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Natural gas — Online gas chromatograph for upstream area

Gaz naturels — Chromatographe en phase gazeuse en ligne pour zone amont

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Foreword

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The committee responsible for this document is ISO/TC 193, *Natural gas*, Subcommittee SC 3, *Upstream area*.

Introduction

Online Gas Chromatograph (GC) is widely used to determine hydrocarbon components in natural gas because of its “Real time” measurement and ease of use. It has become a powerful tool for both custody transfer and upstream process gas monitoring. Especially for the custody transfer which the calorific value and others gas properties such as, relative density, compressibility factor, etc. are needed for energy determination. Therefore, accuracy and reliability of the equipment are crucial.

With proper maintenance and handling, GC can provide an accurate result with a minimum manpower as it analyzes and provides results continuously. With technology today, the unit can do auto-calibration, alarm setting, diagnostic, troubleshooting and configuring through Human Machine Interface (HMI). Its outputs can be linked directly with Flow computer, Distributed Control System (DCS) or any remote personal computer (PC).

The Natural Gas in upstream petroleum industry is normally wet. Then this Technical Report provides recommended application to handling GC focus on design, selection, operation, maintenance and verification of GC and its peripheral. The purpose is to provide the whole process to proper handling the GC until getting the accurate and reliable results. It is also included the sampling system to get the representative sample, data verification, alarm, diagnostic and troubleshooting including how to deal with the data in case of being used for custody transfer purpose. Some acceptance criteria are also identified in this paper based on our historical record and performance of the equipment.

Natural gas — Online gas chromatograph for upstream area

1 Scope

This Technical Report concerns the determination of hydrocarbon components up to C7+ in natural gas in upstream petroleum industry, which describes the principle of operation of GC and provides guidelines for selection, evaluation, and factors impacting upon its performance such as sample probe, sample conditioning, installation, operation and troubleshooting.

2 Principle of measurement

2.1 General

The GC is a technique for separating and analysing compounds that can be vaporized without decomposition in a continuous and automatic manner of sample injection, separation, data integration and reporting. A precise volume of sample gas is injected into the column which contains a stationary phase (packing) that is either an active solid (adsorption partition) or an inert solid support that is coated with a liquid phase (absorption partitioning). The gas is moved through the column by means of a mobile phase (carrier gas). Selective retention of the components of the sample takes place in the column and causes each component to move through the column at a different rate. This action separates the sample into its gaseous constituents.

A detector detects the elution of component from the column and produces electrical outputs proportional to the concentration of each component. Output from the detector are amplified in the electronics, then transmitted to the controller for further processing.

2.2 Gas composition

Natural gas is composed primarily of methane with smaller amounts of higher hydrocarbons and of non combustible gases. Major, minor and trace components are as indicated in Tables 1, 2 and 3:

Table 1 — Major components

Component	Units
Methane	mole %
Ethane	mole %
Propane	mole %
Butanes	mole %
Pentanes	mole %
Hexanes	mole %
Heptanes plus	mole %
Nitrogen	mole %
Carbon dioxide	mole %

Table 2 — Minor component

Component	Units
Hydrogen	mole %
Oxygen	mole %
Carbon monoxide	mole %
Helium	mole %

Table 3 — Trace component

Component	Units
Hydrogen sulfide	mg/m^3
Mercaptan sulfur	mg/m^3
Dialkyl (di) sulfide	mg/m^3
Carbonyl sulfide	mg/m^3
Total sulfur	mg/m^3

