GC3-NGA UG 2011

GC3-Natural Gas Analysis User Guide: Drilling Safety Monitoring

Manual Information

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Changes to User Guide

Summarize requested modifications to this user guide in an e-mail and/or annotate the PDF file and e-mail change requests to ***techdoc@iodp.tamu.edu.***

User Guide Contents

Introduction

Overview

Natural gas analysis for hydrocarbons and hydrogen sulfide (H_2S) is required to avoid natural gas and oil escaping from the hole and is part of the ship's standard drilling safety plan.
The absolute quantity of hydrocarbons is the primary safety risk during shipboard operations. Gas monitoring via gas chromatography is a means of quantifying the hydrocarbon risk. H_2S is another significant risk factor for individuals working in the area. Emergency monitors on the drill floor provide early detection of H_2S, while later quantification is performed on the natural gas analyzer (NGA).

Hydrocarbon Gases

Hydrocarbon generation in sediments is a result of thermal decomposition (maturation) of biogenic organic matter. C_1–C_4 hydrocarbons may be generated in significant quantities in sediment via two processes:

- **Biogenic:** biogenic hydrocarbons, typically characterized by methane, are produced in a sulfate-free environment via the reduction of dissolved bicarbonate.
- **Thermogenic:** thermogenic hydrocarbons are produced in sediments in direct proportion to temperature. C_5 and other heavier hydrocarbons are almost always the result of thermal generation of hydrogen-rich organic matter at temperatures typically ~100°C or greater.

Hydrogen Sulfide

Sulfate-reducing bacteria produce hydrogen sulfide in euxinic sediments. This may occur in a relatively shallow part of the sediment. Thermochemical sulfate reduction of sulfate by hydrocarbons in reservoirs occurs under high temperature (>127°C ~ 140°C).

Theory of Method

Two instruments monitor gases in core headspace and core void samples:

- **GC3:** Agilent 6890 gas chromatograph (GC) with flame ionization detector (FID). This instrument measures C_1–C_3 hydrocarbons:
- Methane (CH_4)
- Ethene (C_2H_4)
- Ethane (C_2H_6)

- Propene (C_3H_6)
- Propane (C_3H_8)
- **NGA:** Agilent 6890 GC with FID and thermal conductivity detector (TCD). This instrument measures C_1–C_7 hydrocarbons as well as some additional compounds:
- Methane (CH_4)
- Ethene (C_2H_4)
- Ethane (C_2H_6)
- Propene (C_3H_6)
- Popane (C_3H_8)
- n-Butane (C_4H_{10})
- iso-Butane (CH_3-C_3H_7)
- n-Pentane (C_5H_{12})
- iso-Pentane (CH_3-C_4H_9)
- n-Hexane (C_6H_{14})
- iso-Hexane (CH_3-C_5H_{11})
- n-Heptane (C_7H_{16})
- iso-Heptane (CH_3-C_6H_{13})
- Nitrogen (N_2)
- Oxygen (O_2)

The FID column on the NGA cannot separately quantify ethene/ethane and propene/propane, and they are reported as combined values. The TCD column does separate these components.

Apparatus, Reagents, & Materials

Instruments

The GC3 and NGA systems are both based on an Agilent 6890 GCs. These systems were further customized with specialized gas injection inlets and various column, detector, and valving systems for gas monitoring.

GC 3

The GC3 system is equipped with a 1/6 inch VALCO union injector with 2 µm screen and an electronically switched 10 port VALCO valve. The column is an 80/100 mesh, 8 ft HayeSep "R" packed column (2.0 mm ID x 1/8 inch OD).
The detector is an FID.

NGA

The NGA gas chromatograph is equipped with 2 detectors:

- Flame ionization detector (FID)
- Thermal conductivity detector (TCD)

The TCD flow path travels through a 6 ft x 2.0 mm ID stainless steel (SS) column packed with Poropak T (50/80 mesh), a 3 ft x 2.0 mm ID SS column packed with molecular sieve 13x (60/80 mesh), and 6 ft x 2.0 mm ID SS column packed with 80/100 mesh HayeSep R (acid washed).
The FID flow path traverses a 60 m x 0.25 mm ID capillary column with 0.25 µm DB-1 film.

Instrument Calibration/Calibration Verification

Overview

Before unknown samples can be analyzed for headspace gases, each GC system must have a valid calibration curve and the calibration curve must have been verified using a calibration verification standard.

