WBEA – Standard Operating Procedure

SOP Title	**Procedures for operating continuous Methan/Non-Methane Hydrocarbon analyzers**
SOP Number	**WBEA SOP-ANA-008 NMHC**
Author	**Kelly Baragar**
Implementation date	**February 19, 2013**

Revision History

Revision #	Date	Description	Author

Table of Contents

Introduction and Background

This document is intended to be used as a reference for use in the calibration, maintenance and operation of continuous analysis of Non-Methane Hydrocarbons in ambient air. The proper utilization of this procedure in conjunction with the operators manual will conform to the current Alberta Air Monitoring Directive (AMD) and enable the data to be included in provincial and national air quality data bases

Principle of the Method

Non-methane hydrocarbon gases are measured using a gas chromatograph column system specifically designed for this application. The only NMHC analyzer make currently in use by WBEA is the TECO 55i. The Thermo Electron Corporation (TEI) Model 55i analyzer is an automated batch analyzer that continuously collects and analyzes small amounts of ambient air. The sample is drawn into the analyzer by a pump and through a system based around an 8-port, two position rotary valve. There are two valve positions or modes, which are referred to as the "Inject" and "Backflush". The cycle starts with the Backflush mode. The sample is drawn into the sample loop (a coil of empty tubing) (see Figure 1.1). The rotary valve now switches to the INJECT position (see Figure 1.1). The valve connects the sample loop to the column and the sample is pushed through the column by the carrier gas. Since the methane component of the gas is lighter (low molecular weight), the methane moves quicker through the column and goes out the column through the rotary valve to the flame ionization detector (FID) for analysis. Once the methane has been detected by the FID, the rotary valve then reverses, returning to the BACKFLUSH mode. The heavy hydrocarbons that are left in the column are now pushed in the reverse direction by the carrier gas through the rotary valve to the FID for analysis. This completes the sample gas cycle. Figure 1.2 shows a typical chromatogram as seen with calibration gas being injected into the analyzer. The graph is showing Volts (vertical) and Time (horizontal) and is connected to the FID output of the analyzer. Calibration gases suggested by the manufacturer are methane (CH_4) and propane (non-methane – C_3H_8). The time required for the analysis of one sample is about 70 seconds but is configurable via the analyzer menu.