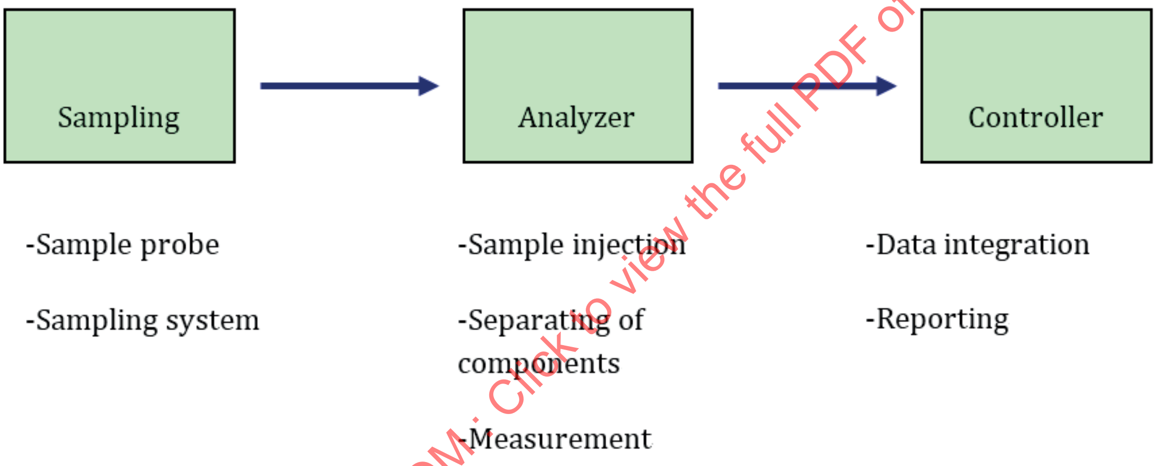


Figure 1 — Online Gas Chromatograph Functional Block Diagram

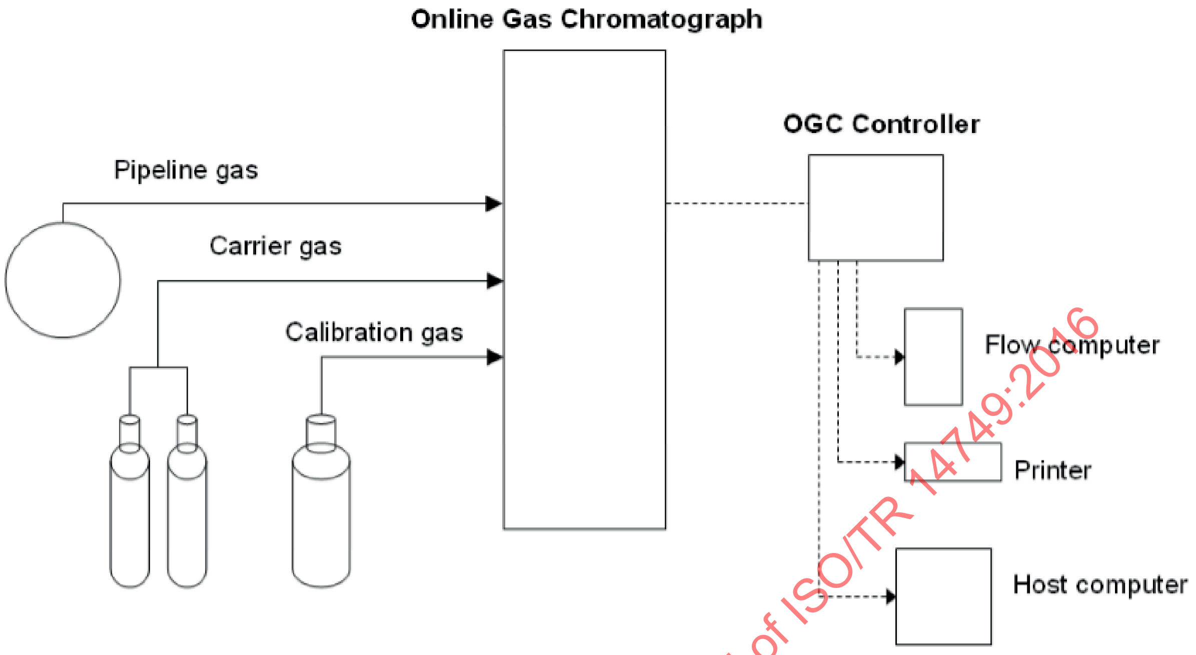


Figure 2 — Online Gas Chromatograph Equipment Diagram

Output from the controller is normally linked to flow computer, DCS, remote personal computer (PC) or a printer. Connection between the GC Controller and others can be accomplished via a direct serial link or Ethernet link.

The GC today has features to report alarm and ignore any fault (report last good value) and also provides good diagnostic and troubleshooting data. To verify the GC performance, repeatability check with Standard gas and baseline check are recommended.

3 Sampling and conditioning

The nature of gas processing in upstream petroleum industry is relied on gas separation and gas dehydration units. There is potential of small liquid droplets in Natural Gas which are able to get into GC causing lots of problems such as incorrect data, failure of GC, etc.

Sample probes and sample conditioning unit have to be properly designed and installed to address liquid carry over and condensing issues. A well designed, installed and maintained sampling system is vital to ensure the provision of a representative sample for GC analysis.

