Determination of Hydrogen Sulfide and Total Sulfur in Natural Gas

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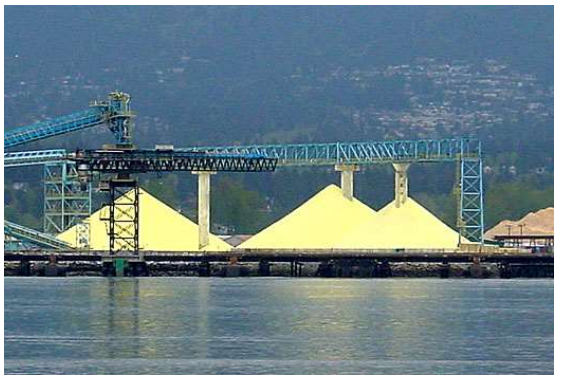
Background on H2S Measurements



Background on H2S

1ppm (1/10,000 of 1%)	=	.0001%	Detectable by odor.
10ppm	=	.001%	Allowable for 8 hours' exposure. (OSHA)
OVER 20ppm			PROTECTIVE EQUIPMENT WILL BE NECESSARY.
100ppm	=	.01%	Kills smell in 3 to 15 minutes. May burn eyes and throat.
200ppm	=	.02%	Kills smell rapidly. Burns eyes and throat.
500ppm	=	.05%	Loses sense of reasoning and balance. Respiratory disturbances in 2 to 15 minutes. Needs prompt artificial resuscitation.
700ppm	=	.07%	Will become unconscious quickly. Breathing will stop and death results if not rescued promptly. Immediate artificial resuscitation.
1000ppm	=	.10%	Unconscious at once. PERMANENT BRAIN DAMAGE MAY RESULT UNLESS RESCUED PROMPTLY.

Background on H2S and Sulfur

Name	Chemical Formula	Abbreviatic
Sulfides		
Hydrogen Sulfide	H_2S	H_2S
Carbonyl Sulfide	COS	COS
Dimethyl Sulfide	CH_3SCH_3	DMS
Methylethyl Sulfide	$CH_3SCH_2CH_3$	MES
Diethyl Sulfide	$CH_3CH_2SCH_2CH_3$	DES
Diallyl Sulfide	$CH_2CHCH_2SCH_2CHCH_2$	DAS
Dipropyl Sulfide	$CH_3(CH_2)_2S(CH_2)_2CH_3$	DPS
Dibutyl Sulfide	$CH_3(CH_2)_3S(CH_2)_3CH_3$	DBS
Mercaptans		
Methyl Mercaptan	CH_3SH	MeSH
Ethyl Mercaptan	CH_3CH_2SH	EtSH
Propyl Mercaptan	$CH_3CH_2CH_2SH$	PrSH
iso - Propyl Mercaptan	$(CH_3)_2CHSH$	i-PrSH
Normal - Butyl Mercaptan	$CH_3(CH_2)_3SH$	n-BuSH or Bu
Secondary - Butyl Mercaptan	$CH_3CH(SH)CH_2CH_3$	s-BuSH
iso - Butyl Mercaptan	$(CH_3)_2CHCH_2SH$	i-BuSH
Tertiary - Butyl Mercaptan	$(CH_3)_3CSH$	t-BuSH
Disulfides		
Carbon Disulfide	CS_2	CS2
Dimethyl Disulfide	$CH_3S_2CH_3$	DMDS
Methylethyl Disulfide	$CH_3S_2CH_2CH_3$	MEDS
Diethyl Disulfide	$CH_3CH_2S_2CH_2CH_3$	DEDS
Dipropyl Disulfide	$CH_3(CH_2)_2S(CH_2)_2CH_3$	DPDS
Tetrahydro Thiophene	$CH_2CH_2CH_2CH_2S$	THT

