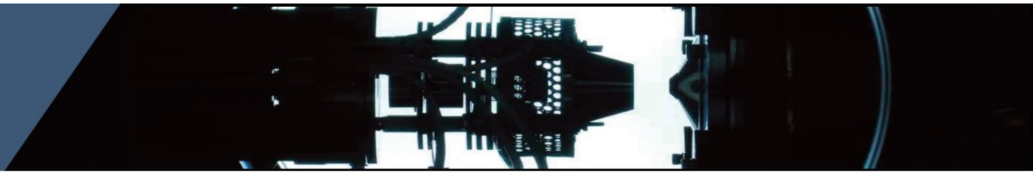
Extrel

ISA Delhi Section



Fertilizer Symposium 2016

“Ammonia Production Control thru Process Mass Spectroscopy”

Dr. Frank A. DeThomas
Extrel CMS LLC
575 Epsilon Drive
Pittsburgh, PA USA

Main use of Ammonia is for Fertilizers

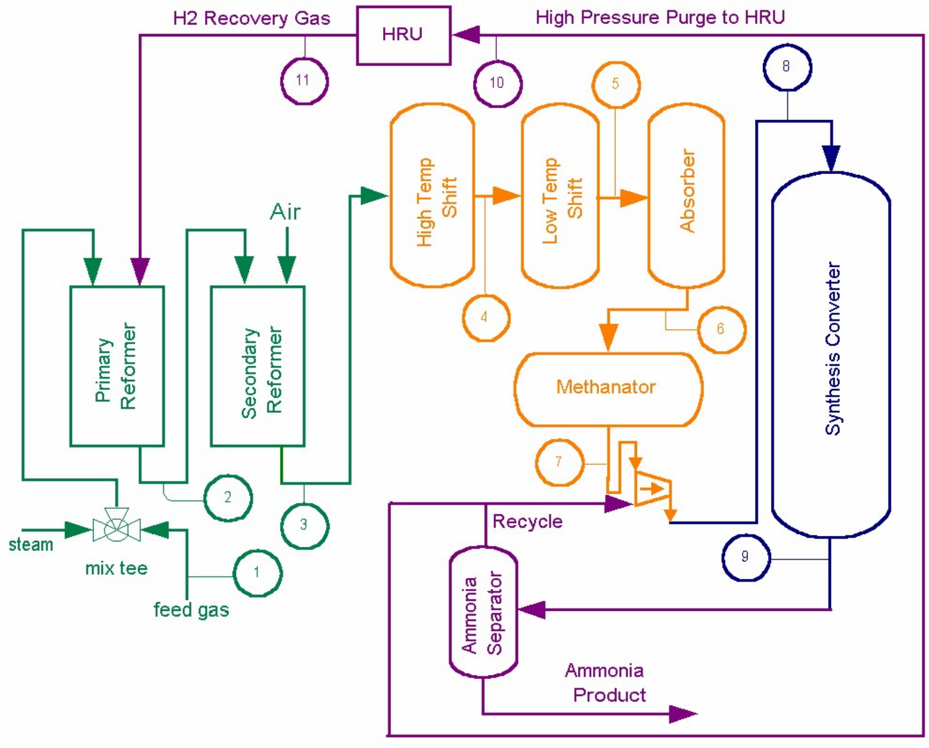
- Fertilizers (~78%)
  - Anhydrous ammonia
  - Urea
  - Ammonium nitrates
  - Ammonium phosphates
  - Other Nitrogen compounds
- Plastics
- Synthetic Fibers and Resins
- Explosives

Mass Spectrometry

- Speed of Analysis
  - 0.4 sec/constituent
  - 10-20 sec/stream
  - Advanced Process Control (APC)
- Selectivity
  - Mass/Charge Ratio (M/Z)
- Multiple Stream
  - 1-46 Process Streams
  - 1-160 Environmental Channels
  - Different Composition
- Dynamic Range
  - Linear Form ppb to 100%
- Accuracy
  - Equal to Calibration Standards
- Precision
  - Better than Primary Method
  - 0.0025 on 1% Ar
- Maintenance
  - Reduced Maintenance
  - Better Than 98% Uptime