The purpose of the sample handling system is not to transfer an exact sample of the process fluid to the GC. Rather, the purpose is to transfer a representative sample of the fluid after it has been conditioned that is compatible with GC sample requirements.

The sampling system consists of sample probes, pressure regulators and sample line.

The sample probe design should take into account the possibility of resonant vibration being induced by high flow velocities in the pipeline. The probe construction can be either a straight tube probe or a regulated probe. An extraction probe should be considered for maintenance purpose without depressurizing shutdown.

Referring to ISO 10715, sample probe should be located directly in the gas stream in such a way that problems induced by aerosols and dust are eliminated. It is recommended that the probe be located a minimum of 20 pipe diameters downstream from any flow-disturbing elements such as elbows, headers, valves and tees. However, due to retriction in the upstream petroleum industry, a distance of at least 5 pipe diameters downstream of custody metering is accepted.

The location of the probe should be on the top of a horizontal part of the pipe. The sample probe tip insertion should be located between one-third and centre of the pipeline diameter.

The sampling pressure, especially in upstream petroleum industry is relatively high (more than 4,137 kPa, or 600 psi) but the GC inlet pressure is designed at very low level (less than 138 kPa, or 20 psi), then pressure reduction is relatively important to prevent the liquid into GC. Two different methods are considered:

- Regulated probe with pressure regulator.
- Heated pressure regulator.

The sample should be heated before reducing the pressure and the regulated probe should be equipped with fin in order to reduce liquid droplet from Joule-Thomson effect.

Sampling accessories such as aerosol and/or dust trap, coalescer filter are considered to ensure that liquid droplets are eliminated. The maintenance on the liquid eliminating system should be performed as frequently as practically possible.

The sampling line should be short and have a small diameter to shorten residence time. A bypass or fast-loop line should be considered to reduce residence time. The sampling vent should comply with hazardous area classification.

Whenever ambient temperature is below the hydrocarbon dew point of the stream, heat tracing on the sample line should be used to keep the sample line temperature 10 °C above the gas dew point. This is in order to avoid condensation problems and to provide a representative sample to the GC. The heat tracing should be either electric or steam, however the electrical parts should comply with hazardous area classification.

NOTE Typically any stream over about 38.73MJ/SCM, or 1 040 btu/scf, will need heat tracing and insulation.

If neccessary a pressure safety relief valve can be installed downstream of the pressure reducer in order to protect the GC from pressure regulator failure.

Materials being used in sampling are dependent on gas composition, in most cases stainless steel is recommended, however in some areas where high amount of H2S are present (more than 50ppm) the duplex stainless steel tubing should be considered. Seats and seals should be made of (elastic) material appropriate for the intended service.

