# ANALYSIS OF REFINERY GAS STREAMS USING THE SCION INSTRUMENTS REFINERY GAS ANALYSER

## Introduction

SCION Instruments offers a solution for refinery gas streams: The Refinery Gas Analyser, RGA. The RGA determines the chemical composition of reformed gas and similar gaseous mixtures containing the following components: Helium, Hydrogen, Oxygen/Argon (not separated), Nitrogen, Carbon monoxide, Carbon dioxide, C1-C6+ Hydrocarbons isomers and Hydrogen Sulphide, in a single analysis under 30 minutes. CompassCDS software will provide complete analyser control, data acquisition and flexible report generation. Moreover, The Rapid RGA provides a substantial reduction in overall analysis time; less than six minutes including $H_2S$. This is another analyser in the SCION Instruments portfolio.

The RGA configuration is optimised for compliance with ASTM D1946 and ASTM D2163. Other methods which can be met by the SCION Instruments RGA are for example ASTM D1945. ASTM D2504, ASTM D7833, ASTM D2593, ASTM D4424, IP405/ISO7941/EN27941, EN15985 and UOP539, although minor modifications may be required. Additionally, for enhanced sample introduction, the RGA can be optionally equipped with an integrated micro-gasifier. This sample conditioning device ensures complete vaporisations of LPG's and high-pressure samples to prevent any sample discrimination prior to injection. Another option for the RGA is the use of liquid sampling valves. The chemical composition of previous mentioned components can be used to calculate important physical properties of the gas, such as heating (calorific) value, and relative density. Physical properties can be calculated with specialist Gas Calculation Software, Eclipse.

## Experimental

The standard RGA is a three channel 456-GC with a multi valve design using both capillary and packed columns. Figure 1 shows the Refinery Gas Analyser. The first channel is optimised for the analysis of helium and hydrogen, with the second channel optimised for the analysis of permanent gases. Finally, the third channel is designed for light hydrocarbons.

For the Helium-Hydrogen channel, the sample is injected by means of a gas-sampling valve onto a Hayesep column. The first fraction containing Helium and Hydrogen is flushed onto a Molecular Sieve column; the rest is backflushed to the vent. Helium and Hydrogen are detected by a TCD.

The Permanent Gas channel is developed for the simultaneous determination of $CO_2$, the C2 isomers, $H_2S$, Oxygen/Argon, Nitrogen, Methane and CO. The sample is injected by means of a gas-sampling valve onto a series of Hayesep columns. The fraction containing Oxygen, Nitrogen, CO and Methane is flushed onto a Molecular Sieve column and parked. $CO_2$, the C2 isomers and $H_2S$ elute to the TCD, bypassing the Molecular Sieve column. After the elution of $H_2S$, the Molecular Sieve column is set in flow again, giving the separation of Oxygen/Argon, Nitrogen, Methane and CO.

The Light Hydrocarbon channel determines the range of low boiling hydrocarbons and isomers, C1 – C5 and C6+ (as composite peak). The sample is injected by means of a gas-sampling valve onto the pre-column (SCION-1). The components with a boiling point of below C6 are transferred onto the Al2O3/Na2SO4 column. The highly selective column separates all individual isomers from the light hydrocarbon fraction. The fraction with a boiling point of C6 and higher is backflushed from the pre-column to the FID, resulting in a peak representing the higher boiling fraction.

The backflush time determines the range of hydrocarbons which will be separated on the Al2O3/Na2SO4 column.

When liquid sample valves are added to the configuration, LPG's can also be injected onto the RGA.

## Results

Figures 2a, 2b and 2c show the chromatograms obtained from the three RGA channels, when a Refinery Gas Standard was analysed.

CompassCDS software provides complete analyser control, data acquisition and flexible reporting. The composition of the sample will give important information about the physical properties. To calculate the physical properties, Eclipse Software was used.

