On-line GC Solution to comply with Flare Measurement Requirements

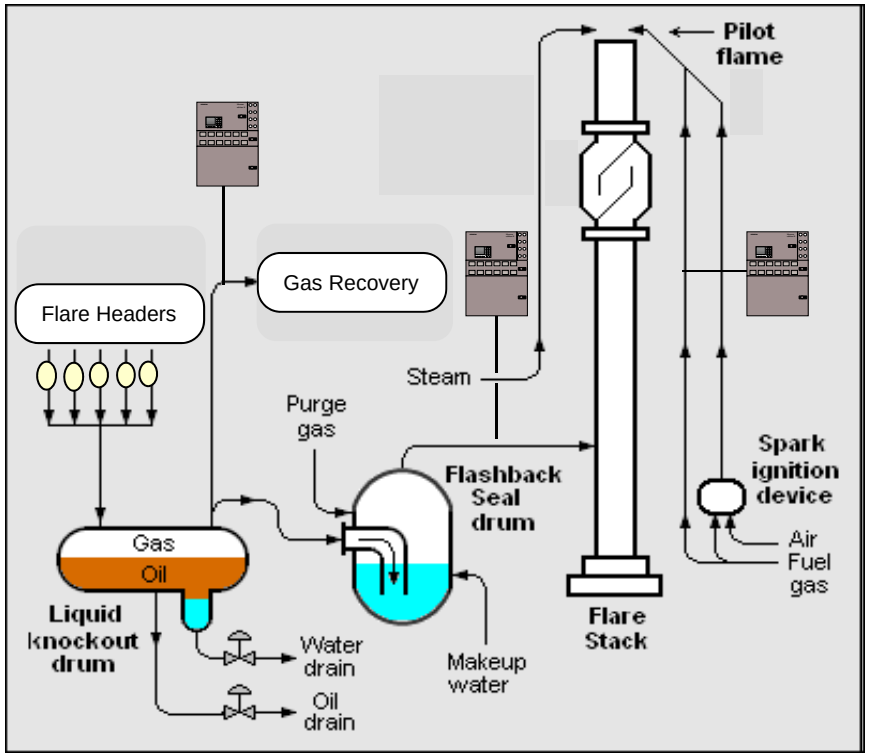
SIEMENS

Ulrich Gokeler
Analytical Products & Solutions
Houston, TX

Objectives

Numerous federal, state and regional regulations require to monitor industrial flares with the objective to quantify emission and optimize combustion efficiency. There is the just implemented federal regulation 63.670 Refinery Sector Rule (RSR), the recent Sub Part Ja also targeting refinery flares, Chapter 115 (HRVOC) of the Texan TCEQ targeting olefin emission in the Houston-Galveston area or Rule 1118 of the South Coast Air Quality Monitoring District (SCAQMD) just to mention a few. There are similarities between a number of those regulations, although with some subtle differences, permitting to share the same analytical configuration and measurement system to satisfy different regulations. Often GCs are the default choice because reliability, familiarity and maintainability which over many years has been proven often to be the best choice. However, as with many on-line analyzers the success of reliable measurement is not necessarily the analyzer but sample transport, sample conditioning, measurement system understanding, validation needs and simplicity of maintenance. This presentation discusses similarities and differences of some of those regulations and Process GC measurement solutions proven over many years of operation.

Flare Measurement



- **Rules**
  - RSR — Refinery Sector Rule 40CFR Part 63.670
  - HRVOC — TCEQ Chapter 115
  - Rule 1118 — South Coast Air Quality Monitoring District
  - Consents — Bilateral consent agreements
  - J — 40 CFR 60 Sub Part J
  - Ja — 40CFR 60 Sub Part Ja