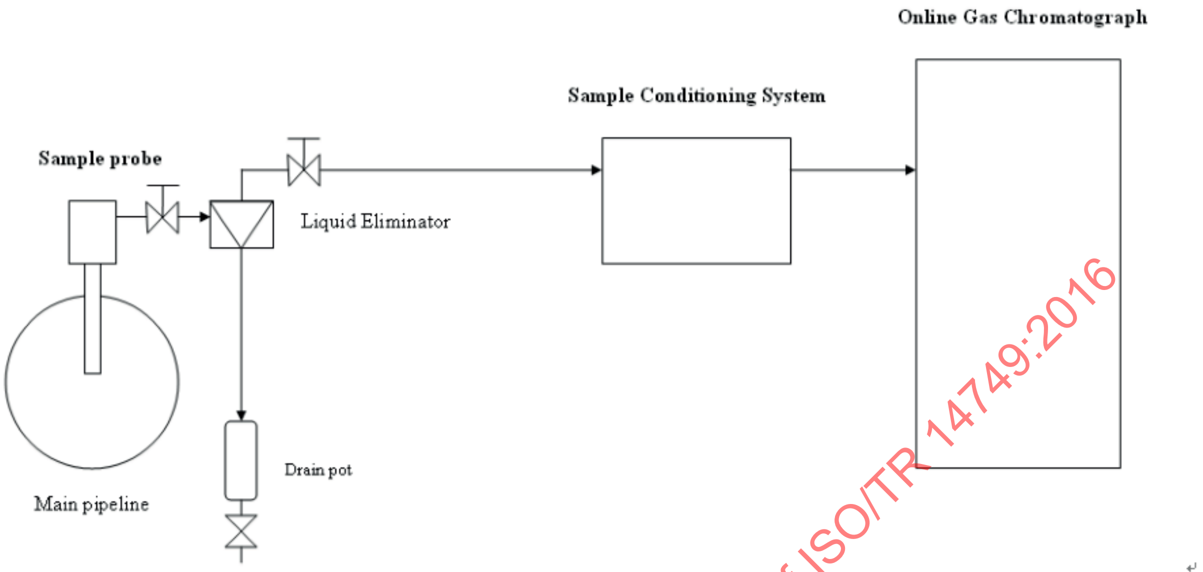
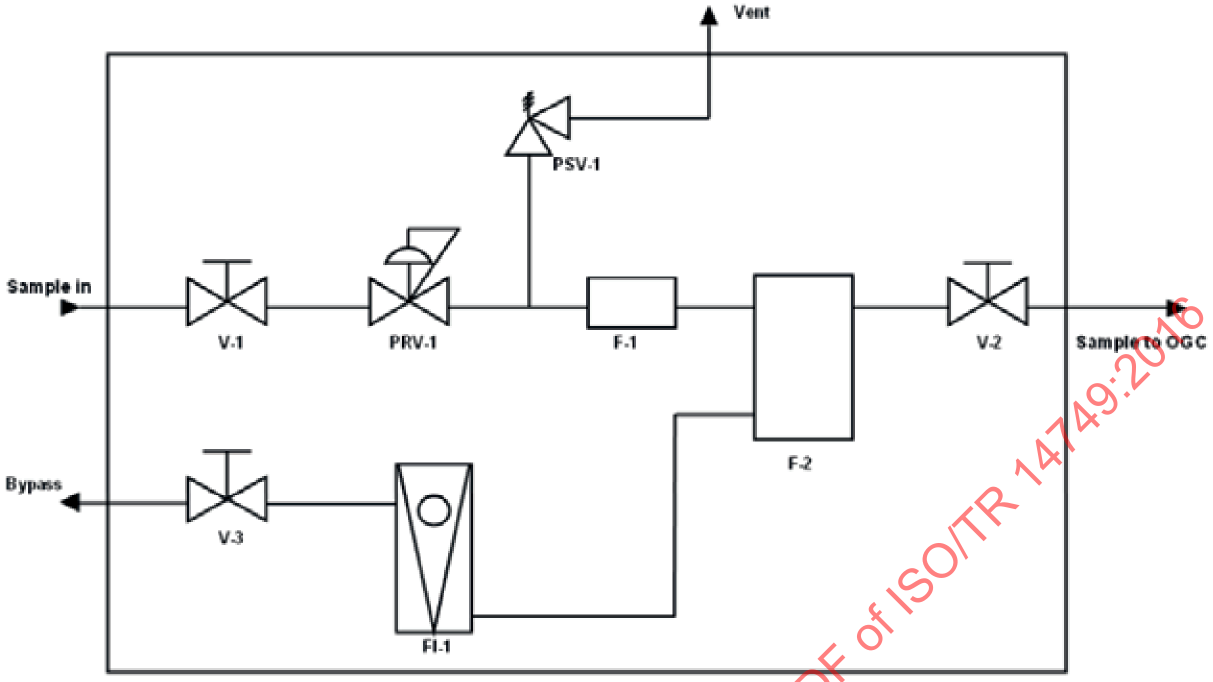


Figure 3 — Online Gas Chromatograph Sampling System Components

A Sample Conditioning System (SCS) is located between the process stream and the analyser inlet. The standard configuration SCS should be as represented in Figure 4.



Key

V-1	inlet valve (sample in)
V-2	outlet valve (sample to GC)
V-3	outlet valve (bypass)
PRV-1	pressure reducing valve
PSV-1	pressure safety valve
F-1	dust filter
F-2	membrane filter
FI-1	flow indicator

Figure 4 — Online Gas Chromatograph Sample Conditioning System (typical)

4 Online gas chromatograph selection guideline

The GC selection guideline is described below.

- Gas composition: number of gas components of interest as agreed with concerned parties. The typical available analyzers can analyse hydrocarbon up to C6+ and C7+.
- Analysis method: any system providing adequate peak separation and analytical performance should be accepted, typical detectors used are TCD, FID and FPD. In case the trace level (ppm order of magnitude) specific equipment may be considered.
- Electrical equipment should comply with hazardous area classification.
- Instrument system should be equipped with
  - Temperature controller should be monitored and adjustable.
  - Column with tag to indicate the column information (material, length). The column should be capable of separating each gas component completely.