CompassCDS was optimised to integrate Eclipse results automatically, generating a physical properties report. The physical properties of interest can be selected from a list for full customisation and reporting.

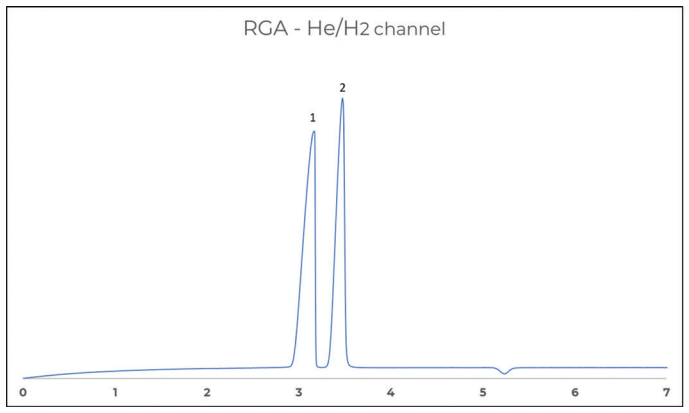
The software uses specific peak identification tables to determine the components on each of the three channels. Every channel has its own peak identification table. Each peak in this table can be calibrated on detector response using a single or multi-level calibration technique.

The peaks of a sample are identified, and the concentrations are calculated using the calibration data. All peaks can be normalised to 100 mol%. The normalised results are used to calculate the desired physical properties.


*Figure 1: SCION 456 Refinery Gas Analyser.*

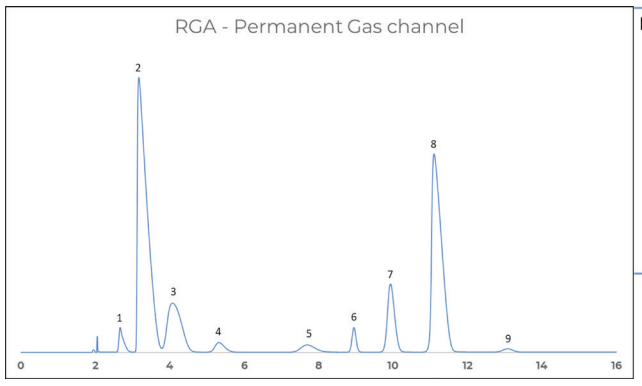
For the analysis of refinery gas, application EN15984 is used as an example. Figure 3 profiles a typical report generated, customise to report all physical properties possible for that application.

Eclipse has also a special enhancement for oxygen/nitrogen correction. It recalculates the concentration of nitrogen based on the amount of detected oxygen, due to leakage of air during sampling. The SCION Instruments RGA is also able to analyse natural gas. For natural gas analysis the physical properties can also be calculated in Eclipse, with extended physical property options.



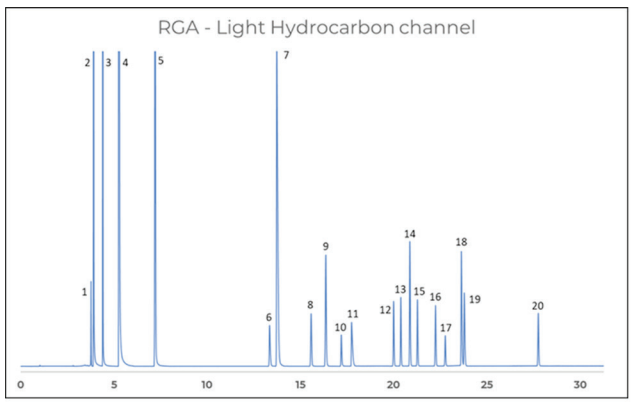

| Peak ID | Compound Name |
|---|---|
| 1 | Helium |
| 2 | Hydrogen |

*Figure 2a: Chromatogram of Refinery Gas Standard Front TCD Channel of RGA*




| Peak ID | Compound Name |
|---|---|
| 1 | Carbon dioxide |
| 2 | Ethylene |
| 3 | Ethane |
| 4 | Acetylene |
| 5 | Hydrogen sulfide |
| 6 | Oxygen/Argon |
| 7 | Nitrogen |
| 8 | Methane |
| 9 | Carbon monoxide |