Figure 1.0: Rotary Valve

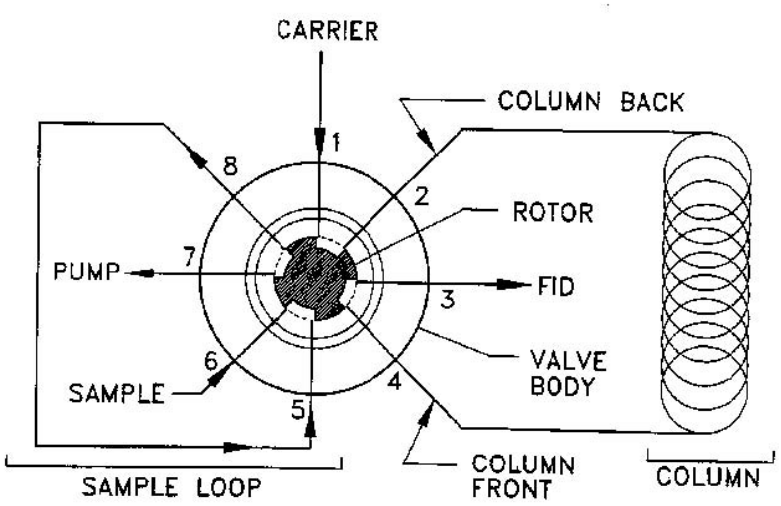


Figure 1.1: Backflush and Inject Positions

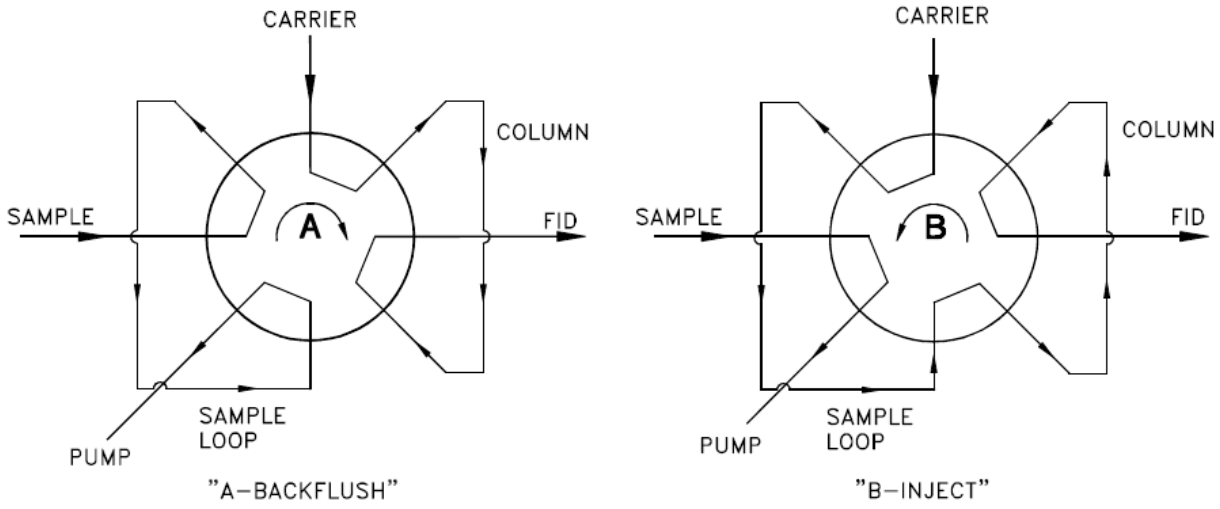
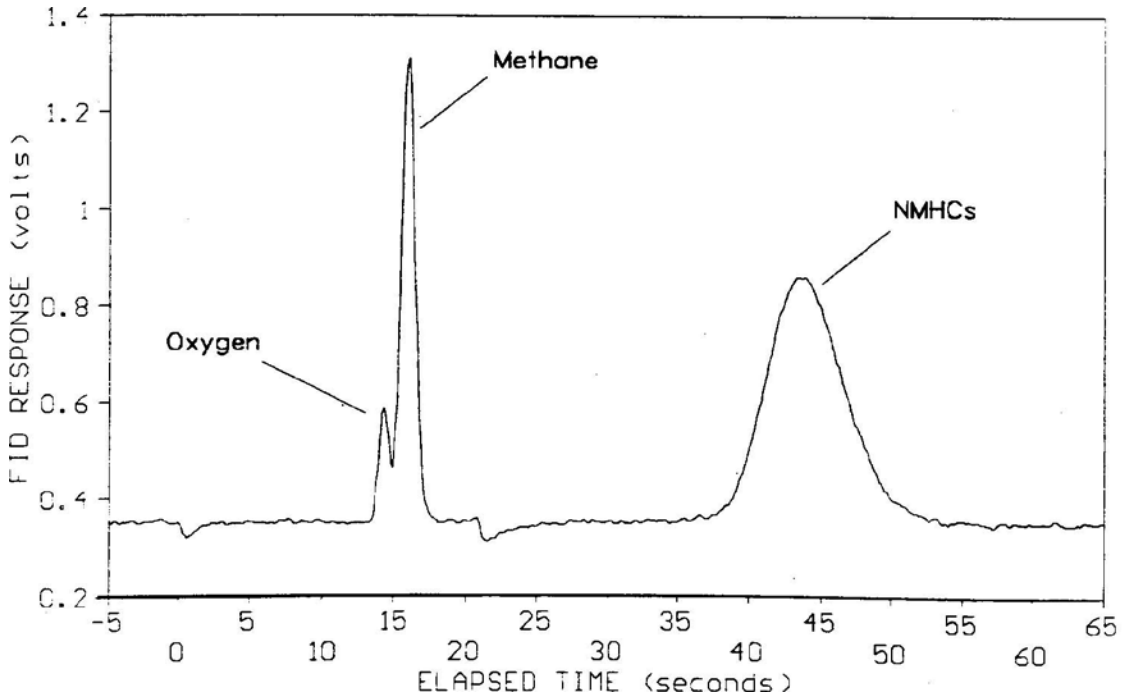


Figure 1.2: Typical baseline FID response



Measurement Range and Sensitivity

The NMHC analyzer used in this method are commercially available models. The range is set by factory based on the sample loop requested and is 0 to 100 ppm for THC and 0 to 50 ppm for CH_4 and NMHC within the WBEA network.