  - Carrier gas should be equipped with pressure switch to shut off the analyser when pressure is too low.
- Controller should
  - Be equipped with HMI display.
  - Have a diagnostic program connected to controller.
  - Have the output signal which can be either an analog communication via serial data or ethernet data.
  - Provide chromatograph of calibration and analysis.
  - Keep calibration and analysis result.
  - Keep alarm and event log.
  - Report the hourly, the daily, the weekly and the monthly average.
  - Calculate the un-normalized mole percent.
- Carrier gas should be inert gas, typically helium or hydrogen. The carrier gas should be of zero grade purity (99,995 % pure), with less than 5 ppm water and less than 0,5 ppm hydrocarbons. The carrier gas should be in dual cylinders with an automatic switch to one cylinder to another when pressure in one cylinder is deemed lower than required. This will reduce chances of analyser shut-off.

5 Calibration guidelines

5.1 Calibration procedure

5.1.1 General

The calibration of an instrument for the routine measurement of the composition of natural gas is a corrective metrological procedure. Its consists of using the value recorded by the instrument for one certified reference gas mixtures (calibration gases) in order either

- To make adjustments to the instrument that reduce to zero the difference between the measured and certified value, or
- To derive a correction that, when applied to the measured value, produces the corrected value.

5.1.2 Calibration

It is recommended to ignore the first run of calibration sequence. Typically, the deviation of the response factor (RF) of each component between at least two consecutive runs should be less than 5 %. (If the atmospheric pressure change, RF deviation for each component will change the same way).

5.1.3 Calibration frequency

The calibration interval is defined as the period of time during which the analytical system would normally be used between recalibrations. Experience shows over how long a period instrument is judged to be stable, and hence what the calibration frequency should be.

The calibration frequencies should be agreed by contractual agreement. The GC may operate for 24 h a day with an automatic recalibration once a day. However, in case daily calibration is not established, the verification and calibration program should be performed once a month.

5.2 Calibration gases

Calibration gases for custody transfer should be certified reference mixtures (CRM), where the certification is for the composition of natural gas values, including a statement of the associated uncertainty. For non-custody transfer, the calibrated gas mixture (CGM) is accepted when the correct term is clarified in the level traceability. Typically, they are synthetic mixtures. Moisture-free gas mixtures of known composition are required for comparison with the test sample. They should contain known percents of the components that are to be determined in the unknown sample. For hexane and heavier components the corresponding normal alkanes in the standard gas (normal hexane, normal heptanes, etc.) are used for calibration. Calculated amounts for individual carbon number components that are heaxane and heavier are the sum of their isomers.

The calibration gas mixture should be homogenous in the vapor state at the time of use. The concentration of a component in the gas calibration standard should no less than one half or more than twice the concentration of the corresponding component in the test gas. The composition of the calibration gas will be calibrated by an accrediated laboratory according to ISO 17025.

The calibration gas used for gas chromatography should be selected very carefully and handled properly throughout the service period.

The calibration gases should be at a temperature at least at least 10°C above the hydrocarbon dew point calculated at the cylinder fill pressure using common equation of state (such as Peng-Robinson). However, it is not neccessary to calculate the hydrocarbon dewpoint, as the manufacturer gives the minimum storage temperature, which the calibration gas should not be used. And the calibration gas storage temperature should not exceed 125 °F (52 °C).

5.3 Chromatogram verification

Run the gas standard and check that all peaks are clearly defined and separated. See Annex B for a typical chromatogram.

5.3.1 Response Factor (RF)

The response factor is an important parameter to monitor the performance of the GC system for the abnormality of equipment such as, valve setting, time event or the sampling system. The recommended limit for response factor value is ± 5 %. When conducting the calibration, the software should have a function that gives an alarm and inhibits the calibration which contains response factors that are outside the setting limits. If the response factor deviates by more than 5 %, the possible causes are a calibration gas leak in the sample line leading to low gas introduced into the column; or a separation system error which leads to the partially inhibiting actual component peaks; or a faulty auto-calibration solenoid.

5.3.2 Retention Time (RT)

The output of the chromatogram is monitored with the help of retention time, parameter which indicates whether the peaks are eluted at the correct time. The recommended alarm setting for the retention time is ± 0,5 %. If the RT caused by the flow rate of carrier gas or the flow rate of output gas. The stability of the temperature should be monitored within the set point. The temperature control card should be replaaced if there is a malfunction.