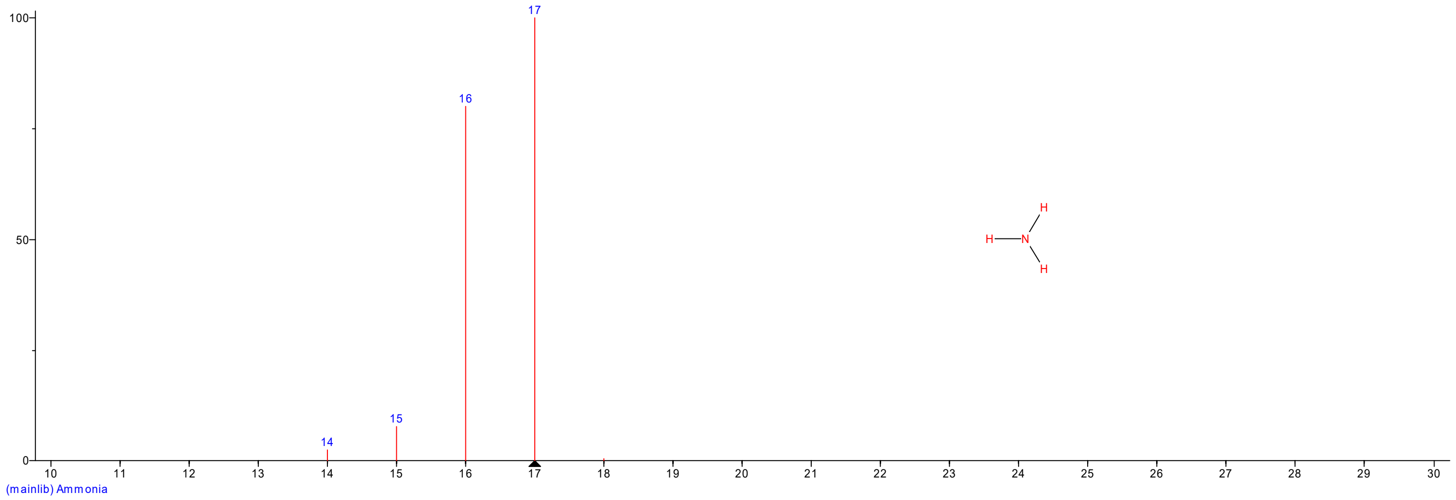
Ammonia Background

Ammonia is made in a multistage process based on steam methane reforming of a natural gas feed



Some plants are designed to use alternative feed stocks such as petroleum feedstock

How Does a Mass Spectrometer Work?

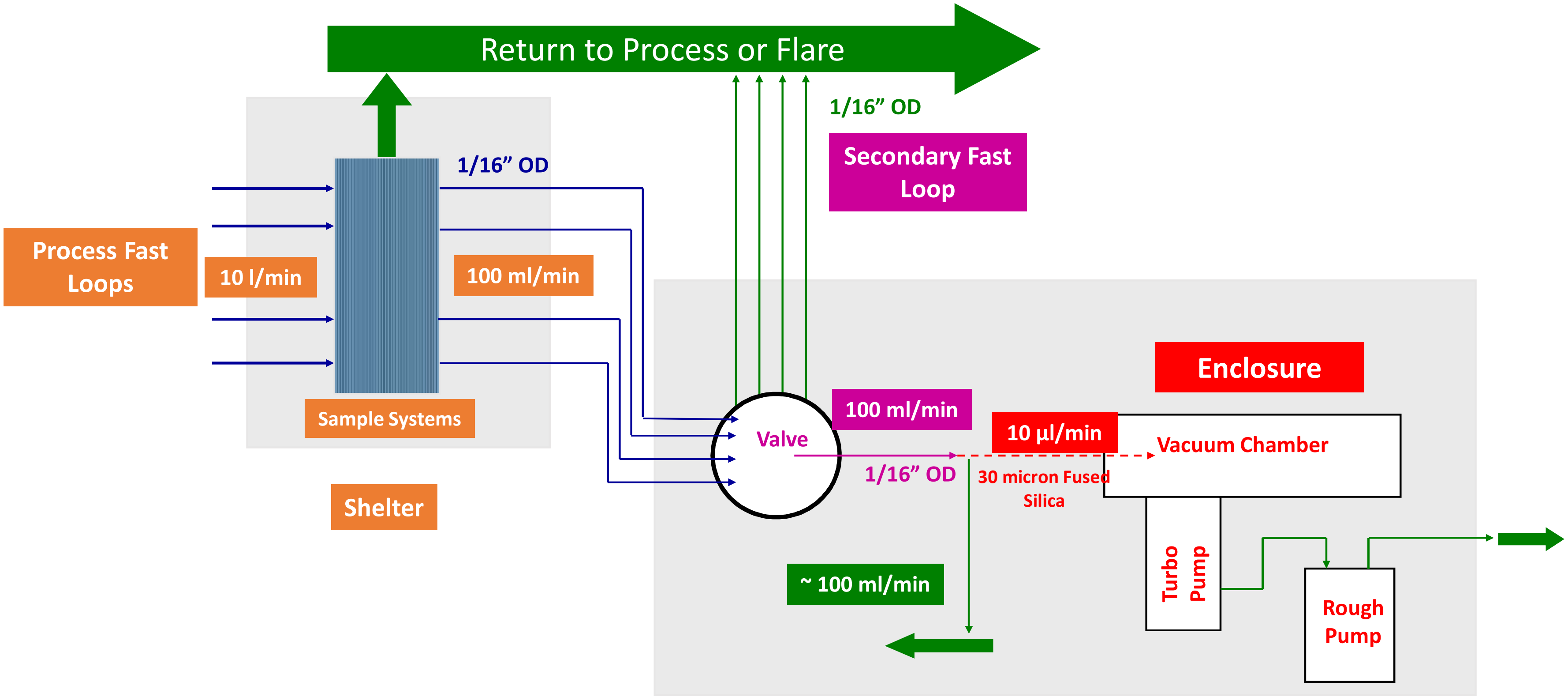


- Constant flow of gas enters the analyzers
- Sample gas is ionized and scanned electronically
  - Each scan produces a set of peaks specific to the composition of the ionized gas
  - All gas samples can be analyzed with a mass spectrometer