Expecting

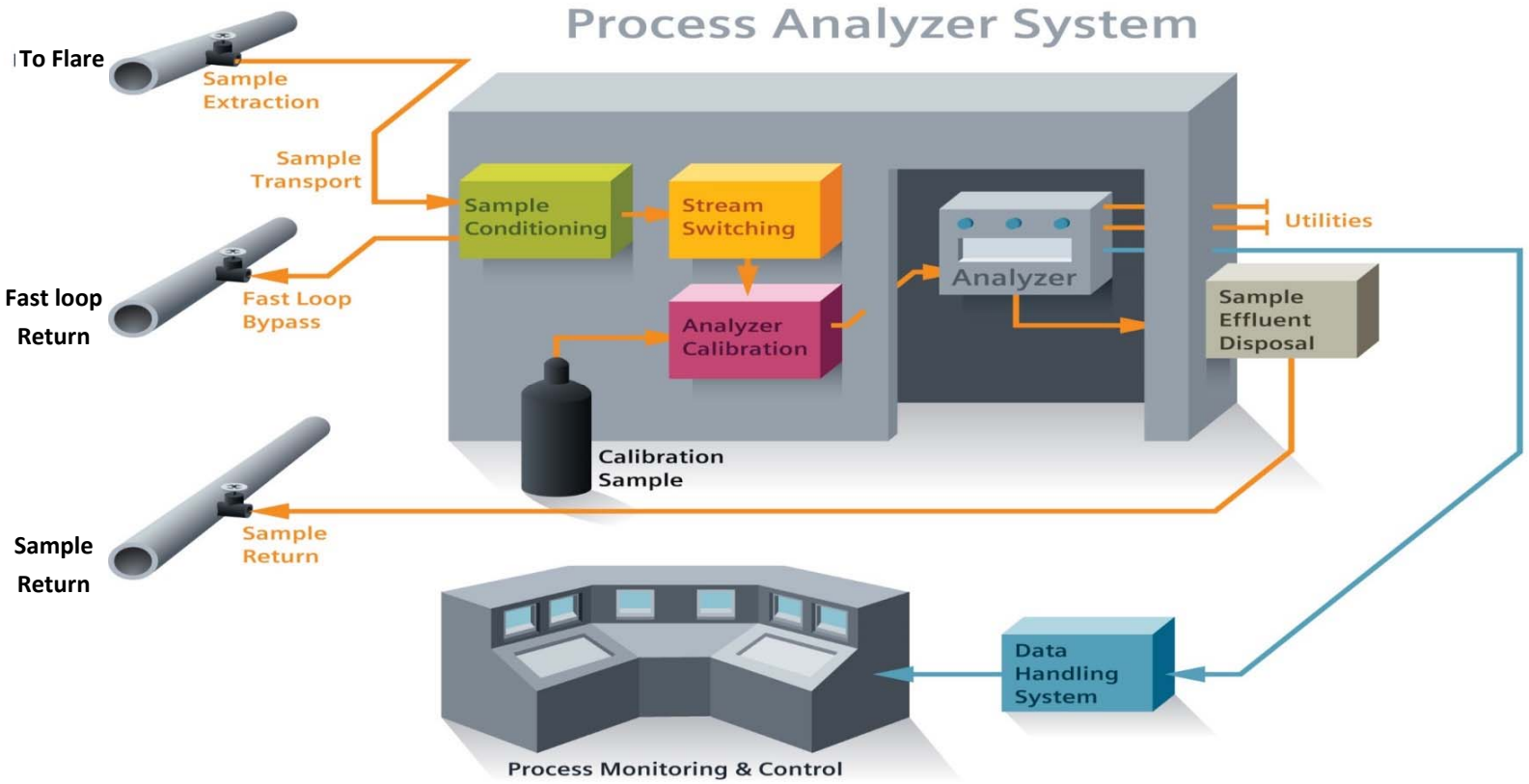
- ESR — Ethylene Sector Rule
- CSR — "Chemical" Sector Rule

Flare Measurement

- **Discussions often focus on analyzer**
- **System Solution**
  - Not often discussed in detail
  - Is decisive
  - Needs experience

www.us.siemens.com/processanalytics
www.industry.usa.siemens.com/automation/us/en/process-instrumentation-and-analytics/solutions-for-industry/environmental-monitoring/Pages/environmental-monitoring.aspx
www.union-instruments.com/en/products/calorimeter-cwd
www.deltainstrument.com/calorimeters.html
www.precisive-instruments.com
www.extrel.com