6 Verification procedure

6.1 General

Verification and acceptance is normally carried out on site with a frequency agreed by concerned parties. The purpose criteria for GC verification is to demonstrate that an instrument is capable of operating within an agreed envelope of satisfactory performances, for the whole range of expected operational conditions.

It is recommended to perform GC verification and audit annually.

6.2 Visual inspection of Sample system

The sample probe and peripheral are installed properly.

Sample line size, sample line distance and sample fast loop vent are installed properly, in order to ensure the sample delay time as per design.

No gas leakage present

6.3 Visual inspection of analyser

GC and its peripheral are in good condition as per drawings.

No gas leakage present.

Verify that the power is on.

Establish HMI connection with the chromatography software.

Verify that the configuration is set correctly.

6.4 Carrier Gas

Carrier gas pressure is present and correct as per manufacturer's guidelines.

It is recommended to install an automatic change-over on carrier gas cylinders.

Check the function of automatic change over switch for carrier gas pressure.

6.5 Calibration Gas

Verify that calibration gas component and concentration identified in the manufacturer's certification is corrected as per requirement.

Calibration gas filling pressure is present and correct as per manufacturer's certification.

6.6 GC verification

The GC oven temperature should be within manufacturer's limit.

The sampling pressure should be within manufacturer's limit.

Baseline verification by putting the sampling gas on hold and verifying the noise level of detectors with only carrier gas.

Check that the calibration gas composition in the controller is same to the calibration gas certificate.

Perform calibration as per calibration guidelines.

The RF for each component should be consistent over time.

Repeatability checks and reproducibility check should pass the criteria in "repeatability and reproducibility topic".

Un-normalized sum of components should be within ± 3 mol %. (97 mol % to 103 mol %).

Day-night effect test: run the known gas for 24 h to ensure that the GC's performance is not affected by a change of ambient temperature from day-night effect. The calorific value deviation throughout 24 h should be within ± 0,2 %.

7 Maintenance and Corrective maintenance

7.1 Preventive maintenance

It is normal practice to carry out, as a minimum, all maintenance procedures as recommended by the manufacturer, and at the prescribed frequency. It is recommended to perform maintenance and verification once a year or at a frequency set per contractual agreement.

7.2 Corrective maintenance

Corrective maintenance is any set of operations carried out in order to repair an instrument malfunction. The malfunction in question can be either the instrument shutting down or it can be that routine verification procedures show that the recent record is unsatisfactory (inaccurate).

It is not possible to give general guidelines for the content of corrective maintenance procedures, but procedures relevant to various types of failure can likely be found in the particular manufacturer instrument manuals. Calibration of an instrument is mandatory after the performance of corrective maintenance.

However, the common problems and troubleshooting to the GC system are:

- Sample conditioning system:
  - Sample pressure fluctuation or sample flow blockage causes a too low or too high un-normalized total. The sample pressure regulator should be checked.
  - Liquid carry-over causes high error in result for higher hydrocarbons analysis. The sample system should be flushed and cleaned.
- Leakage:
  - Carrier gas pressure too low or tube leakage causes RT shift. The carrier gas pressure regulator and leakage should be checked.
  - Switching valve passing or leak causes RT shift, some gas peaks disappear of the chromatogram. The switching valve should be checked and replaced if applicable.

8 Alarm and diagnostic

The alarm system is the powerful tool to alert and remind the user or operator for the abnormality of the system, either on the GC itself or the process gas. The hardware alarms should have factory settings, and provide user an easy way to investigate the root causes. Moreover, the software should provide the function to allow the user to set threshold limits for GC analysis data. When a limit is exceeded, an alarm is activated and logged.

The hardware alarms which indicate the abnormality of the GC and its possible causes are listed below:

- Application Check Failure/ROM Check Failure.

The possible cause for this alarm is bad EPROM, change the CPU board.

- Alarm.
  - Carrier gas is gone or too low pressure.

    Check the availability of carrier gas and set the pressure to the factory recommended set point.
  - Detector failed.

    Check the function of the detector, change the new board if it failed.

  - Preamplifier out of balance or failed.

    Check the balance of the preamplifier and run a chromatogram to ensure the peak actually exists and is in its normal position.

  - Analyser temperature low.

    Ensure that the temperature is constant at the set point in both detector and oven. If it was found that the temperature cannot reach the set point, replace the board.

  - Interconnection wiring.

    Make sure all wirings are firmly connected.

  - Power failure.

    In any case of power failure and recovery, the controler should log by itself with calendar date and time.