1	Create/refresh calibration curve (start at least 1 day before reaching site) (see ***Creating a Calibration Curve***).
2	Verify calibration (***Running a Calibration Verification Standard***).
3	Perform a work flow test (***Running a Gas Sample***).

Creating a Calibration Curve

1	Prepare 5–7 registered standard gases.
2	Activate GC3/NGA LIMS uploader located at **Start > Program Files > IODP > MegaUploadaTron.** The uploader must be activated before the calibration is run.
3	In the ChemStation Main menu, click **Run Control > Sample Info**.
4	Fill in the specific fields on the screen as follows: • *Operator name*: LIMS user account (your last name) • *Sample name*: name of the standard (e.g., STD_D) and the replicate number (STD_D-1, STD_D-2, etc.) • *Comment*: text ID of the standard (scan the label) Click **OK** to close screen.
5	Slowly inject 5000 µL of the first standard gas and observe the floating ball in the flow meter move upward. Keep the outflow rate on the flow meter <80 mL/min.
6	When the ball in the flow meter indicates flow has fallen to just above 0 (is about to hit 0), press the **Start** button on the control panel of the GC.
7	When the run has finished, open the *Data Analysis* screen in ChemStation and click **Calibration**.
8	On the *Main* ChemStation menu, select **Calibration** > **Recalibrate**.
9	On the *Recalibration* screen, select **Level #** and **Replace** (or **Average**) as applicable for that level.
10	Repeat Steps 5–9 for 3 replicate standards (CH_4: A 25%, B = 50%, C 75%, D = 99%).
11	Click **OK** to change the calibration value. For NGA calibration, the same standard can be applied to both the appropriate TCD and FID level; you do not need separate standards for TCD and FID.

Running a Calibration Verification Standard

1	Ensure the uploader is activated and the CV standard is registered in LIMS.
2	Click **Run Control** in the main menu of ChemStation and select **Sample Info**.
3	Fill in the specific section on the window as follows: • *Operator name*: LIMS user account (your last name) • *Sample name*: common name for standard (e.g., STD_D-1) • *Comment*: text ID of the standard (scan the label) Click **OK** to close the sample info screen.
4	Prepare the CV standard at approximately the mid-point concentration of the curve.
5	Slowly inject 5000 µL of the standard gas, keeping the outflow rate <80 mL/min.
6	Press **Start** on the GC control panel when the flow meter is just above 0.
7	When the run is finished, the report will automatically display the values. Click **Upload** in the uploader to submit the data to LIMS.

Running a Blank

1	To run a blank, in the Main menu click **RunControl > Sample Info**.
2	Fill in the following fields: • Operator name: your last name • Sample name: "BLANK" • Comment: text ID of the blank (scan the label) Click **OK** to close window and save information.
3	Prepare laboratory air (5000 µL) and inject it into the GC in the same fashion as the standards above when the ChemStation software shows Ready.
4	Press the **Start** button on the GC control panel to start the run.
5	Confirm the chromatogram on the screen shows no peaks. If peaks are present, the system contamination must be found (injector, detector, sample loop, etc.).

Running a Gas Sample

1	Ensure the uploader has been activated.
2	Click Run Control in the main menu of ChemStation and select Sample Info.
3	Fill in the specific section on the window as follows: • Operator name: LIMS user account (your last name) • Sample name: Exp/site/hole/core/coretype/section/interval (e.g., 324-U1351A 5H4 32-35) • Comment: text ID of sample (scan label) Click OK to close sample info screen.
4	Prepare a headspace or void gas sample.
5	Slowly inject 5000 µL of the gas sample, keeping the maximum gas outflow <80 mL/min.
6	Press Start on the GC control panel when the ball on the flow meter is just above 0.

Sample Preparation & Analysis

Overview

There are two primary sample types used for natural gas analysis.

- Headspace gas, which is obtained from core samples by heating a sample to ~70°C.
- Void gas collected with a vacuum vial.

Occasionally, cores that come on deck have voids with large amounts of free gas. Free gas must be sampled using a sampling device that penetrates the liner and provides a channel for the gas to be drawn into a gas-tight syringe, vacuum vial, or gas sampling bag.