Flare Measurement System

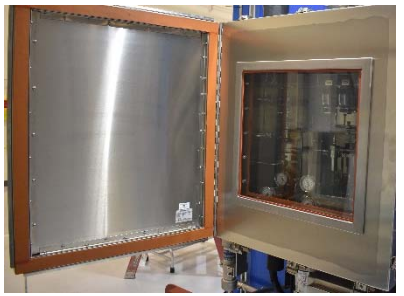


Flare Measurement System

- **Sample Conditioning**
  - Heating
    - **“**Cold” flares
    - “Hot” flares
  - Filter
    - Particulates & Coalescent
  - Traditional Design
    - Periodic visual inspection of P, T, F, condensate
  - Smart Design
    - T,P and flow of analytical loop and possibly fast loop
    - Multivariable smart devices bus linked to analyzer
    - Monitored via analyzer and workstation
  - Valving
    - Stream / Flare select
    - Purge
    - Cal/Val selection

Sample system at 120°C

Smart Sample System at 60°C



Flare Measurement System

- **Validation**
  - Analyzer
  - Measurement System
- **Standards**
  - Number of cylinders
    - GC, BTU typically 3 (multi components)

Heated Cabinet for Calibration/Validation

Flare Measurement System

- **Validation**
  - Analyzer
  - Measurement System

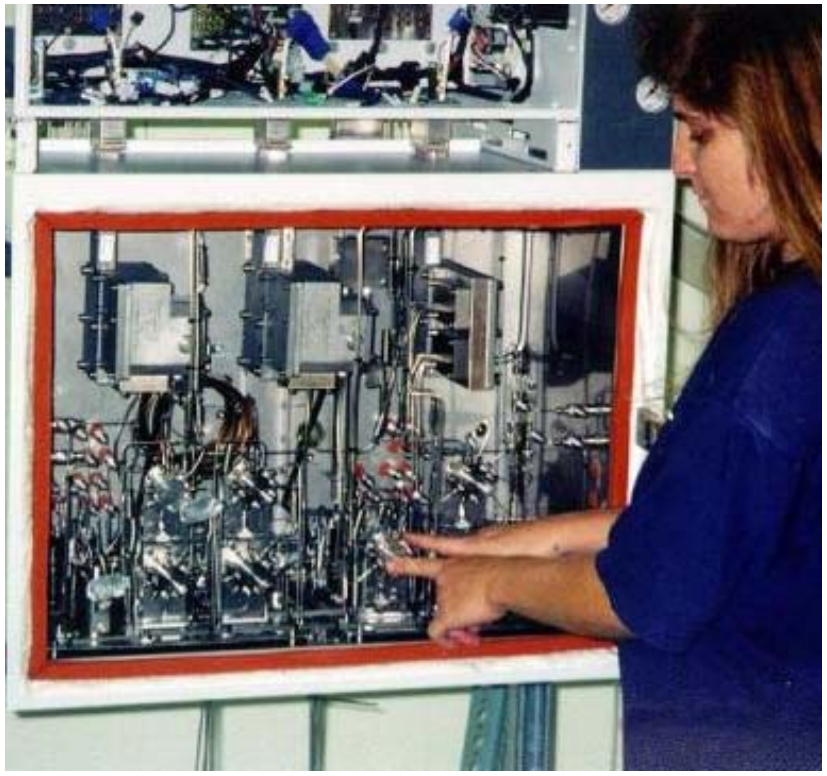
- **Standards**
  - Number of cylinders
    - GC, BTU typically 3 (multi components)
    - MassSpec 8+ (few comp./cylinder)
    - IR Interferential Lab analysis, or GC, or MS