Sampling Requirements

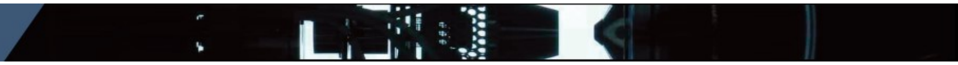
- Requirements are the same for any Gas Analyzer
  - Vapor Phase
    - non-condensing
  - Particulates
    - 5 micron filter
  - Pressure Range
    - 20PSI to 0.1PSI (1034 to 5 torr)
  - Flow
    - 100 cc/min
  - Temperature
    - Max. 250C

Typical Sample Flow for Rotary Valve



Ammonia Sampling

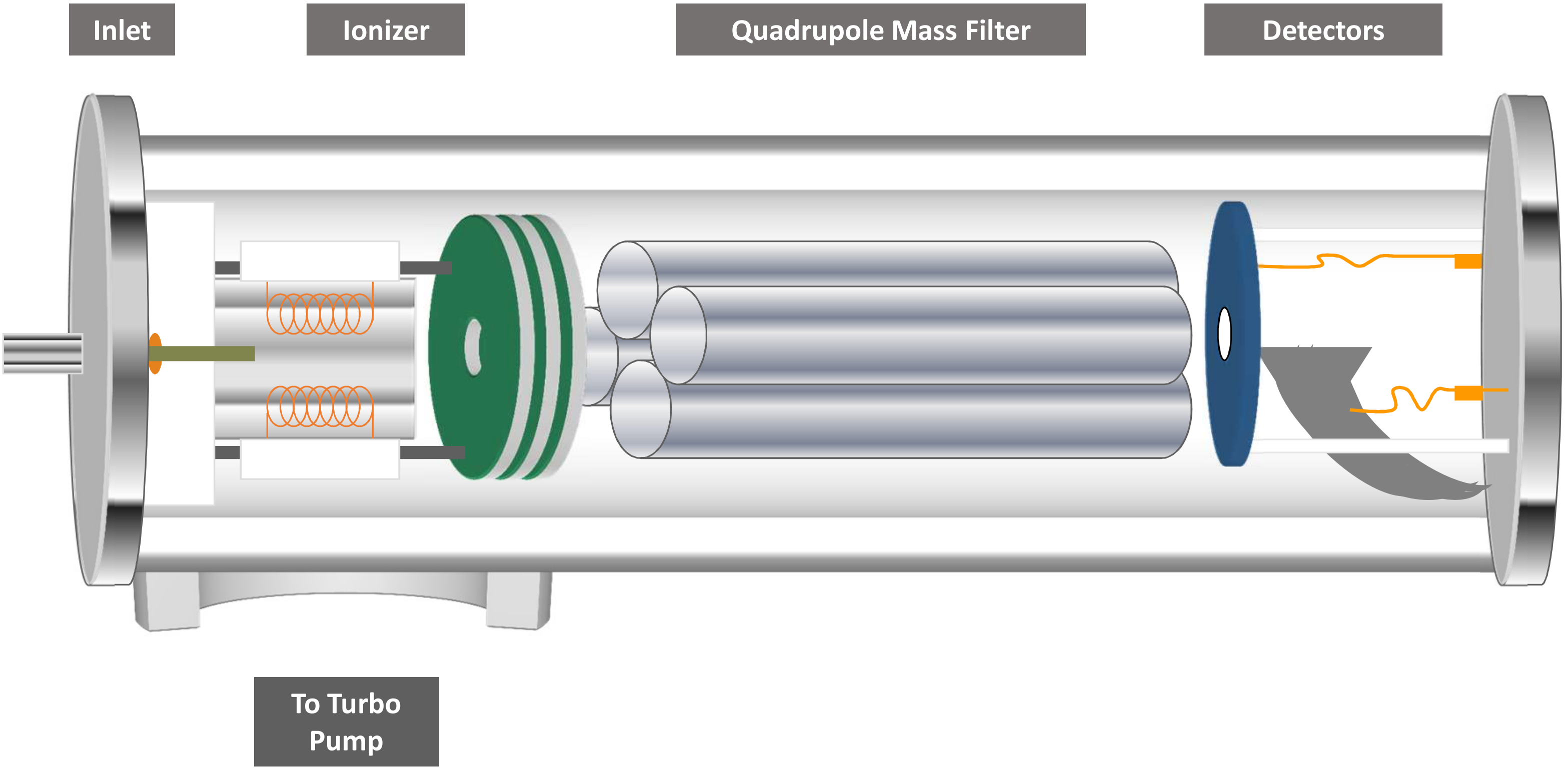
- Samples are measured on Dry basis
- High and Low Moisture Sampling Points
- Water must be removed from high moisture streams (20-50%)
  - Initial water condensing at sample tap.
  - Secondary water removal with Coalescing Filter (Membrane) close to analyzer
- Plant Upset Conditions
  - Consider isolation Solenoids tried to DCS emergency shutdown system.