*Figure 2b: Chromatogram of Refinery Gas Standard Middle TCD Channel*




| Peak ID | Compound Name |
|---|---|
| 1 | C6+ |
| 2 | Methane |
| 3 | Ethane |
| 4 | Ethylene |
| 5 | Propane |
| 6 | Cyclopropane |
| 7 | Propylene |
| 8 | i-Butane |
| 9 | n-Butane |
| 10 | Propadiene |
| 11 | Acetylene |
| 12 | t-2-Butene |
| 13 | 1-Butene |
| 14 | i-Butene |
| 15 | c-2-Butene |
| 16 | i-Pentane |
| 17 | n-Pentane |
| 18 | 1,3-Butadiene |
| 19 | Propyne |
| 20 | Butyne |

*Figure 2c. Chromatogram of Refinery Gas Standard Rear FID Channel*

## Conclusion

SCION Instruments provides a robust, high resolution, complete solution for refinery gas streams; the Refinery Gas Analyser. This analyser determines the chemical composition of reformed gas and similar gaseous mixtures, including natural gas.

The hardware and columns of the Refinery Gas Analyser are chosen in such a way that the analysis of refinery gas and other product streams can be achieved with a standard configuration.

In combination with Eclipse, gas calculation software, an extended list of physical properties can be calculated which will give important information about the characteristics of the gas streams.

The combination of the Refinery Gas Analyser with Eclipse software is a complete solution for analysing refinery gas streams.

## Peak Report

**Signal 1 Front (TCD)**

| Time | Area | Conc | Norm | Name |
|---|---|---|---|---|
| 3.4680 | 47.654e03 | 9.995 | 9.995 | Helium |
| 3.7880 | 41.392e03 | 4.949 | 4.949 | Hydrogen |

**Signal 2 Middle (TCD)**

| Time | Area | Conc | Norm | Name |
|---|---|---|---|---|
| 2.6863 | 31.455e03 | 0.998 | 0.998 | Carbon Dioxide |
| 7.5610 | 30.016e03 | 1.001 | 1.001 | Hydrogen Sulfide |
| 8.9417 | 33.100e03 | 0.999 | 0.999 | Oxygen |
| 9.8610 | 158.240e03 | 5.000 | 5.000 | Nitrogen |
| 12.8790 | 10.613e03 | 0.496 | 0.496 | Carbon Monoxide |

**Signal 3 Rear (FID)**

| Time | Area | Conc | Norm | Name |
|---|---|---|---|---|
| 3.4053 | 5.417e03 | 1.216 | 1.216 | Further compounds with Carbon atoms ≥ 5 |
| 3.7763 | 23.653e03 | 24.960 | 24.960 | Methane |
| 4.2273 | 11.309e03 | 5.999 | 5.999 | Ethane |
| 5.0033 | 47.065e03 | 24.980 | 24.980 | Ethylene |
| 6.7797 | 14.249e03 | 5.017 | 5.017 | Propane |
| 12.9240 | 1.390e03 | 0.501 | 0.501 | Cyclo Propane |
| 13.2250 | 13.560e03 | 5.002 | 5.002 | Propylene |
| 14.9447 | 1.756e03 | 0.504 | 0.504 | i-Butane |
| 15.7617 | 3.579e03 | 1.004 | 1.004 | n-Butane |
| 16.8263 | 806.715e00 | 0.500 | 0.500 | Propadiene |
| 17.4103 | 1.717e03 | 1.003 | 1.003 | Acetylene |
| 19.5253 | 1.706e03 | 0.510 | 0.510 | trans-2-Butene |
| 19.8797 | 1.755e03 | 0.519 | 0.519 | 1-Butene |
| 20.3703 | 3.450e03 | 1.005 | 1.005 | i-Butylene |
| 20.5983 | 866.598e00 | 0.200 | 0.200 | neo-Pentane |
| 20.8023 | 1.699e03 | 0.512 | 0.512 | cis-2-Butene |
| 21.6127 | 1.735e03 | 0.405 | 0.405 | i-Pentane |
| 22.1820 | 883.307e00 | 0.202 | 0.202 | n-Pentane |
| 23.2420 | 3.422e03 | 1.004 | 1.004 | 1,3-Butadiene |
| 23.3843 | 2.150e03 | 1.021 | 1.021 | Propin |
| 27.2467 | 1.540e03 | 0.500 | 0.500 | Butyne |
| | | **100.00** | **100.00** | |