Open Air Cabinet for Flare MassSpec Calibration/Validation

Process GC Flare Measurement Solution

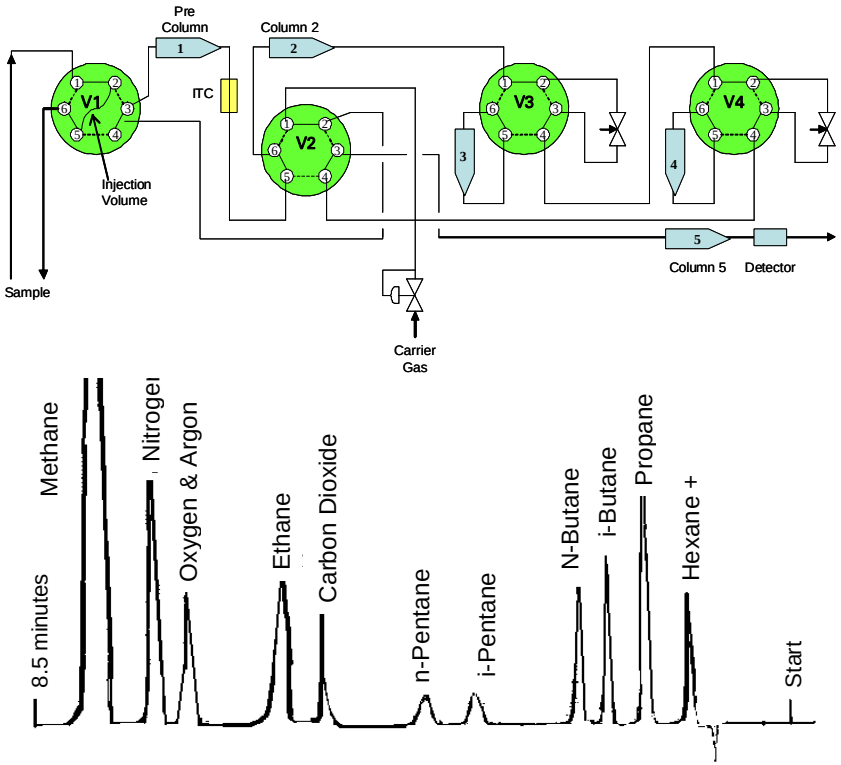
- **On-Line Process Gas Chromatograph**
  - Most flexible analytical technology
  - Most widely used multi component analyzer
  - Physical separation of target components
  - Direct measurement of components, not inferred
  - High uptimes
  - Predictable
  - Maintainable

Process GC – Complexity?



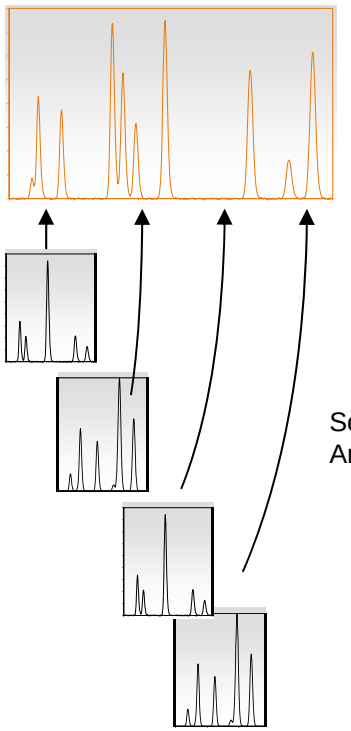
- **Process Gas Chromatograph**
- **Perception of**
  - Complexity
  - Long cycle Times
  - Long time experience
- **Not if done correctly!**

Process GC - Separation



- **Traditional**
  - Multi valve and multi separation columns
  - Complexity leading to challenges
    - Understanding
    - Maintainability
    - Cycle time
  - Traditional GC analytics needs simplification

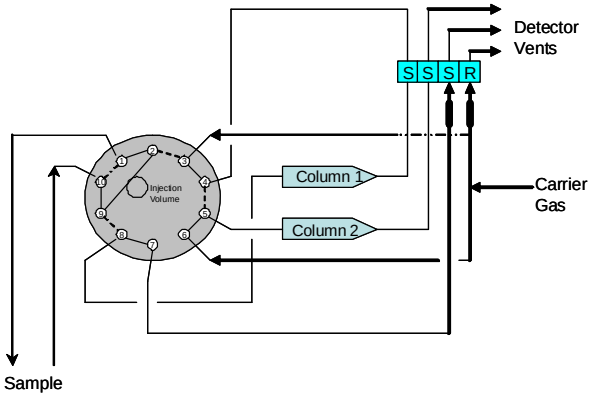
Process GC - Separation



Serial Chromatography

Segmentation of analytical task –
Analyze each segment independently

- **Parallel Chromatography**
  - Multiple simple column trains
    - Simple Backflush
    - Multiple detectors