H_2S and Sulfur Compounds

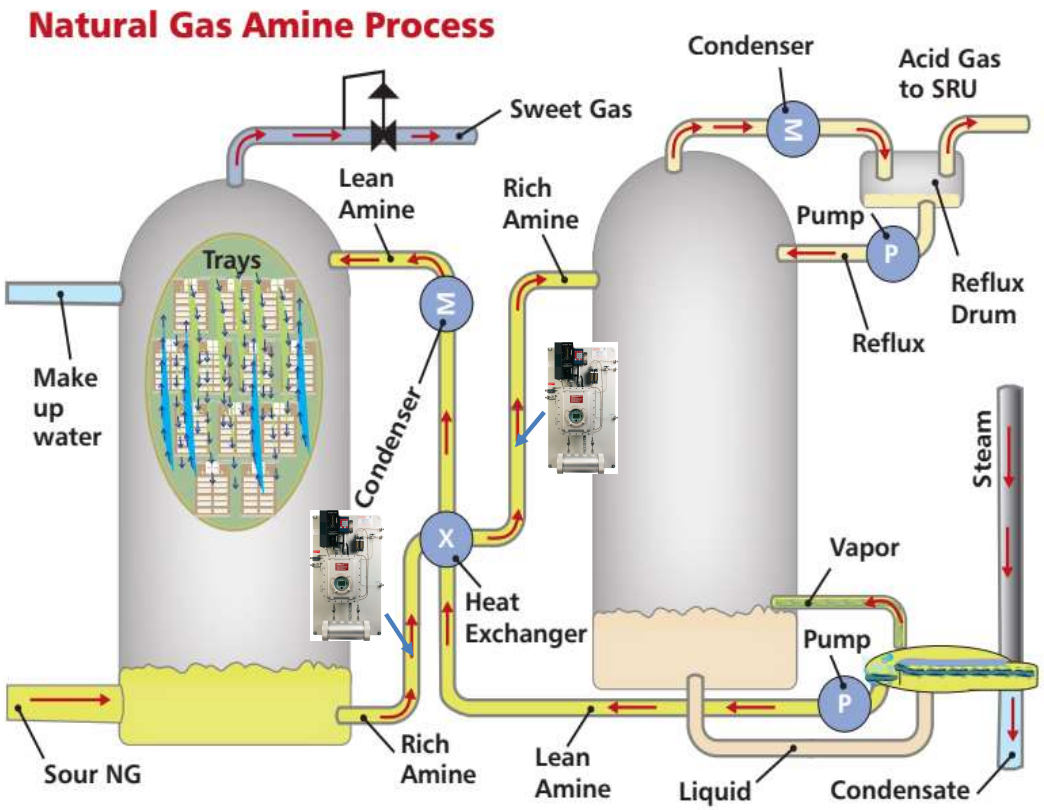
- H_2S and other sulfur compounds occur naturally with oil and gas deposits around the world.

- In general, sulfur compounds are considered undesirable and are removed from hydrocarbons.

- H2S is colorless, toxic, highly reactive and flammable. Distinctive "rotten egg" odor at low concentration.

Amine stripping and sulfur recovery.
Chemical absorbents.

- Sulfatreat
- Activated Carbon
- ZnO



Monitoring the inlet and outlet of the absorber is critical to optimizing the acid gas removal process and realize significant reductions in costs.

e.g., contact temperature, pressure, total acid gas loading, NG and amine feed flow rates, location of lean amine feed point on the absorber structure, and amine fluid degradation.

Measurement in Refining

Liquefied Petroleum Gases (Propane/Butane)

- Product Quality
- Feedstocks

Fuel Gas

- Emission Reporting

Sulfur Recovery

- Process H_2S/SO_2 Air Demand
- Acid Gas, Pit Gas, SO_2 Emissions

Vent Stack Emissions

- Total Reduced Sulfur
- SO_2 Reporting

Measurement in Petrochemical

Ethylene / Propylene

- Product Quality
- Catalyst Protection

Liquefied Petroleum Gases

- Feed Stock - Catalyst Protection

Syngas

- H_2, CO, CO_2, CH_4
- Product Quality / Catalyst Protection
- Total Sulfur Measurement

Fertilizer

- Catalyst Protection
- Feedstock is generally Natural Gas
  Trace (ppb) H_2S and TS