The detection limit of the analyzer is specified by the manufacturer and specific settings applied to the analyzer when placed in the field. This is also governed by the noise level of the output signal, whether analog or digital. Two times the noise level is generally accepted as the lower detectable limit (LDL); the manufacturer states it to be at 20 ppb for CH_4 and 50 ppb for NMHC as Propane based on optimum operating conditions.

Equipment and Apparatus

NMHC analyzers in use are all AMD compliant monitors including the TEI 55i.

The design of the analyzer requires the use of support gases. WBEA network analyzers are integrated with hydrogen for fuel, a zero air source (generator) for FID supply air, Nitrogen (N_2) for carrier gas, and a pressurized air source for actuator control. All cylinders utilized for the network are rated Ultra High Purity (UHP). Refer to the respective operating manuals for specifics regarding setup and settings of the support gases as required.

Interferences

As this system is GC based, any compounds detectable by the FID are typically retained on the column and then flushed off the column during the backflush cycle.

Particulate matter may interfere with analyzer response. This problem is normally eliminated by using a particle filter of 5.0µm pore size made of inert material, such as Teflon, at the sample inlet of the instrument.

Precision and Accuracy

The measurement precision is generally considered to be the “repeatability of the measurement”. Precision of the data output by the analyzer is established by the manufacturer, but confirmed during daily span checks and monthly calibrations.

The accuracy of the sensor is generally considered the “deviation from true”. This means how close it is to what it should be. The benchmark of “what it should be” is provided by the Alberta Environment Audit Program staff and the use of high quality standards such as available from the National Institute of Standards and Technology (NIST). As with precision, accuracy is confirmed by the daily span and monthly calibration checks. Refer to the sections identified above for further information on accuracy relating to calibration and audit procedures.

Site Requirements

All THC analyzers are housed in a temperature controlled ambient air monitoring shelter in a standard instrument rack. Sample air is brought into the shelter using a glass sample inlet system and made available to the THC analyzer. The station is sited according to appendix A-2, Station Site Criteria section of the AMD. Site location for THC monitoring should be determined according to the intended application of the monitoring data.

Installation Requirements

All the installation requirements are specified by the manufacturer in the installation procedures of the manual. General requirements listed below must also be followed:

- The ¼ inch outside diameter connection tubing from the manifold to the analyzer inlet must be made of Teflon or equivalent material for chemical inertness.
- A Teflon particulate filter with a pore size of no larger than 5.0µm must be placed in the sampling line before the air sample enters the detection cells and is recommended to be located as close as possible to the inlet manifold. The holder for such filter must also be made of Teflon, Stainless Steel or Delrin.
- A data acquisition system (DAS) should be connected to the analyzer to record or download the signal output from the analyzer. For connection to record analog voltage signals, the system should be set to match the voltage range of the analyzer output. In the WBEA network the standard is 5V full scale and is scaled to convert the output signal to the concentration range outlined in section 3. For serial or LAN connection there must be a station router in place and configurations made to the analyzer settings, the router, and the data logger. See the DAS operations manual for instructions on configuring these channels.
- The monitoring station temperature should be controlled within the range of 15 to 30°C. It is important to note that the analyzer will operate properly at any temperature within this range; however, the stability of the station temperature is most important.
- Range Set – the range is factory preset to 0 to 100 ppm for THC and 0-50 ppm for CH4 and NMHC based on the sample loop size.

Operational and Maintenance Requirements

The following activities must be performed when operating a continuous automated NMHC analyzer in Alberta. All operational activities conducted at any ambient monitoring station must be documented in the Doc-It system. This allows other operators to access a history of the station if the regular technician is not available. The following documentation must be available to the operators on site: operational and maintenance manual(s), quality system manual and station site documentation.

Daily Requirements

Zero/Span Check – a zero/span cycle is required every day to verify the analyzer's performance. This involves diverting the sample flow of the analyzer so that the analyzer subsequently samples zero air for the zero cycle and air with a known amount of CH_4 and C_3H_8 for the span cycle. These two sources are provided by the in-situ calibration system. A zero air point of dilution air only is generated through a saved sequence in the calibrator, and span is generated by a saved calibration point in the calibrator, typically the high point of the routine multipoint calibration sequence. This cycle is controlled by the

data system in the station, as it also flags the collected data as calibration and not sample data. The DAS is programmed to close contacts that are connected to the sample/span solenoid contacts on the analyzer. During the daily zero/span cycle WBEA runs zero for twenty minutes to ensure stability, followed by a twenty minute span. The remaining twenty minutes of the hour is flagged down as Ambient Return to ensure data recorded as the analyzer returns from span to stable ambient readings won't be misinterpreted. Refer to the analyzer manual for more information.