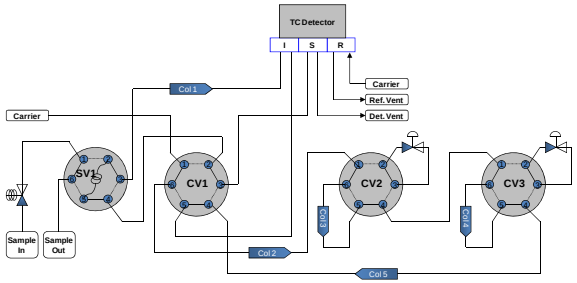


Applet

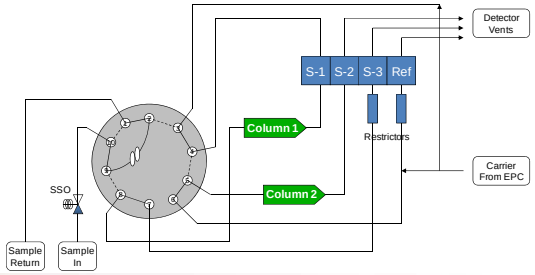
Single Column Train

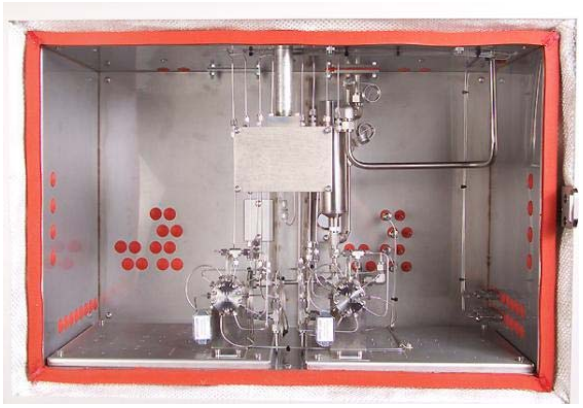
Process GC - Separation

Old Style “Serial GC”

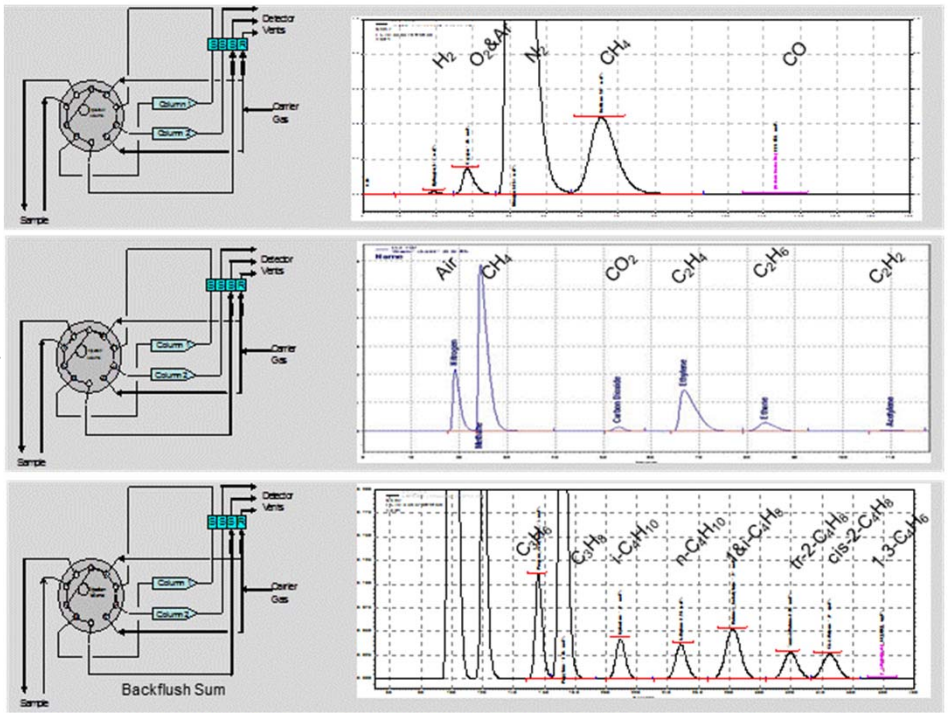


Maxum “Parallel GC”





Process GC - Flare Measurement



- **Example of full H2-C5+ analysis**
- **Parallel Chromatography**
  - Multi simple column trains
    - Simple Backflush
    - Multiple detectors
- **Simplification**
  - Understanding
  - Maintenance
  - Shorter cycle time
- **Performance Improvement**
  - On-line time 98-99.5%
    (possible 99.7%)

Process GC - Flare Measurement

- **Maintenance in Place**
  - Utilized widespread
  - Familiarity
  - Experience
- **Maintenance by Exchange**
  - Module based
  - Module consist of separation columns, valves and detectors on common mating base plate
  - Standard column trains
  - Exchange, heat-up and validation ~2-3 hours.