Measurement in Natural Gas

Pipeline

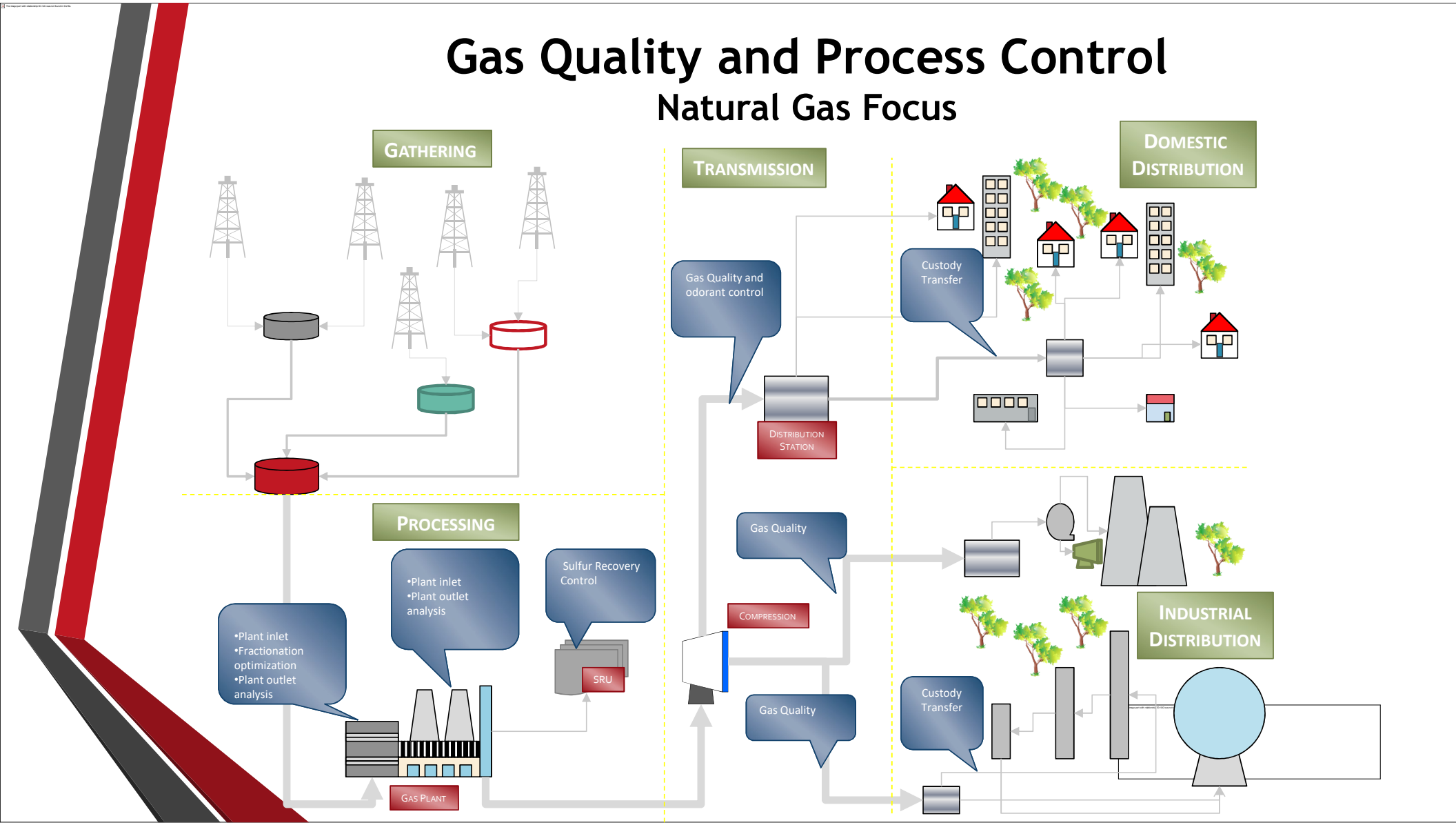
- Product Quality / Custody Transfer
  - -Tariff Levels- U.S.- 4 ppm, Canada- 16 ppm, EU- 3.5 ppm
- Odorants Total Sulfur analysis to ensure gas is properly odorized.
- Corrosion Control
  - -H_2S measurement

Production – Gas Plant

- Product Quality, Plant Outlet
- Plant Inlet
  - -High concentrations of H_2S
- Flare Lines
  - -High concentrations of H_2S
  - -Environmental regulations