Sampling Tools

- Sample coring tool (metal cylinder)
- Sample coring plunger
- Puncture tool (to penetrate plastic liner)
- Headspace vial
- Headspace gasket with crimp top
- Crimping tool
- Permanent marker for labeling

Sampling Procedure and Gas Sample Preparation

Headspace Gas

Collect samples from a freshly cut core section at a position within 0.5 inch of the inner side of the core liner (where sample has not been disturbed by contact with drilling fluid or core liner). In addition, the sample must be taken prior to the use of acetone or any other organic solvent in the catwalk area.
The curator authorizes the sampling plan before coring; therefore, the chemistry specialist must know the catwalk sampling plan before taking samples.

Collecting a Headspace Gas Sample

1	Locate a freshly sectioned core (consult with the curator).
2	Gently push the sample coring tool into the core section slightly inward of the edge.
3	Gently pull out the tool. If the sample recovery (% of coring tool with sample) is >80% (~5–7 cm^3), proceed; otherwise repeat Steps 1 and 2.
4	Place the open end of the sample coring tool over a clean headspace gas vial and use the plunger to push the sediment into the vial.
5	Immediately place a gasket with a crimp top over the vial and crimp shut.
6	After sealing the vial, immediately write down the sampling interval, location, and any other information for the sample that was just taken. Generate a proper label and apply it to the vial as soon as possible.
7	Place the vial with the sample in a 70°C oven for 30 min to degas the sediment (use timer).

8	Inject extracted gas sample into the GC using syringe (see ***Running a*** Sample).

Collecting a Void Gas Sample

1	Use the puncture tool to make a hole in the core liner to make a channel for the gas.
2	Quickly collect a free gas sample from the small hole with a syringe.
3	Immediately introduce the gas sample into the GC instruments in the same manner as the headspace samples.

Running a Sample

1	Start GC and operation system at least 1 day before reaching site (the system should be fully calibrated and ready for analysis) (see Advanced User Guide).
2	Ensure LIMS uploader is running.
3	Inject 5 mL of headspace gas after the sample has heated in the oven for 30 min.
4	Click **Upload** if the uploader is not in automatic mode.

Quality Assurance/Quality Control

Overview

QA/QC for GC3/NGA analysis consists of instrument calibration and continuing calibration verification using check standards, instrument blanks, and replicate samples.

Analytical Batch

An analytical batch is a method-defined number of samples with which QC samples including calibration verification, blank, and replicate samples are run. Samples are implicitly grouped into batches based on the spacing between CV samples.

QC Samples

Blank

- The blank determines the level of contamination originating from the laboratory environment (air) and sample path in the GC (injection port with screen, sample loop, and separation column).
- Run a blank with each batch of samples by injecting 5 mL of ambient laboratory air into the GC using the same syringe used to inject headspace gas samples.
- All calibrated values other than O_2 and N_2 should be nondetectable in the blank. If aberrant peaks appear, bake the column for 8 hr and repeat the blank analysis.

Calibration Sample

- Five to seven levels of calibration samples (standard gases) are used to create a calibration curve, which is saved with the measurement data (see ***Instrument Calibration/Calibration Verification***).
- Correlation coefficient values for calibration curves should be 0.99 or better, except O_2 and N_2, which should be 0.95 or better.

Calibration Verification (CV) Sample

- Select one of the 5–7 calibration samples from the calibration curve for the calibration verification sample.
- Run a CV sample at least every shift that samples are taken (see ***Instrument Calibration/Calibration Verification***).
- The CV should fall within 3% of the calibrated value; O_2 and N_2 should be within 10% of the calibrated value.

Control Limits

For a system to be considered in control, all QA/QC samples (blank and calibration verification) must be in control.

In Control

A QA/QC sample is in control when the sample analysis result is within a certain tolerance of acceptable limits (see above). Calibration verification samples should be within acceptable limits of the actual value calculated against the calibration curve (see ***Calibration Verification (CV) Sample***) and blanks should be within acceptable limits of background levels of headspace hydrocarbons and gases (see ***Blank***). When the system is in control, as indicated by acceptable results on QA/QC samples, analytical results for unknown samples are considered to be reliable.

Out of Control

If the control limits are exceeded, the instrument system is considered out of control and all samples in the current analytical batch are invalid and must be rerun after the system is proved to be in control.

