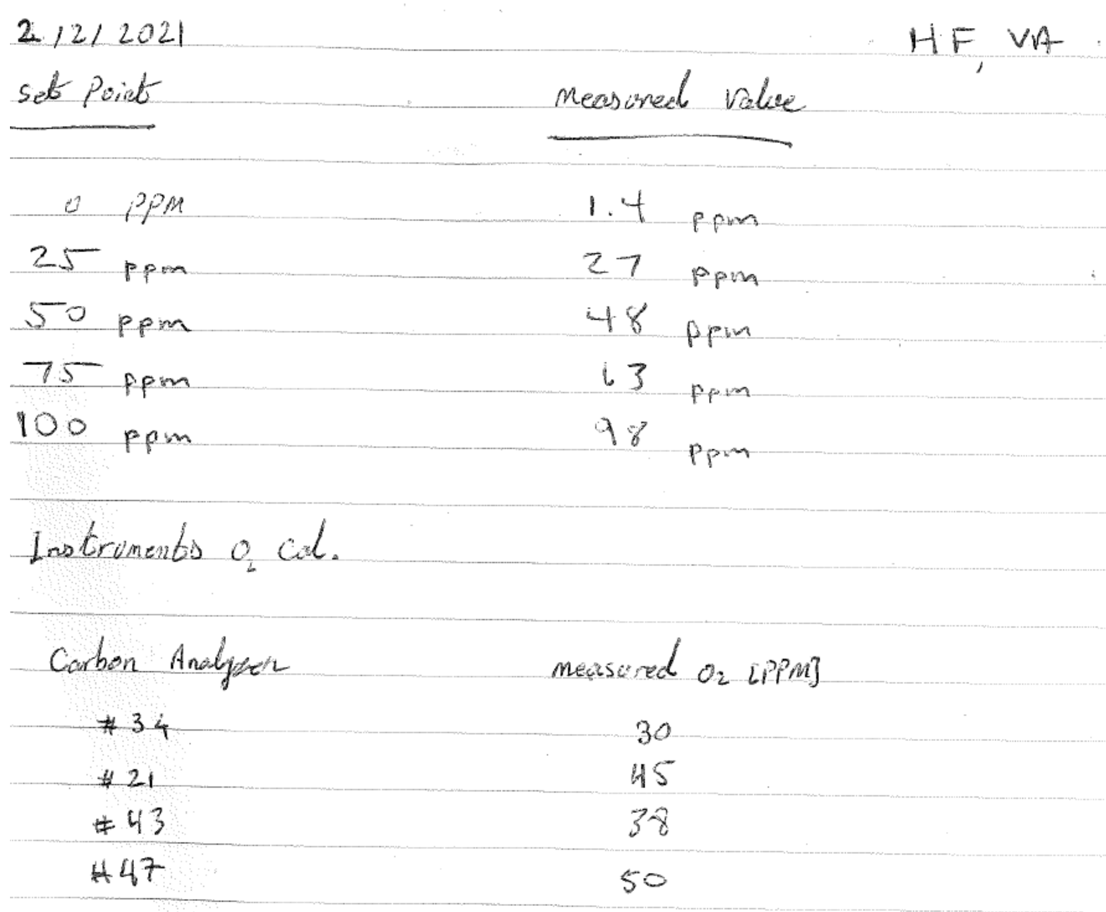
- NTRON SENZTX-200 electrochemical sensor
- LDH2O-T moisture trap
- Three-way valve
- Metering valve
- 1/8" Teflon tubing and 1/16" stainless steel tubing
- Injection septa- Thermogreen, LB-1 cylindrical injection septa, 6mm x 9mm (Sigma-Aldrich, St. Louis, MO, SKU: 20668).

2.3 Regents

- Ultra-high-purity (UHP) helium as the zero gas
- Calibration gas of O_2 (25, 50, 75, and 100 ppm) in helium, for example
  - Airgas 103L-M8-25P
  - Airgas 103L-M8-50P
  - Airgas 103L-M8-75P
  - Airgas 103L-M8-100P

2.4 Forms, Paperwork, and Logbook

Sensor calibration and carbon analyzer O_2 concentration measurement are recorded in the laboratory logbook as shown in Figure 2-1.