Components of a Mass Spectrometer

- Inlet
  - Stream Selection
  - Sample Introduction
  - Membrane Pre-Concentration
- Ionizer
  - Electron Impact (EI) Ionization
- Mass Filter
  - Quadrupole
- Detector
  - Faraday and Electron Multiplier
- Data System
  - Signal Acquisition, Processing and Display

“Cutaway” of Mass Spectrometer Vacuum Chamber



Inlet

Ionizer

Quadrupole Mass Filter

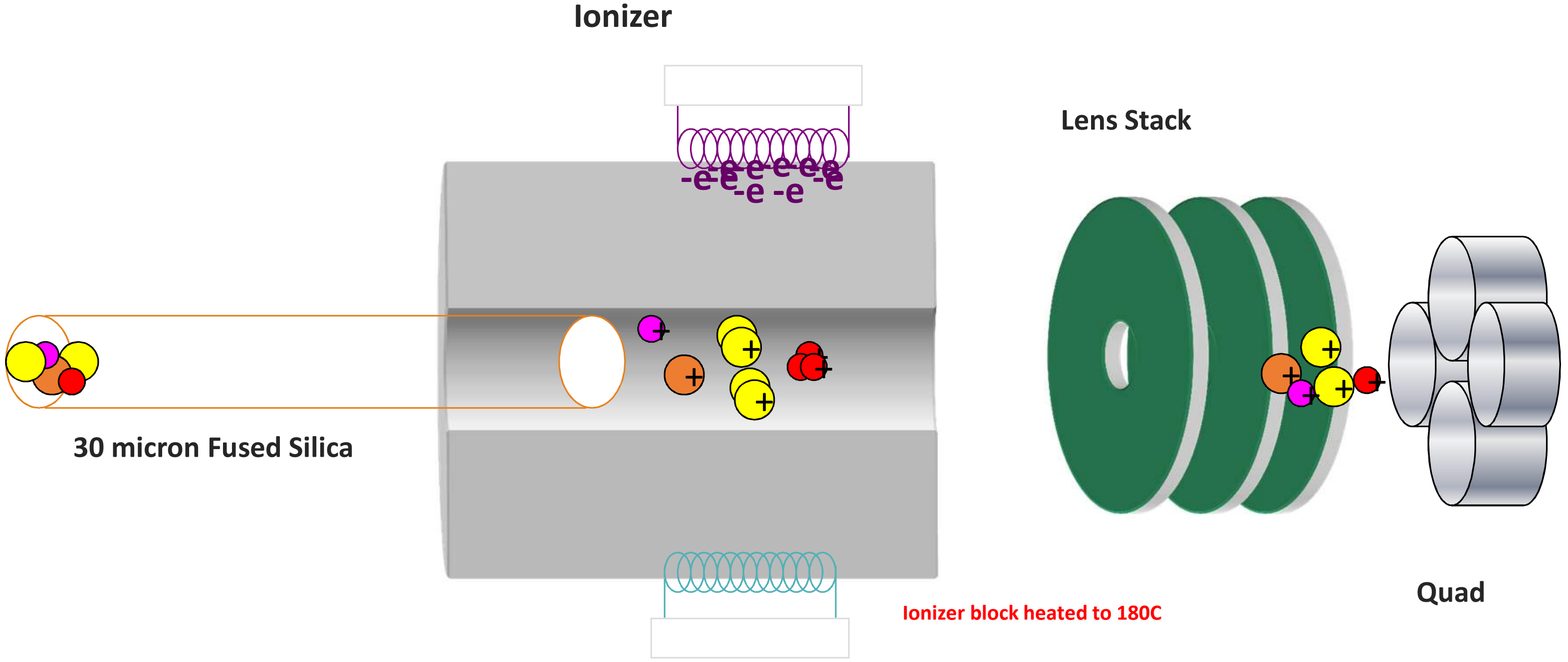
Detectors

To Turbo Pump

The capillary leaks a small amount of sample into the ionizer …

A current is applied to the (active) filament to heat it up and emit electrons

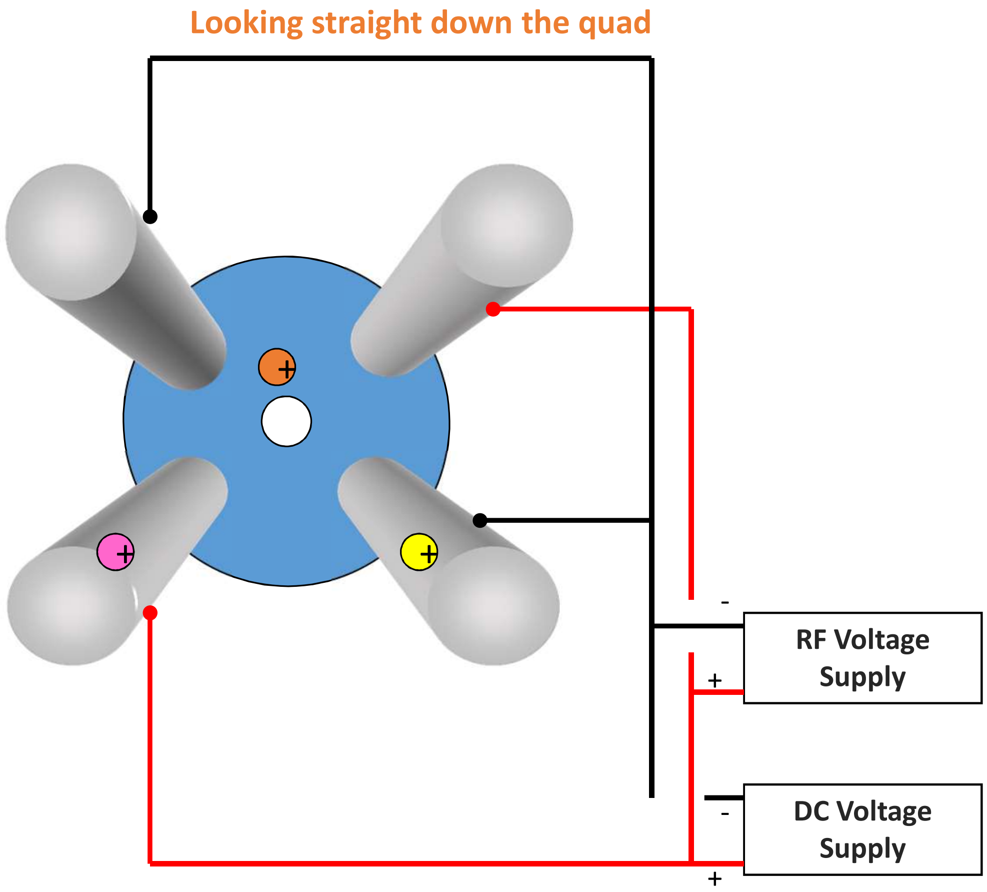
Positive charged ions are attracted towards the lens stack where there is a negative voltage …