Process GC - Flare Measurement Performance

Linearity R^2 = 0.999-1 (0.01-100%)

Component	Range	Linearity R^2
MSR - Hydrogen	0-100%	0.999
MSR - Argon/Oxygen	0-100%	0.9999
MSR - Nitrogen	0-100%	1
MSR - CO	0-100%	0.9999
Methane	0-100%	0.9999
CO2	0-100%	1
Ethane	0-100%	1
Ethylene	0-100%	1
Acetylene	0-100%	1
Propane	0-100%	1
Propylene	0-100%	1
i-Butane	0-100%	0.9999
n-Butane	0-100%	0.9999
i-Butylene	0-100%	0.9993
cis-2-Butylene	0-100%	0.9999
trans-2-Butylene	0-100%	0.9995
1.3-Butadiene	0-100%	0.9997
i-Pentane +	0-100%	1

Why 3-point validation?

Repeatability RSD 0.2-0.6% (6 days)

Component	% rel. STDev. 6 days	Component Concentrations Mol %
MSR - Hydrogen	0.75	5.90
MSR - Argon / Oxygen	0.45	0.41
MSR - Nitrogen	0.35	23.80
MSR - Carbon Monoxide	1.26	0.16
Methane	0.32	16.00
Carbon Dioxide	0.24	0.68
*Ethylene	0.23	5.60
Ethane	0.23	6.30
Acetylene	0.27	0.57
Propane	0.20	15.20
*Propylene	0.20	11.50
i-Butane	0.35	2.00
n-Butane	0.24	4.30
*i-Butene & Butene-1	0.22	8.50
*Trans-2-Butene	0.24	3.50
*Cis-2-Butene	0.25	3.36
*1,3-Butadiene	0.31	3.80
i-Pentane (Plus)	0.46	0.53

Why daily validation?

Process GC – Cycle Time

Measurement		Cycle Time (min)	Objective	Applicability
Hydrogen		0.5-0.75	BTU Benefit	RSR, HRVOC
Nitrogen		1 - 1.5	Flowmeter	All regs
Air, C1-C4+		2	BTU	RSR
Air, C1-C5+		3	BTU	RSR
H2, N2, CO2, C1-C5+	Paraffins	3	BTU	RSR, HRVOC
H2, N2, CO, CO2, C1-C5+	Paraffins & Olefins	7.5	BTU	HRVOC
H2S		3-5	Sulfur Emission	J, Ja
Total Sulfur		3	Sulfur Emission	Ja, 1118

Flare Measurement - Similar Regulations

	RSR
Objective	Combustion Efficiency
Control	BTU in combustion zone
Flow quantification	T, P, F
Measurement	All or H_2, C_2-C_5 N_2
Measurement Frequency	minimum 4 results/hr.
Validation	BTU
	PS 9
	min. 60°C
Validation Frequency	daily mid point (single analysis)
	quarterly low/mid/high
Validation Target	"All" or H_2 & C1-C5 n-Paraffins

Flare Measurement - Similar Regulations

	RSR	HRVOC
Objective	Combustion Efficiency	Olefin Emission
Control	BTU in combustion zone	>300 BTU
Flow quantification	T, P, F	T, P, F
Measurement	All or H_2, C_2-C_5 N_2	C_2-C_4 Olefins as present H_2, N_2, C_1-C_5+, H_2O a.o.
Measurement Frequency	minimum 4 results/hr.	minimum 4 results/hr.
Validation	BTU	individual components
	PS 9	PS 9
	min. 60°C	min. 60°C
Validation Frequency	daily mid point (single analysis)	weekly mid point (triplicate)
	quarterly low/mid/high	quarterly low/mid/high
Validation Target	"All" or H_2 & C1-C5 n-Paraffins	Olefins, "all" or main BTU contributors

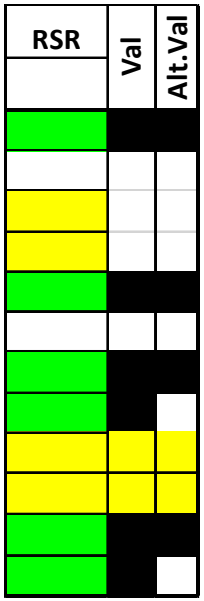
Flare Measurement - Validation

Components	Range %	RSR	Val
Hydrogen	0-100		
Oxygen & Argon	0-100		
Carbon Monoxide	0-100		
Nitrogen	0-100		
Methane	0-100		
Carbon Dioxide	0-100		
Ethane	0-100		
Ethylene	0-100		
H2S	0- 100		
Acetylene	0-100		
Propane	0-100		
Propylene	0-100		