2/12/2021 HF, VA

Set Point	Measured Value
0 ppm	1.4 ppm
25 ppm	27 ppm
50 ppm	48 ppm
75 ppm	63 ppm
100 ppm	98 ppm

Instruments O_2 Cal.

Carbon Analyzer	measured O_2 [PPM]
#34	30
#21	45
#43	38
#47	50

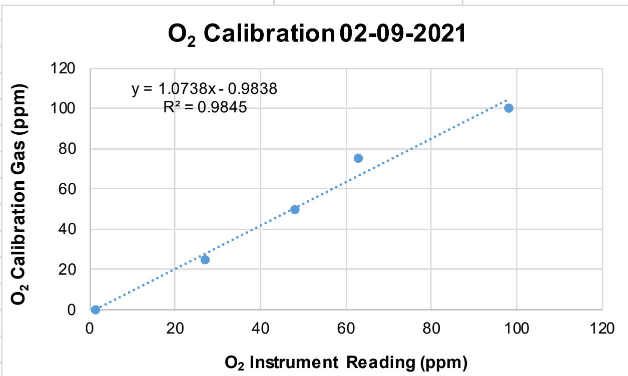
Figure 2-1. Laboratory logbook recording of LDetek LD8000 O_2 sensor calibration and carbon analyzer trace level O_2 measurement.

The calibration data are then entered into an Excel file named by the calibration date under the folder \\eaf-srvr19-file\EAFSQL\2015 Carbon Analyzers\O2 Testing. An example of the data entry sheet is shown in Figure 2-2.

Instrument Name & Model:	LD8000 Trace Impurity Analyzer
O2 Instrument Calibration Date:	2/2/2021
Calibrated By:	HF, VA
O2 Testing Date:	2/2/2021
Tested By:	WR, HF

Calibration Gas Part#	Calibration Gas (ppm)	O2 Instrument Reading (ppm)
	0	1.4
	25	27
	50	48
	75	63
	100	98

y-intercept:	-0.98
slope:	1.07



CA#	CA Reading (ppm)	Calibrated Value (ppm)
21	45.00	47.34
31	N/A	N/A
32	N/A	N/A
34	30.00	31.23
35	N/A	N/A
36	N/A	N/A
37	N/A	N/A
38	N/A	N/A
40	N/A	N/A
41	N/A	N/A
42	N/A	N/A
43	38.00	39.82
47	50.00	52.71

Figure 2-2. An example of the Excel spreadsheet with O_2 sensor calibration and carbon analyzer trace level O_2 measurements. The orange cell shows where data should be entered.

3. PROCEDURES

3.1 Calibration setup

The experimental setup is schematically shown in Figure 3-1 and the setup pictures are shown in Figure 3-2. The UPH gas tank and the O_2 calibration tank are connected to a 3-way valve. The calibration pressure is regulated to 1-15 PSIG (recommended 5 PSIG). The flow passes through the moisture trap and enters the sample inlet port of the LD8000 analyzer. The detector vent flow is connected to the Drycal flowmeter to measure total flow rate.

After the setup is complete, use a helium leak detector to check all connections to make sure that there are no leaks.