## Physical Properties

| | | |
|---|---|---|
| Metering Temperature (t2) | 15 | °C |
| Metering Pressure (p2) | 101.3250 | kPa |
| Combustion Temperature (t1) | 15 | °C |
| Combustion Pressure (p1) | 101.3250 | kPa |
| Molar Mass (dry) | 26.102 | g/mol |
| Z Mix (t2,p2, dry) | 0.9951 | |
| Carbon Content | 73.67 | g/100g |
| Rel. Ideal Density (dry) | 0.90122 | |
| Rel. Density (t,p, dry) | 0.90567 | |
| Ideal Density (dry) | 1.10390 | kg/m3 |
| Real Density (t,p, dry) | 1.10935 | kg/m3 |
| Inferior Cal. Value (t1, dry) | 1,101.97 | kJ/mol |
| Inferior Cal. Value (t1, dry) | 4,221.83 | kJ/100 g |
| Inferior Cal. Value (t1,V(t2,p2), dry) | 46.60 | MJ/m3 |
| Real Inferior Cal. Value (t1,V(t2,p2), dry) | 46.83 | MJ/m3 |
| Vapor Pressure | 1,327.12 | psi at 100 °F |
| Motor Octane Number | 44.3 | |
| Density LPG | 719.5 | kg/m3 at 15 °C |
| Abs Vapor Pressure Grade A | 6,319 | kPa at -10 °C |
| Gauge Vapor Pressure Grade A | 6,218 | kPa at -10 °C |
| Abs Vapor Pressure Grade B | 6,791 | kPa at -5 °C |
| Gauge Vapor Pressure Grade B | 6,690 | kPa at -5 °C |
| Abs Vapor Pressure Grade C | 7,289 | kPa at 0 °C |
| Gauge Vapor Pressure Grade C | 7,188 | kPa at 0 °C |
| Abs Vapor Pressure Grade D | 8,363 | kPa at 10 °C |
| Gauge Vapor Pressure Grade D | 8,261 | kPa at 10 °C |
| Abs Vapor Pressure Grade E | 9,546 | kPa at 20 °C |
| Gauge Vapor Pressure Grade E | 9,445 | kPa at 20 °C |
| Abs Vapor Pressure Grade F | 12,260 | kPa at 40 °C |
| Gauge Vapor Pressure Grade F | 12,159 | kPa at 40 °C |
| Abs Vapor Pressure 37.8 | 2,514 | kPa at 37,8 °C |
| Gauge Vapor Pressure 37.8 | 2,413 | kPa at 37,8 °C |
| Abs Vapor Pressure 50 | 3,082 | kPa at 50 °C |
| Gauge Vapor Pressure 50 | 2,981 | kPa at 50 °C |
| Carbon Emission Factor | 70.46 | g CO2/mol |
| Carbon Emission Factor | 2.70 | g CO2/g |
| Carbon Emission Factor | 2.99 | g CO2/m3 |
| Carbon Emission Factor (inferior) | 63.94 | g CO2/MJ |
| Carbon Emission Factor (inferior) | 63.94 | ton CO2/TJ |

*Figure 3: Customised reporting of RGA results*

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