where it is bombarded by electrons to make positively charged ions

the ions are pulled out of the ionizer and propelled into the quadrupole mass filter.

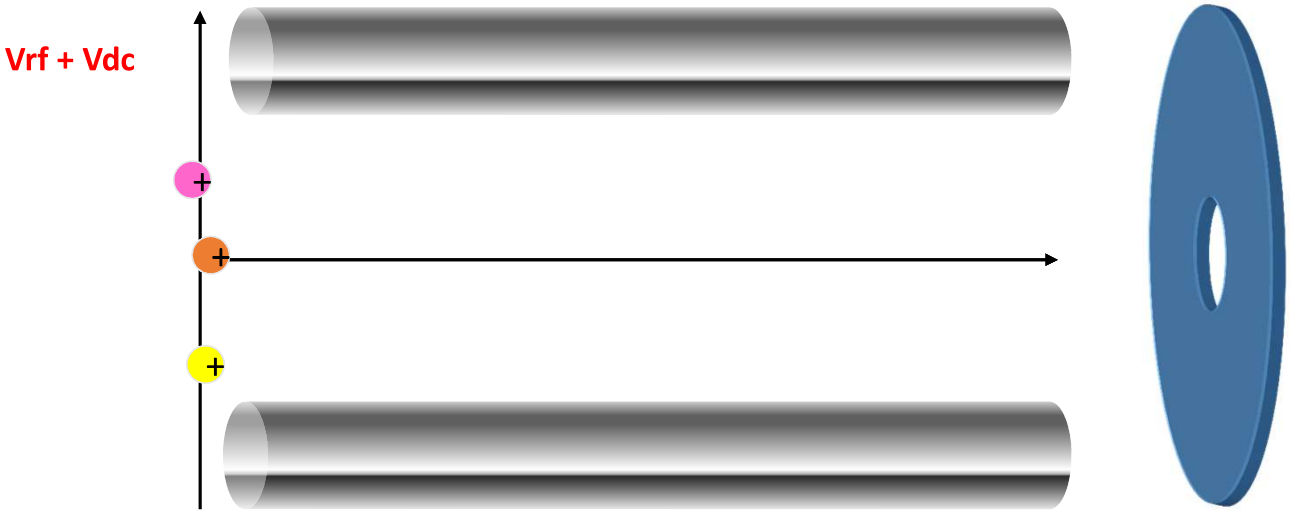
How does a mass filter work?



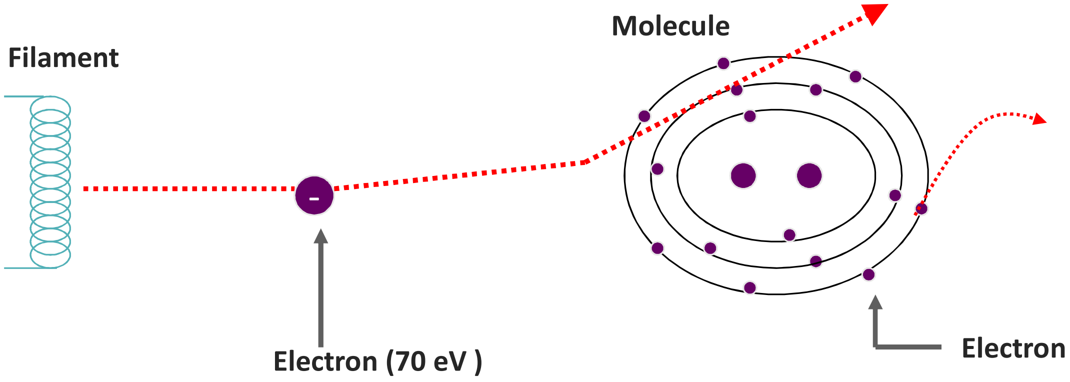
- RF and DC voltage is applied to opposite rods
- Only ions of the right mass make it all the way down the quad
- Other masses are unstable and will strike the quad and be neutralized and pumped away

How does a mass filter work?