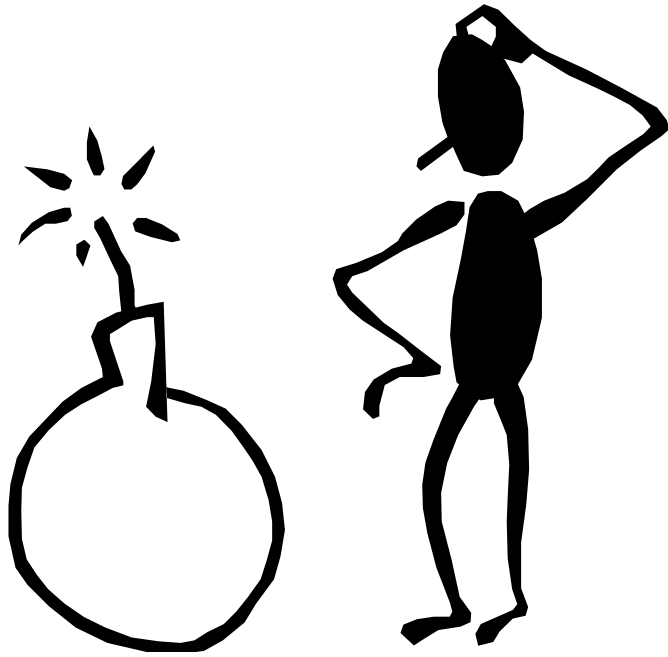
Gas Quality and Process Control

Natural Gas Focus



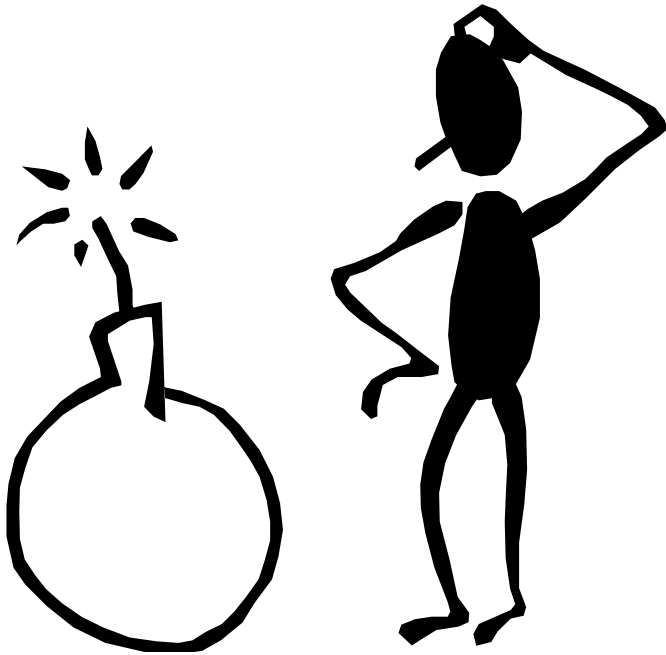
Why Some Gas Compounds like H2S Are Difficult To Monitor?

- Sample Concentration and Chemistry Concerns
- Sample Transport and Handling vs Analysis
- Process Conditions- Pressure, Temp, Flow Sample Return
- Reporting Requirements- Accuracy, Time…
- Analysis Technique- Optical, Color, GC, TDL
- Budget, Resources, Cost Versus Analysis Time



Sample Chemistry

- Concentration (%, ppm, ppb, ppt)
- Sample state
- Polar versus Non-Polar
- Solubility
- Reactivity
- Toxicity and Safety
- Corrosive



Sample Transport and Handling

- Materials of Construction for Wetted Surfaces
  - Hastelloy, Inconel, Teflon, SilcoSteel
  - Monel, Sulfinert, Stainless Steel

Process Temp./Pressure

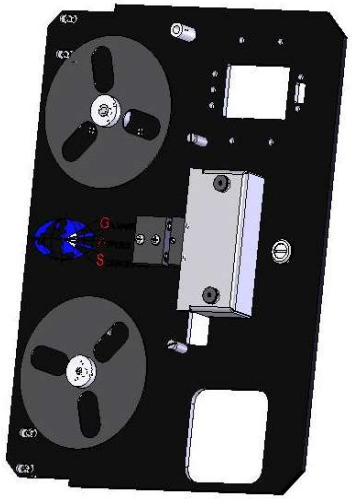
- Distance to Analyzer (fast loop?)
- Heated Lines and Enclosures
- Sample Exhaust (process, flare, air)

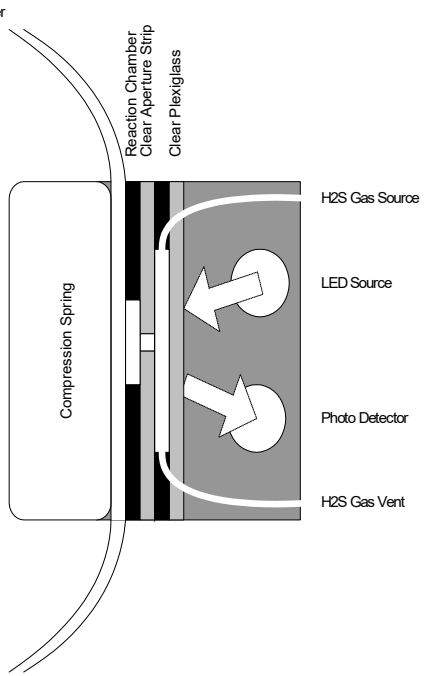
Common Analysis Techniques for H2S/Sulfur Compounds