LIMS Integration

LIMS Components

Analysis	Component	Unit	Description
GC3	dat_asman_id	—	Serial number of chromatographic data file in digital asset management database (ASMAN)
	dat_filename	—	File name of chromatographic data file containing measurements
	run_test	—	Test number of related calibration or QA/QC test
	propene	ppmv	Relative concentration of propene in the sample
	propane	ppmv	Relative concentration of propane in the sample
	ethene	ppmv	Relative concentration of ethene in the sample
	ethane	ppmv	Relative concentration of ethane in the sample
	methane	ppmv	Relative concentration of methane in the sample
GC3_QAQC	dat_asman_id	—	Serial number of chromatographic data file in ASMAN
	dat_filename	—	File name of chromatographic data file containing measurements
	run_test	—	Test number of related calibration or QA/QC test
	propene	ppmv	Relative concentration of propene in the sample
	propane	ppmv	Relative concentration of propane in the sample
	ethene	ppmv	Relative concentration of ethene in the sample
	ethane	ppmv	Relative concentration of ethane in the sample
	methane	ppmv	Relative concentration of methane in the sample
GC3_QCAL	mtd_asman_id	—	Serial number of chromatographic method in ASMAN
	mtd_filename	—	File name of the chromatographic method file containing measurements
	ethene_corr2	R^2	Ethene calibration coefficient
	ethene_intercept	—	Intercept of ethene calibration curve
	ethene_slope	—	Slope of ethene calibration curve
	ethane_corr2	R^2	Ethane calibration coefficient
	ethane_intercept	—	Intercept of ethane calibration curve
	ethane_slope	—	Slope of ethane calibration curve
	propene_corr2	R^2	Propene calibration coefficient
	propene_intercept	—	Intercept of propene calibration curve
	propene_slope	—	Slope of propene calibration curve
	propane_corr2	R^2	Propane calibration coefficient
	propane_intercept	—	Intercept of propane calibration curve
	propane_slope	—	Slope of propene calibration curve
	methane_corr2	R^2	Methane calibration coefficient
	methane_intercept	—	Intercept of methane calibration curve
	methane_slope	—	Slope of methane calibration curve

NGAFID	dat_asman_id	—	Serial number of chromatographic data file in ASMAN
	dat_filename	—	File name of chromatographic data file containing measurements
	run_test	—	Test number of related calibration or QA/QC test
	iso_butane	ppmv	Concentration of iso_butane in a sample
	iso_heptane	ppmv	Concentration of iso_heptane in a sample
	iso_hexane	ppmv	Concentration of iso_hexane in a sample
	iso_pentane	ppmv	Concentration of iso_pentane in a sample
	n_butane	ppmv	Concentration of n_butane in a sample
	n_heptane	ppmv	Concentration of n_heptane in a sample
	n_hexane	ppmv	Concentration of n_hexane in a sample
	n_pentane	ppmv	Concentration of n_pentane in a sample
	ethane_ethene	ppmv	Concentration of ethane + ethene in a sample
	propane_propene	ppmv	Concentration of propane + propene in a sample
	methane	ppmv	Concentration of methane in a sample
NGAFID_QA	dat_asman_id	—	Serial number of chromatographic data file in ASMAN
	dat_filename	—	File name of chromatographic data file containing measurements
	run_test	—	Test number of related calibration or QA/QC test
	iso_butane	ppmv	Concentration of iso_butane in a sample
	iso_heptane	ppmv	Concentration of iso_heptane in a sample
	iso_hexane	ppmv	Concentration of iso_hexane in a sample
	iso_pentane	ppmv	Concentration of iso_pentane in a sample
	n_butane	ppmv	Concentration of n_butane in a sample
	n_heptane	ppmv	Concentration of n_heptane in a sample
	n_hexane	ppmv	Concentration of n_hexane in a sample
	n_pentane	ppmv	Concentration of n_pentane in a sample
	ethane_ethene	ppmv	Concentration of ethane + ethene in a sample
	propane_propene	ppmv	Concentration of propane + propene in a sample
	methane	ppmv	Concentration of methane in a sample
NGAFID_QC	mtd_asman_id	—	Serial number of chromatographic method in ASMAN
	mtd_filename	—	File name of the chromatographic method file containing measurements
	iso_butane_corr2	R^2	Iso-butane calibration coefficient
	iso_butane_intercept	—	Intercept of iso-butane calibration curve
	iso_butane_slope	—	Slope of iso-butane calibration curve
	iso_heptane_corr2	R^2	Iso-heptane calibration coefficient
	iso_heptane_intercept	—	Intercept of iso-heptane calibration curve
	iso_heptane_slope	—	Slope of iso-heptane calibration curve
	iso_hexane_corr2	R^2	Iso-hexane calibration coefficient
	iso_hexane_intercept	—	Intercept of iso-hexane calibration curve
	iso_hexane_slope	—	Slope of iso-hexane calibration curve
	iso_pentane_corr2	R^2	Iso-pentane calibration coefficient
	iso_pentane_intercept	—	Intercept of iso-pentane calibration curve
	iso_pentane_slope	—	Slope of iso-pentane calibration curve
	n_butane_corr2	R^2	n-butane calibration coefficient
	n_butane_intercept	—	Intercept of n-butane calibration curve
	n_butane_slope	—	Slope of n-butane calibration curve
	n_heptane_corr2	R^2	n-heptane calibration coefficient