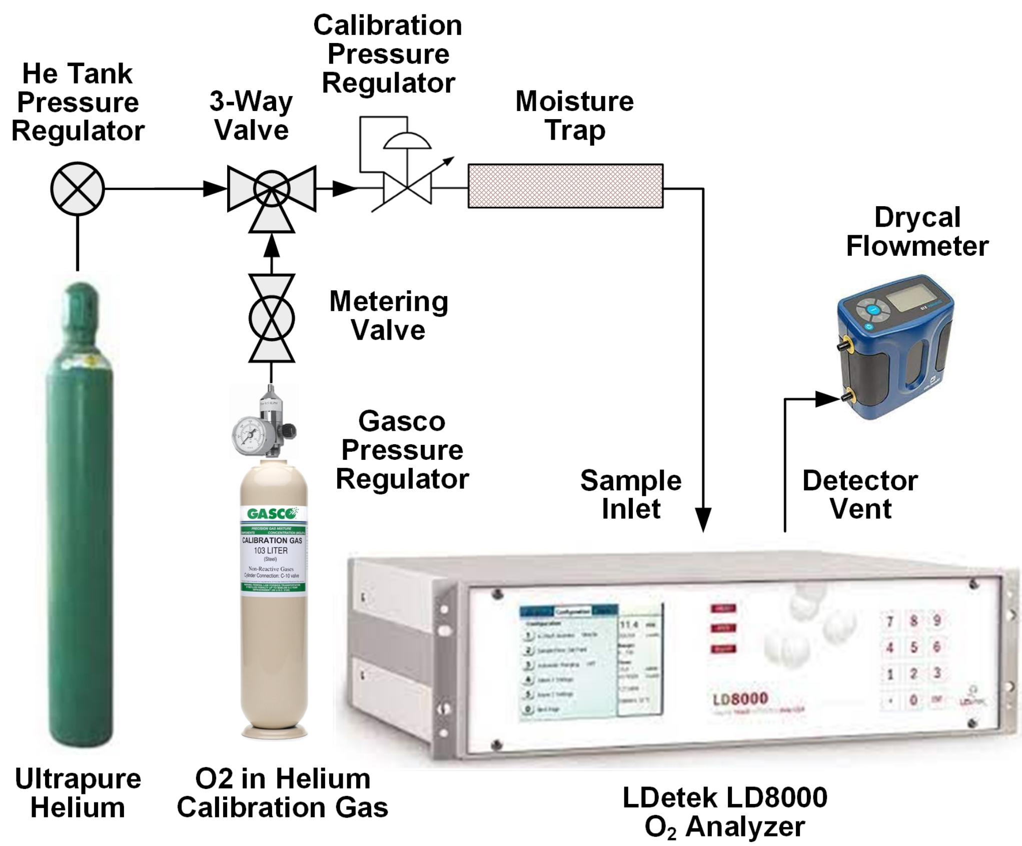


Figure 3-1. A schematic diagram of O_2 analyzer calibration setup.

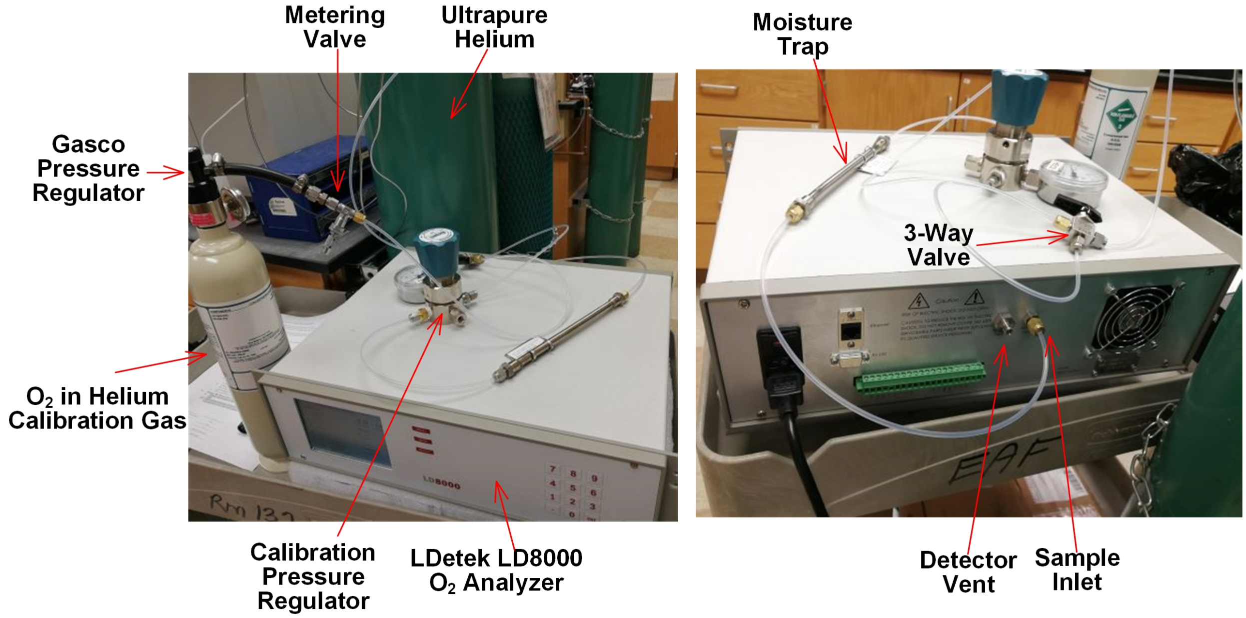


Figure 3-2. Pictures of the O_2 analyzer calibration setup (the Drycal flowmeter was not connected).