- Analyser Failure.
  - Carrier gas is low or runs out.
  - Bad Solenoid.
  - Carrier gas leak in the system.
- Noisy Baseline.

A noisy baseline can be caused by carrier gas leaks, an electronic failure in the preamplifier, an interference in the power supply, grounding system, defective detector, or contamination in the column. If the baseline is still noisy after correcting for leaks, then perform the Detector Bridge Balance before replacing the detector or the preamplifier board.

However, the software also allows the user to set the threshold limit of the analysis data. The alarm setting for following parameters and its threshold limit are recommended below:

- Total percentage of un-normalized concentration.

The recommenced value is ± 3 mol %. If the un-normalized total is not within acceptable limits, it may caused from the following abnormalities:

- The amount of sample gas in the sample loop is not constant which may be caused from the atmospheric pressure and/or back pressure.
- The sample line regulator has failed.
- The leakage of carrier gas system.
- The flow rate of by- pass loop (fast loop) is too low or too high.

All the above abnormalities can cause the amount of sample introduced into the sample loop to not be equivalent to the calibration standard. Check the regulator output pressures and sample flow rates, including the Stream switching solenoid valve that may not work properly. It is also possible that the % un-normalized concentration has dropped to zero for a few analysis cycle per day, in that case check concerned solenoids to ensure their functionality.

- Mole percent of each component.

Alarm setting on mole % of each component should be half and twice as much as normal gas composition (for instance for a concentration of 1,0 mol %, the alarm lower and upper limits should be respectively

0,5 mol % and 2,0 mol %). If some components have suddenly dropped to zero, it may be caused by the following errors:

- The solenoid valve is malfunctioning and failed to activate sample into the column.
- The peaks of each component in the chromatogram have shifted from their normal interval due to possible temperature control failure. Check the temperature controller for proper cycling and set point level.
- The carrier gas regulator has failed to maintain proper flow. Check the regulator set point.
- The preamplifier is out of balance or has failed. Check the balance of preamplifier and run the chromatogram to ensure the peak actually exists and is in its normal position.

9 Repeatability and Reproducibility

9.1 Repeatability

The difference between two successive results obtained by the same operator with the same analyser under constant operating conditions on identical test materials should be considered suspect if they differ by more than the following amounts:

Component, mole %	**Repeatability**, mole % absolute
$x < 0,1$	0,01
$0,1 < x < 1,0$	0,04
$1,0 < x < 5,0$	0,07
$5,0 < x < 10,0$	0,08
Over 10,0	0,10

9.2 Reproducibility

The difference between two results obtained by different analyzers or different laboratories on identical test materials should be considered suspect if they differ by more than the following amounts (refer to ISO 6974-3):

Component, mole %	**Reproducibility**, mole % absolute
$x < 0,1$	0,02
$0,1 < x < 1,0$	0,07
$1,0 < x < 5,0$	0,10
$5,0 < x < 10,0$	0,12
Over 10,0	0,15

10 Data handling during GC failure

The alarm system is another tool to alert the user or operator in order to be able to rectify the problem as early as possible after alarm. In most cases, the GC data are used for custody transfer purposes. When the GC fails to generate reliable data, it will cause problems with the billing process, since the gas compositions analysed from the GC may or may not be used for Volume and Calorific Value calculations.

When the GC fails, then the following alternative methods may be used if the parties hereto agree:

- Use gas compositions analysed from backup GC if available. In some cases, a duplicated GC is installed to ensure that there is no problem with the fiscal measurement system. However, it should be ensured that the duplicated unit is in good maintenance, calibration, etc as equivalent with the main unit.

- Use gas compositions analysed from backup gas sampler system if available. If the duplicated GC is not available, it is recommended to have the continuous gas sampler system to collect gas into a gas cylinder.
- Use the average of correct value retrieved from the GC software. Since the software of GC has the ability to allow the user to retrieve the previous data for further verification, the unaccepted data should be deleted and manual calculation for those reliable data.
- Use the average gas composition before and after GC failure. If there is no data available, this option is the only choice.

Other alternative methods rather than the ones mentioned above can also be used if the parties hereto agree.

11 Quality Control of analysis data

Quality control is the process to monitor the accuracy and reliability of the GC in order to ensure its proper functioning and stability after calibration and throughout the analysis period. The quality control check should be conducted periodically on one or more of following guideline:

- Check against the certified reference gas mixtures.