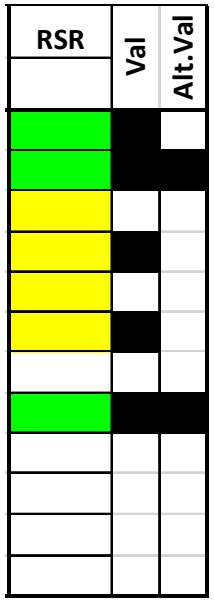
Components	Range %	RSR	Val
i - Butane	0-100		
n-Butane	0-100		
i-& 1-Butene	0-100		
tr-2-Butene	0-100		
cis-2-Butene	0-100		
1,3-Butadiene	0-100		
i-C5+	0- 50		
n-C5+	0- 50		
n-Pentane	0- 50		
i-C6+	0- 20		
Water	0- 30		
a.o. Benzene	0- 10		

Flare Measurement - Validation

Components	Range %
Hydrogen	0-100
Oxygen & Argon	0-100
Carbon Monoxide	0-100
Nitrogen	0-100
Methane	0-100
Carbon Dioxide	0-100
Ethane	0-100
Ethylene	0-100
H2S	0- 100
Acetylene	0-100
Propane	0-100
Propylene	0-100



Components	Range %
i - Butane	0-100
n-Butane	0-100
i-& 1-Butene	0-100
tr-2-Butene	0-100
cis-2-Butene	0-100
1,3-Butadiene	0-100
i-C5+	0- 50
n-C5+	0- 50
n-Pentane	0- 50
i-C6+	0- 20
Water	0- 30
a.o. Benzene	0- 10



Alternative Surrogate Calibration/Validation simplifies => fewer cylinders, higher pressure/gas volume

Flare Measurement - Validation Similarities

Components	Range %	HRVOC	Val		RSR	Val	Alt.Val
Hydrogen	0-100						
Oxygen & Argon	0-100						
Carbon Monoxide	0-100						
Nitrogen	0-100						
Methane	0-100						
Carbon Dioxide	0-100						
Ethane	0-100						
Ethylene	0-100						
H2S	0- 100						
Acetylene	0-100						
Propane	0-100						
Propylene	0-100						

Components	Range %	HRVOC	Val		RSR	Val	Alt.Val
i - Butane	0-100						
n-Butane	0-100						
i-& 1-Butene	0-100						
tr-2-Butene	0-100						
cis-2-Butene	0-100						
1,3-Butadiene	0-100						
i-C5+	0- 50						
n-C5+	0- 50						
n-Pentane	0- 50						
i-C6+	0- 20						
Water	0- 30						
a.o. Benzene	0- 10						

Utilize same analyzer for multiple regulatory requirements

Multi Purpose Flare Analyzer System

- Similar Regulations
  - RSR, TCEQ Chapter 115, SCAQMD 1118, Consent Agreements
- Objectives
  - Regulation compliance
  - Internal objectives
- Sample Temperature
  - Sample transport
  - Sample system
- Validation
  - Single
  - Triplicate
  - Analyzer
  - Measurement System
- BTU Calculation
  - Heat Values according individual rules
- Downtime
  - Validation according different rules may incur additional down time

Technological Options & Suitability

	Specia-tion	HRVOC Olefins	HRVOC BTU	RSR	H2	N2	Speed	Complexity	Standards	Cost
Calorimeter					Add H2		<30 sec	User	1-3	0
IR Inferential	Add GC for optimization						<30 sec	Vendor	multiple	0
Mass Spec							<30 sec	Vendor/User	8 - ?	+
Process GC							90-450 sec (scope dependent)	User	1 - 3	-

Based on public information and comments by customers.