3.2 Flow and pressure conditions

Sample flow: 15 sccm (min) - 200 sccm (max), 100 sccm (recommended)
Calibration regulator pressure: 1 PSIG (min) – 15 PSIG (max), 5 PSIG (recommended)
Do not pressure the LD8000 to >15 PSIG to prevent instrument damage!

3.3 Calibrating LD8000 Trace Impurity Analyzer

To minimize O_2 intrusion into the calibration system and reduce purging time, steps 2-5 below need be performed quickly.

1) Set the calibration pressure regulator to 0 (loosen all the way).
2) Loosen the cap on the LD8000 sample inlet port and connect it to the tube coming out of the moisture trap.
3) Turn the 3-way valve so it is getting its input from the UHP He tank. Make sure the flow rate is set to 0 on the Gasco regulator connected to the 103-liter O_2 calibration gas tank, and the metering valve is fully closed.
4) Open the UHP He tank and set the tank regulator output pressure to ~10 PSIG. Make sure the pressure regulator reading is zero.
5) Remove the cap on the LD8000 detector vent port, and immediately set the calibration pressure regulator to 5 PSIG.
6) Turn on the power of the LD8000, and check that the flow is set to 100 cc/min (default). Verify that the flow is ~100 cc/min with the Drycal connected to the detector vent, and then disconnect the Drycal.

7) Leave the analyzer under purge for 24 hours or more to bring the reading down to near zero. The analyzer power can be turned off to eliminate the pump noise. Note: Pressurizing the instrument will cause damage, so verify the detector vent is open and monitor the pressure regulator to keep it at about 5 PSI.
8) On the following day after the LD8000 was turned on, verify zero counts against previous calibrations. For reference, the zero count was 3565250 when the analyzer was shipped by the manufacturer on October 1, 2020.
9) Once the O_2 reading has stabilized, select the "Set Zero" button, set zero to 0.1, and press accept.
10) Push the "ReZero" button to re-zero instrument, which takes 10-15 minutes. After the re-zero is completed, accept changes.
11) Press the "Set Span" button to 100 and save.
12) Connect the 100 ppm O_2 standard to the instrument, set the Gasco pressure gauge flow to 0.3 LPM, open the metering valve, and turn the 3-way valve so the input is from the 100 ppm O_2 standard. On the LD8000 screen, an initial spike in the O_2 reading or even saturation may appear before it stabilizes close to 100 ppm. Once it is stable, press the "ReSpan" button. Wait approximately for 15 minutes till it complete and then accept changes.
13) Now the LD8000 is ready for calibration verification. Turn the 3-way valve back to the UHP He tank to get the zero point. Record instrument reading (ppm) in the lab notebook (Figure 2-1).
14) Connect the 25 ppm, 50 ppm, 75 ppm, and 100 ppm calibration tanks one by one and record the instrument reading in lab notebook. Once completed, transcribe data into the spreadsheet for electronic records (Figure 2-2).
15) Plot a calibration curve on the spreadsheet and obtain the regression slope and intercept (Figure 2-2).

3.3 Testing DRI Model 2015 Carbon Analyzers for O_2

1) Connect the 25 ppm O_2 standard to the LD8000 analyzer and direct the 3-way valve to that tank. Flow is set to 0.3 LPM and the metering valve is open.
2) Turn off the power to the LD8000 analyzer. Close off the helium tank and disconnect the helium tank line from the 3-way valve. In its place, connect the 1/8" sample tubing with needle (Figure 3-3a).
3) Move the calibration cart to be close to a carbon analyzer. Turn on the power to the LD8000 analyzer.
4) Place the needle into the inject port of the DRI Model 2015 Carbon Analyzer.
5) In the calibration screen of the carbon program, set instrument flows to 80 cc/min for He1, 40 cc/min for He2, and 0 for He/O_2. Leave the back valve open and front valve closed.