Looking horizontally along the quadrupole



Mechanism of Electron Impact Ionization



$M + e \longrightarrow M^{+} + 2e$	Single Ionization
$M + e \longrightarrow M^{++} + 3e$	Double Ionization
$M + e \longrightarrow M_1^{+} + R^{\bullet} + 2e$	Fragmentation

Fragmentation of Methane

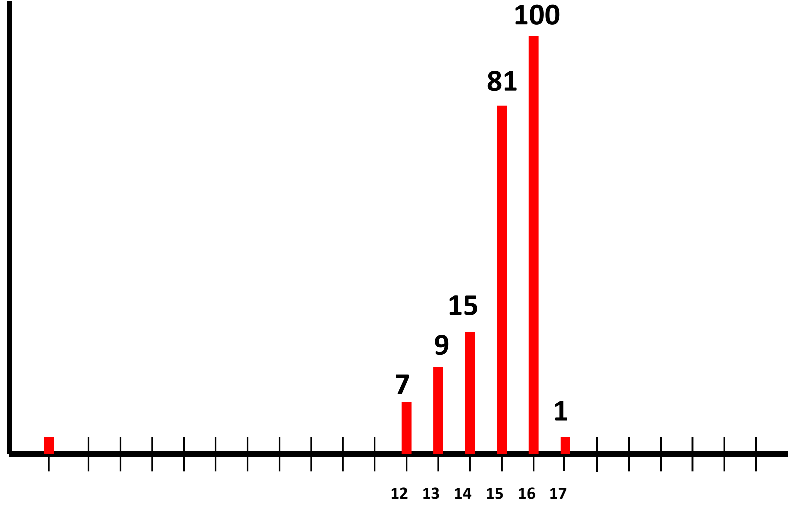
(16) $CH_4^+ \longrightarrow CH_3^+ + H$ (15)

$\longrightarrow CH_2^+$ (14)

$\longrightarrow CH^+$ (13)

$\longrightarrow C^+$ (12)

$\longrightarrow H^+$ (1)

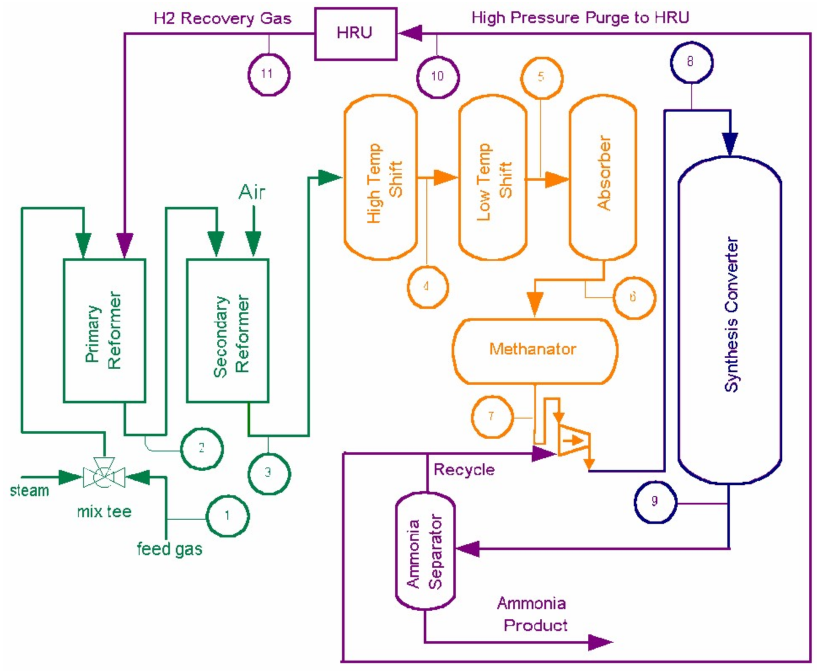


- Single Ionization occurs when electron impact (EI) causes CH_4 to lose an electron, becoming CH_4^+
  - Largest peak at mass 16
- Fragmentation occurs when a bond breaks during ionization, CH_3^+ is produced when CH_4 loses a H
  - Mass 15 peak
- Less frequently, additional fragmentation generates CH_2^+,CH^+ and C^+ and H^+

Ammonia Application Information

Analysis of streams to increase efficiency, reduce waste and extend equipment life

1. Feed Gas
2. Primary Reformer
3. Secondary Reformer
4. High Temperature Shift
5. Low Temperature Shift
6. Absorber Outlet
7. Methanator Outlet
8. Converter Inlet
9. Converter Outlet
10. Purge Gas
11. H_2 Recovery Gas



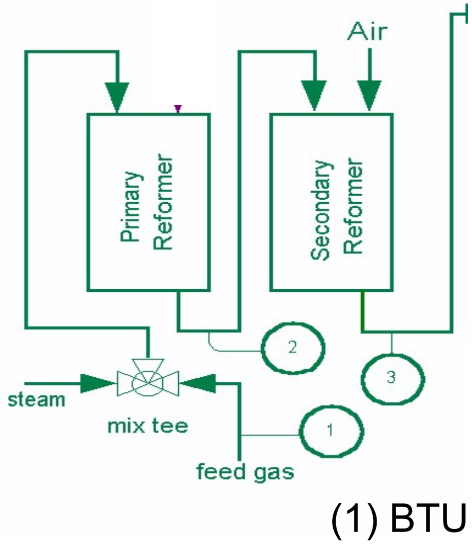
First Stage: Hydrogen from Feedstock

(3) Air is added at the secondary reformer to convert the remainder of the feedstock.