- Paper Tape (Colorimetric)
- Ultraviolet Spectroscopy (UV)
- Gas Chromatography (GC)
- Tuneable Diode Laser (TDLAS)

Paper Tape

An advanced colorimetric sensor that continuously measures the rate of darkening caused by the reaction of H_2S on white tape impregnated with lead acetate in accordance with ASTM methods D4084-94, D4323-97 and D4468-95.





Principle of Operation

- $H_2S + Pb(CH_3COO)_2 \rightarrow PbS + H_2O$
- Lead Sulfide (PbS) is left on tape as brown stain
- Rate of stain formation is proportional to amount of H_2S present
- Rate of stain is monitored by photodiode sensor
- Lead Acetate Tape is 100% H_2S specific
- No interferences

Paper Tape Advantages:

- Highly sensitivity
- No interferences
- Low cost to acquire and low cost of ownership
- Simple technology
- H_2S and or Total Sulfur (reduction path- H_2S)
- Multipoint capability

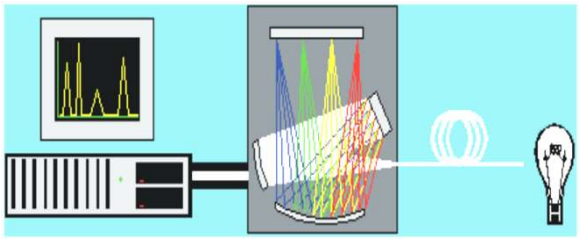
Disadvantages:

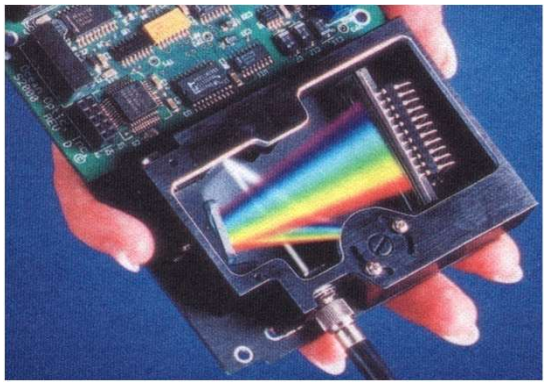
- Expendables
- Speed of analysis
- Dynamic range
- Temp./Humidity

Ultraviolet Spectroscopy (UV)

Absorbance, Fluorescence, Diode Array, Non-dispersive

UV spectroscopy is type of absorption spectroscopy in which light of ultraviolet region (200-400 nm.) is absorbed by the molecule. Absorption of the ultraviolet radiations results in the excitation of the electrons from the ground state to higher energy state. The energy of the ultraviolet radiation that is absorbed is equal to the energy difference between the ground state and higher energy states.





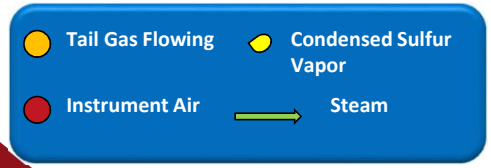
Ultraviolet Advantages:

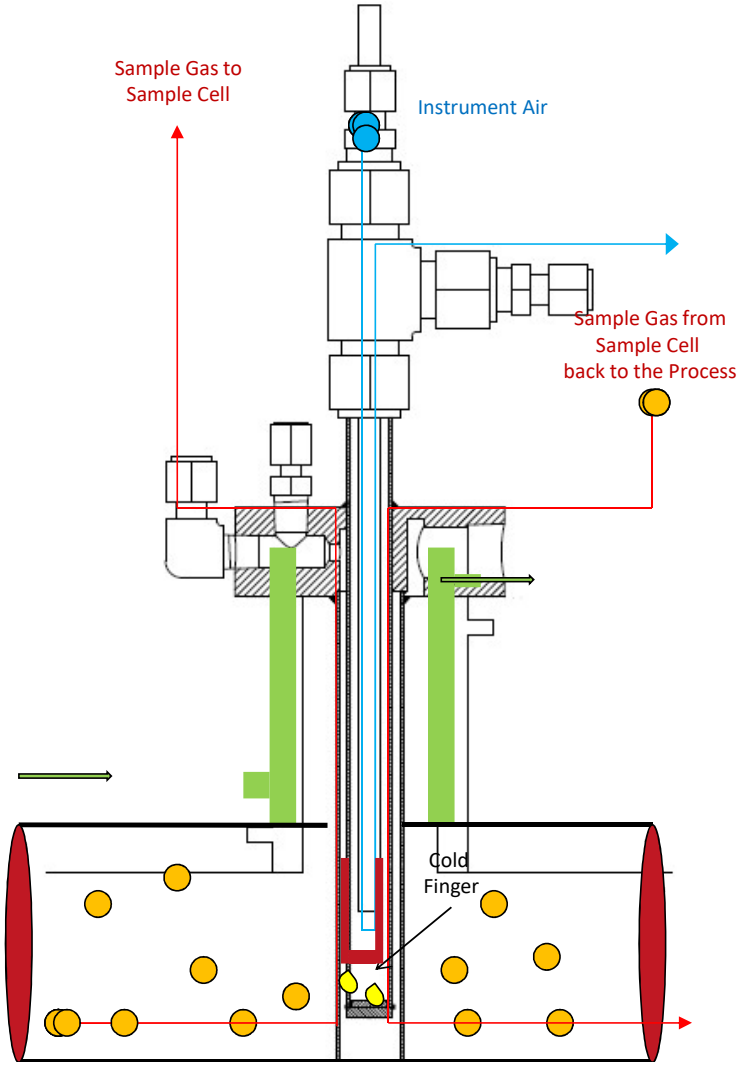
- Speed of measurement
- Dynamic range
- moderate cost to acquire and low cost of ownership
- H_2S and some sulfur compounds (oxidation path- SO_2)
- Multipoint capability

Disadvantages:

- UV source lifetime
- Moderate sensitivity with absorbance
- Interferences

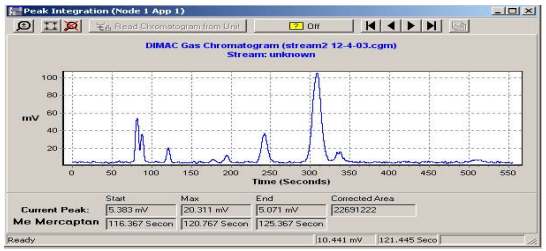
UV Sample Probe in Klaus SRU





Gas Chromatography (GC)

A chemical analysis instrument for separating chemicals in a complex sample. A gas chromatograph uses a flow-through narrow tube known as the column, through which different chemical constituents of a sample pass in a gas stream (carrier gas, mobile phase) at different rates depending on their various chemical and physical properties and their interaction with a specific column filling, called the stationary phase. As the compounds exit the column they are detected and identified.



Gas Chromatography Advantages:

- Speciation of compounds
- Moderate complexity
- Low to moderate cost to acquire
- H_2S as well as all sulfur compounds/or in addition to other compounds
- Multipoint capability

Disadvantages:

- Speed of analysis
- Sensitivity is detector dependent (chemiluminescence vs TCD)
- Carrier gas supply (helium, hydrogen)
- Cost of ownership and maintenance

Tunable Diode Laser (TDLAS)

TDLAS uses a tunable near infrared Laser. A Tuneable Diode Laser is a type of semiconductor based laser that can be tuned to optically select a very specific wavelength (or color) of light. The laser emits near-infrared radiation with a line width less than 0.003 cm-1, which is narrower than molecular absorption line widths (typically 0.1 cm-1 at atmospheric pressure). Tuning to a specific wavelength is done by varying the diode temperature and the diode current going through it.

Tuneable Diode Laser Advantages:

- Multi-compound capability
- Speed of analysis
- Dynamic range
- Multipoint capability

Disadvantages:

- Sensitivity to H_2S in near infrared
- Repeatability for H_2S varies by sample type
- High cost to acquire
- No speciation of sulfurs

Conclusions:

- Put Real Effort Into the Sampling and Calibration System
- Get as Close to the Process as Possible
- H_2S, H_2S/TS or other compounds/H_2S
- When all Criteria Appear Equal the Most Sensitive Analyzer is Usually Best
- More Time Makes for Better Decisions
- Multipoint-Sampling, Cost Versus Time

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