After conducting the calibration or whenever there are any doubts about the analysis results, verify the calibration response factors against certified reference gas mixtures that were not used for calibration. The analysis results obtained from the GC compared to its certificate should conform to the reproducibility.

- Check against the back up GC.

In some cases, especially when the GC is used for custody transfer purposes, the duplicated GC is installed in parallel. Monitor the daily averages of the component concentration from both GCs to validate whether their composition is within the reproducibility.

- Check against the gas sampling cylinder.

Gas sampling can be done by spot or continuous sampling. Time and location should be the same as GC. Gas sample should be analysed by another GC. The different of calorific value should be not more than ± 0,2 % or as agreed by contractual agreement.

Annex A
(informative)

Example, comparison between duty and backup GC

GC1 is duty and GC2 is back up. Both have identical installation, verification and maintenance for a 6 month period.

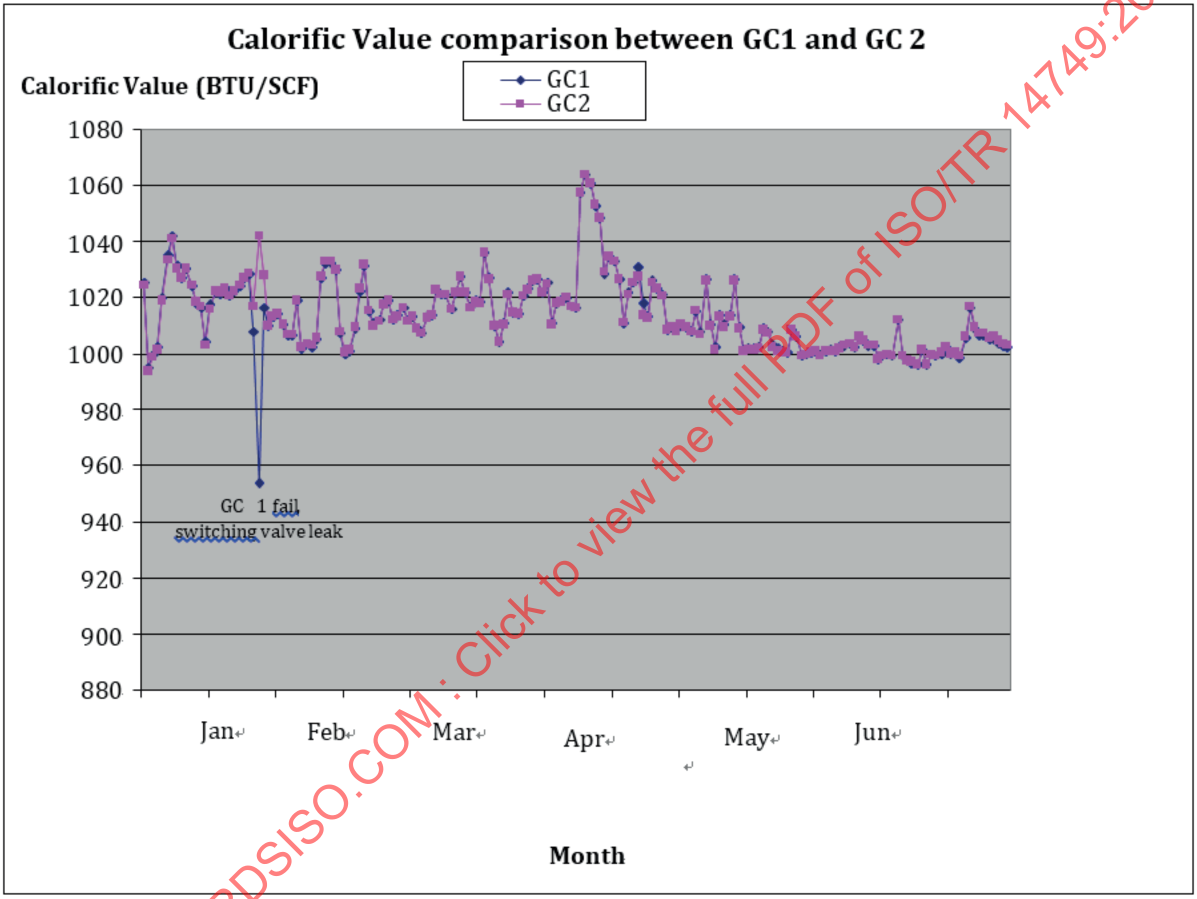


Figure 1 — Comparison between GC1 and GC2 for C7+ application