$$H_2 + \text{AIR} \longrightarrow 3H_2 + N_2 + (CO_2 + CO)$$

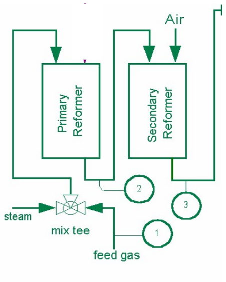
(2) Steam is added at the Primary Reformer.

$$CH_4 + H_2O \longrightarrow CO + 3H_2 + (CH_4)$$



(1) BTU and H_2S on Feed Gas Stream

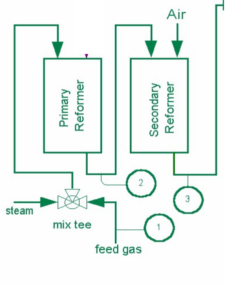
(1) Feed Gas Stream: Typical

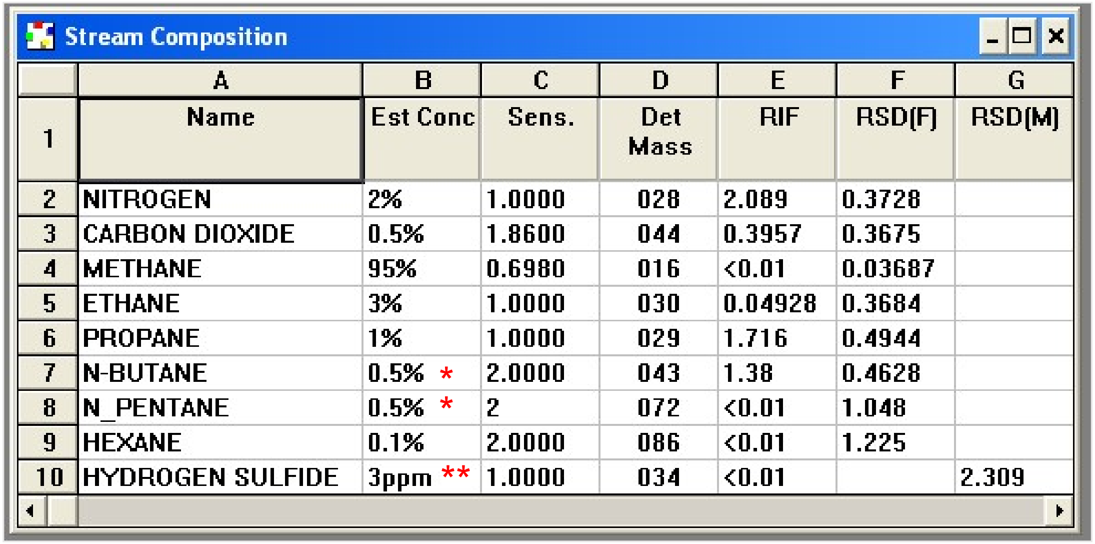


- Save energy and fuel by tightly controlling the steam to carbon ratio to within 0.02%
  - Requires accurate BTU values
  - Steam is expensive to make and tight control can decrease production costs
- Protect the catalyst from being poisoned and deactivated
  - Monitor the feed gas for the presence of hydrogen sulfides

Component	Concentration
Nitrogen	2.00 %
Carbon Dioxide	0.50 %
Methane	95.0 %
Ethane	3.00 %
Propane	1.00 %
Butanes	0.50 %
Pentanes	0.50 %
Hexane	0.10 %
Hydrogen Sulfide	3 ppm

(1) Feed Gas Stream: Results



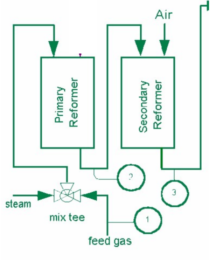


	A	B	C	D	E	F	G
1	Name	Est Conc	Sens.	Det Mass	RIF	RSD(F)	RSD(M)
2	NITROGEN	2%	1.0000	028	2.089	0.3728	
3	CARBON DIOXIDE	0.5%	1.8600	044	0.3957	0.3675	
4	METHANE	95%	0.6980	016	<0.01	0.03687	
5	ETHANE	3%	1.0000	030	0.04928	0.3684	
6	PROPANE	1%	1.0000	029	1.716	0.4944	
7	N-BUTANE	0.5% *	2.0000	043	1.38	0.4628	
8	N_PENTANE	0.5% *	2	072	<0.01	1.048	
9	HEXANE	0.1%	2.0000	086	<0.01	1.225	
10	HYDROGEN SULFIDE	3ppm **	1.0000	034	<0.01		2.309

Calculation of Relative Interference Factor and RSD

*Separation of C4 and C5 isomers
** Measurement H_2S to 1ppm

Reformer Streams: Typical



2. Primary Reformer Stream

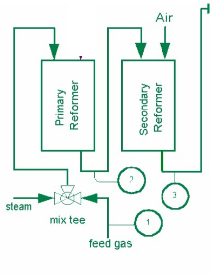
Component	Concentration
Hydrogen	67.00 %
Nitrogen	1.50 %
Carbon Monoxide	8.00 %
Carbon Dioxide	11.50 %
Argon	0.10 %
Methane	12.00 %