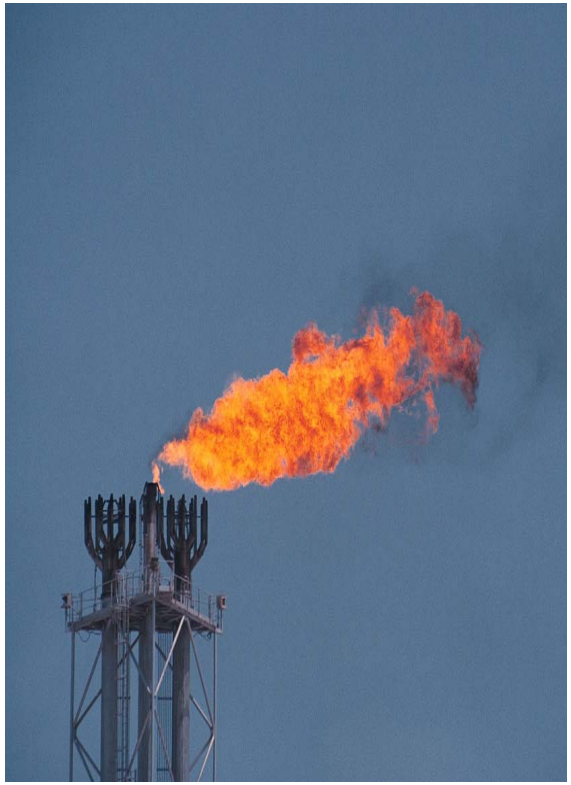
Extractive, need Sample System & Basic Weather Protection

Objective is BTU value in Combustion Zone

Composition dependent Steam/Air addition enables optimized combustion

Process GC – Flare Experience

- Flare GCs
  - Since >20 years
  - >500 in operation
- Sample Conditions
  - Liquid Slugs / Sample dew point
    - Steady state
    - Upset conditions
  - Sample system design
    - Coalescence Filter
    - 60^{o}C => 110^{o}C
    - Purge option
    - Smartness
  - Pump
    - Redundancy

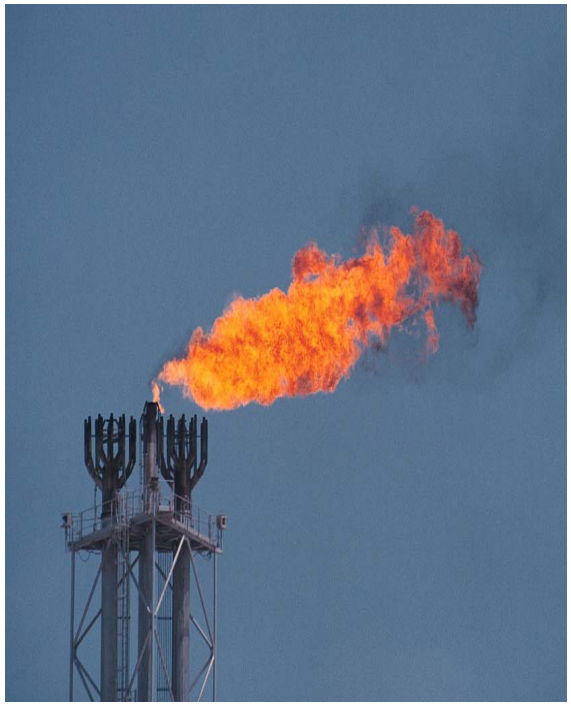


Process GC – Flare Experience

- Validation
  - Standards
    - Number of constituents
    - Number of cylinders
    - Temperature equilibration
  - Memory
    - Sample line inertness
    - Purge volume
- Maintainability
  - Analytical system simplicity
    - On-site understanding
    - On-site maintainability

Process GC - Summary

- **On-line Process Gas Chromatography**
  - Most widely used speciated measurement solution
- **Risk reduction**
  - Proven solutions
  - Front-end measurement assessment
  - Turn-key measurement system including sample extraction, sample conditioning, analyzer, system packaging
- **Permits Minimizing Validation complexity**
  - Minimize validation components/standards
- **Permits Commonly on-site Maintainability by User**
  - Easiest to maintain by on-site technicians
    - Analyzer hit by condensate slugs
    - Composition change/range adaptation
- **Utilize Measurement System for Multiple Rules or in redundant configuration**



SIEMENS

On-line GC Solution to comply with Flare Measurement Requirements

Ulrich Gokeler
Strategic Support
Siemens Industry, Inc.
Analytical Products & Solutions

Houston, TX 77041. USA
Phone: 713 417 3864
E-mail: ulrich.gokeler@siemens.com