	n_heptane_intercept	—	Intercept of n-heptane calibration curve
	n_heptane_slope	—	Slope of n-heptane calibration curve
	n_hexane_corr2	R^2	n-hexane calibration coefficient
	n_hexane_intercept	—	Intercept of n-hexane calibration curve
	n_hexane_slope	—	Slope of n-hexane calibration curve
	n_pentane_corr2	R^2	n-pentane calibration coefficient
	n_pentane_intercept	—	Intercept of n-pentane calibration curve
	n_pentane_slope	—	Slope of n-pentane calibration curve
	ethane_ethene_corr2	R^2	Ethane + ethene calibration coefficient
	ethane_ethene_intercept	—	Intercept of ethane + ethene calibration curve
	ethane_ethene_slope	—	Slope of ethane + ethene calibration curve
	propane_propene_corr2	R^2	Propane + propene calibration coefficient
	propane_propene_intercept	—	Intercept of propane + propene calibration curve
	propane_propene_slope	—	Slope of propane + propene calibration curve
NGAFID_QC	methane_corr2	R^2	Methane calibration coefficient
	methane_intercept	—	Intercept of methane calibration curve
	methane_slope	—	Slope of methane calibration curve
NGATCD	dat_asman_id	—	Serial number of chromatographic data file in ASMAN
	dat_filename	—	File name of chromatographic data file containing measurements
	run_test	—	Test number of related calibration or QA/QC test
	carbon_dioxide	ppmv	Concentration of carbon dioxide in a sample
	ethane	ppmv	Concentration of ethane in a sample
	ethene	ppmv	Concentration of ethene in a sample
	hydrogen_sulfide	ppmv	Concentration of hydrogen sulfide in a sample
	methane	ppmv	Concentration of methane in a sample
	nitrogen	ppmv	Concentration of nitrogen in a sample
	oxygen	ppmv	Concentration of oxygen in a sample
	propane	ppmv	Concentration of propane in a sample
	propene	ppmv	Concentration of propene in a sample

Uploading Data to LIMS

Data are uploaded to LIMS automatically using a process explained in the *GC3-NGA Advanced User Guide*. If the data do not upload to LIMS, contact the laboratory technician.

Health, Safety, & Environment

Safety

- The following parts are dangerously hot. Avoid touching these areas and cool completely to room temperature before servicing them:
- Inlets
- Oven
- Detectors
- Column nuts
- Be careful when working behind the instrument; during cooldown cycle the oven emits hot exhaust that can cause burns.
- Do not place temperature-sensitive items (e.g., gas cylinders, chemicals, regulators, and plastic tubing) in the path of the heated exhaust.
- Insulation around inlets, detectors, and valve box contains refractory ceramic fibers. Avoid inhaling particles and wear personal protective equipment including gloves, safety glasses, and dust/mist respirator when working in these areas.
- Do not leave flammable gas flows on if GC will be unmonitored for long periods of time (however, leave carrier gas on for column flow).
- Always operate the instrument with the cover properly installed.

Maintenance & Troubleshooting (HP6890GC)

Troubleshooting

Faults

- Beeping instrument (cancel beep by pressing **Clear** on the instrument keyboard)
- One beep: instrument fault, warning, or shutdown
- Series of beeps: gas flow cannot reach setpoint and flow will be shut down after 1–2 min
- Continuous beep: thermal shutdown
- Blinking setpoint on GC display
- Control table setpoint blinking: gas flow, valve, or oven shutdown
- Detector On/Off line blinking: pneumatics or detector failure
- Instrument screen messages (press **Clear** to remove message)
- Caution: configuration problems
- Error: setpoint out of range or incorrect hardware
- Popup: shutdown, fault, or warning (see error table)
- FID will not stay lit
- Make sure the dessicant in the hydrogen generator is not saturated with water (replace/recharge as necessary).
- Check water level in hydrogen generator