Analyzer Test Parameters

The analyzer monitors and displays test functions in order for the operator to monitor the performance of specific systems within the analyzer. These test parameters should be recorded digitally via DAS collection or documented on calibration reports. Support gasses of Hydrogen and Nitrogen (and in some cases compressed dry air) are also required for the operation of these analyzers. Pressures of these cylinders in the WBEA network are monitored and alarmed digitally so that cylinders are changed before they run empty. It is necessary for continuous data and the proper maintenance of NMHC analyzers to change the cylinders once they drop below required levels.

Inlet Filter Change

The sample inlet filter is typically replaced when the monthly multipoint calibration is being done. The filter change is completed after the as found points have been completed and before the multipoint calibration is carried out. This is done to establish a reference prior to the removal of the filter.

Analyzer Maintenance

Preventative maintenance tasks should be completed on the analyzer on a periodic basis. These tasks are outlined in the operations manual. A strict regiment of these tasks should be adhered to as they are intended to fix a problem before it happens. Any maintenance must be recorded in the Doc-It system. This is also recorded in the instrument log that accompanies each instrument.

Multipoint Calibration

Multipoint calibrations are conducted on the NMHC analyzer to verify precision, accuracy and linearity of the instrument. This procedure must be completed after the analyzer has been installed following at least a 24 hour warm up period, prior to removal, and monthly to comply with Alberta Environment regulations. This procedure is also completed before and after any major maintenance to confirm the precision and accuracy after repairs. The calibration standard for the WBEA network utilizes a blend of methane and propane for calculation of a THC response.

Analyzer Audit

NMHC analyzers operating in Alberta are required to undergo an on-site audit once per year. This audit involves the Alberta Environment Audit Program staff visiting the site with the NIST traceable standards to verify the accuracy and linearity of the instrument.

Calibration Requirement

The calibration procedure for NMHC analyzers is similar to calibration of other continuous ambient air analyzers. This procedure involves generating a known amount of CH_4/C_3H_8, which is introduced to the analyzer to verify its performance. There are certain specifics to the NMHC calibration that are identified in this section. The main calibration procedure can be referenced in WBEA SOP-OPS-002 Dilution Calibration Procedure.

- Calibration Equipment – NMHC analyzers are calibrated using the dilution method.
- Methane equivalency for propane must be converted in for THC calculated concentration. The equivalency multiplying factor is 2.75.
- Three upscale points must be used, spaced approximately 15%, 30% and 60% of full scale as well as minimum of a single zero point from a separate zero air source.
- Calibration results must be graphed as indicated concentrations (Ci) versus calculated concentrations (Cc) from which the slope of the graph, the intercept and final correction co-efficient are calculated.
- The acceptance criteria are slope of 1.0, ±0.05, and intercept of ±3% full scale and a coefficient of correlation (CC) >0.995.
- A zero/span check cycle is run through the DAS following the calibration to verify the span values and to pick up and zero offset.
- A recorded trace of the instrument, response over time is required to demonstrate stability and accuracy.

Data Collection and Management

The analog output of the NMHC analyzers is typically wired to the analog input channels of the station Campbell's Scientific CR3000 data logger. This data recorded at 5 minute intervals and is then polled remotely via cellular modem. Alternatively the data can be polled digitally via the serial or Ethernet port, and can be accompanied by the diagnostic or meta-data information.

Reference Documents

- *MODEL 55C DIRECT METHANE, NON-METHANE HYDROCARBON ANALYZER*, THERMO ENVIRONMENTAL INSTRUMENTS INC. Franklin MA, 2000, .
- State of California air resources board air monitoring quality assurance volume II standard operating procedures for air quality monitoring, appendix ak station operator's procedures for thermo environmental instruments inc. Model 55c direct methane, non-methane hydrocarbon analyzer monitoring and laboratory division, June 2000