6) Switch the 3-way valve to take gas from the carbon analyzer, set the Gasco regulator flow to 0, and turn off the metering valve.
7) Make sure the carbon analyzer pressure is >3 PSIG and verify that the flow is ~100 cc/min at the LD8000 detector vent port using a Drycal.
8) After the O_2 reading on the LD8000 analyzer stabilizes, record the reading in both laboratory notebook and spreadsheet for electronic records (Figure 2-1 and Figure 2-2). Verify that the calibrated value is <100 ppm (Figure 2-2).
9) After O_2 measurement is completed at a carbon analyzer, switch the 3-way valve to the 25 ppm standard gas tank; set the Gasco regulator flow to 0.3 LPM, and turn on the metering valve. Disconnect the needle from the carbon analyzer, and re-install the septa on the analyzer injection port. Reset the flow to default values: He1: 40 cc/min, He2: 10 cc/min, and He/O2: 10 cc/min. Verify that the carbon analyzer flows and pressure are within specification.
10) Repeat the steps above to measure O_2 from all carbon analyzers that are due for O_2 measurement.
11) After measurement is completed for all analyzers, turn off the LD8000 power and cap both sample inlet and detector vent ports to prevent O_2 intrusion.

(a) Probe connected to the carbon analyzer **(b) Setup to measure O_2 level in carbon analyzer**

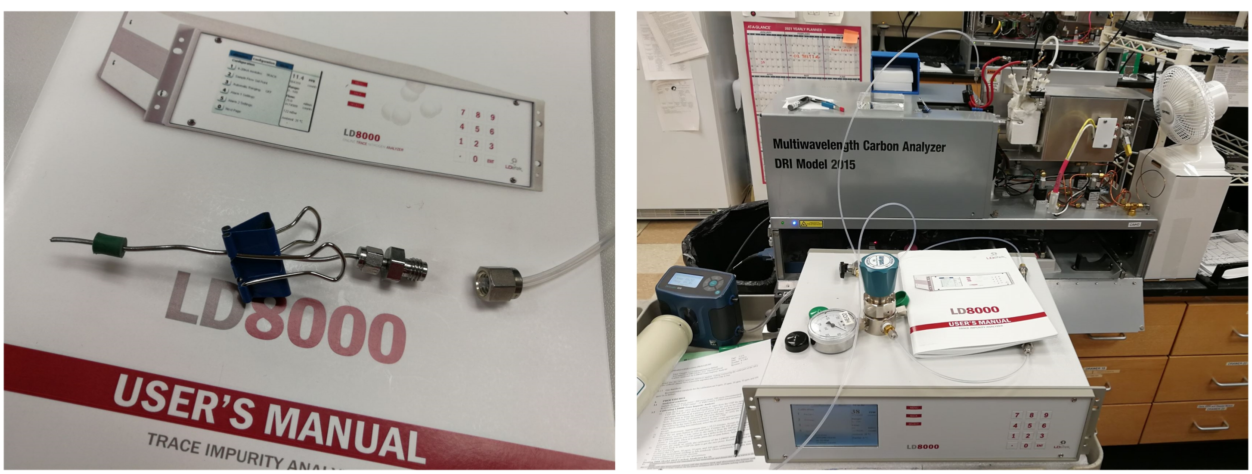


Figure 3-3. Pictures of: (a) probe connecting LD8000 to carbon analyzer; and (b) measurement of trace level O_2 in a carbon analyzer.

4. QUANTIFICATION

4.1 LD8000 O_2 sensor calibration

Results from the calibrations are summarized in an Excel plot with the standard gas concentration on the y-axis and LD8000 analyzer reading on the x-axis (Figure 2-2). A linear regression line fits through the data points to obtain the slope, intercept, and coefficient of determination (R^2). A calibration with $R^2 < 0.95$ is rejected and the calibration is redone.

4.2 Calculations

Results from the oxygen testing of the DRI Model 2015 Carbon Analyzers are input into the Excel spreadsheet with the calibration curve (Figure 2-2). The raw analyzer readings are converted to calibrated values using the linear regression equation. Calibrated values must be below the acceptance criteria of 100 ppm for the carbon analyzer to pass.

5. REFERENCES

- LD8000 Trace Impurity Analyzer User's Manual

6. CHANGE DOCUMENTATION

- 9/21/2021: New SOP 4-119r0