3. Secondary Reformer

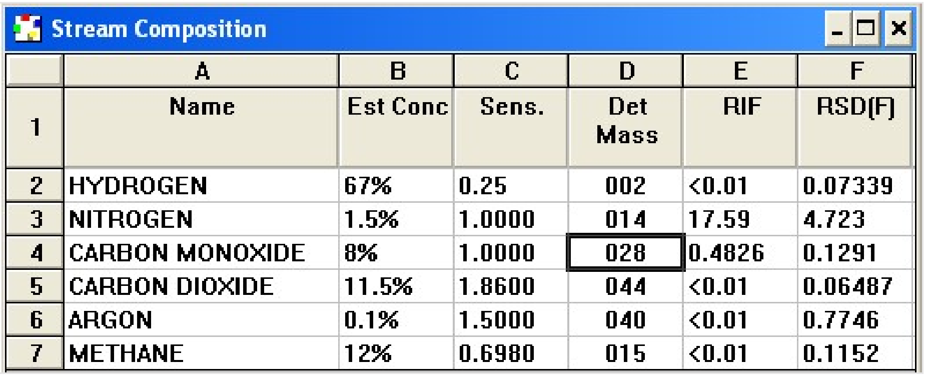
Component	Concentration
Hydrogen	57.50 %
Nitrogen	22.50 %
Carbon Monoxide	12.00 %
Carbon Dioxide	8.50 %
Argon	0.30 %
Methane	0.40 %

- Tight control of methane slippage maximizes equipment life
  - Amount of unreacted Methane is an indication of reformer efficiency
  - Wide dynamic range for methane analysis is required
    - > 90% in Feed
    - 10% in Primary Reformer
    - <0.5% in Secondary Reformer
    - Control the methane slippage with +/ 50ppm accuracy
- Accurate H_2 analysis is required in order to control Air injection rate for a 3:1 H_2:N_2 ratio at the exit

Reformer Streams: Results



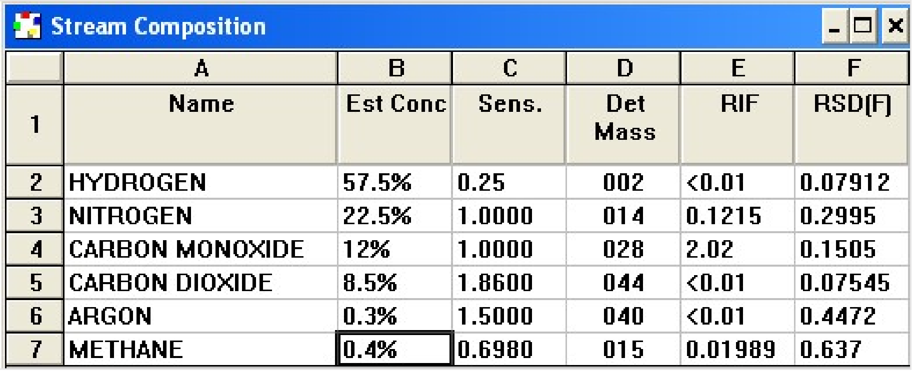
2. Primary Reformer Stream



	A	B	C	D	E	F
1	Name	Est Conc	Sens.	Det Mass	RIF	RSD(F)
2	HYDROGEN	67%	0.25	002	<0.01	0.07339
3	NITROGEN	1.5%	1.0000	014	17.59	4.723
4	CARBON MONOXIDE	8%	1.0000	028	0.4826	0.1291
5	CARBON DIOXIDE	11.5%	1.8600	044	<0.01	0.06487
6	ARGON	0.1%	1.5000	040	<0.01	0.7746
7	METHANE	12%	0.6980	015	<0.01	0.1152

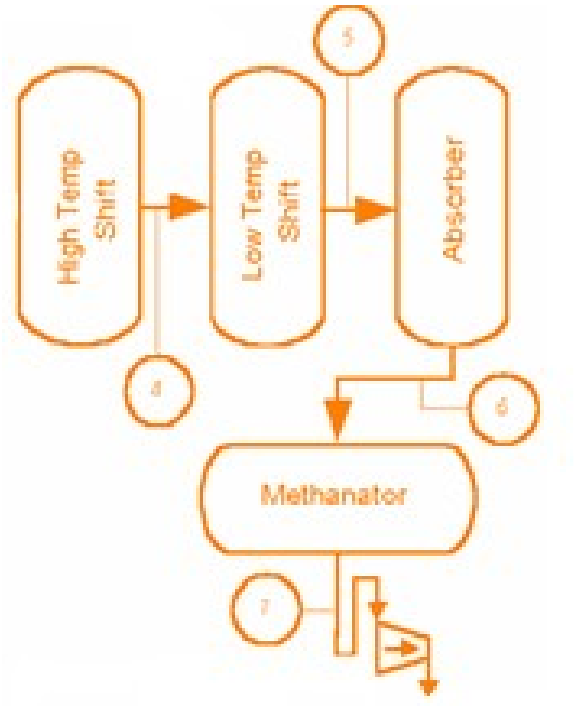
Calculation of Relative Interference Factor and RSD

3. Secondary Reformer



	A	B	C	D	E	F
1	Name	Est Conc	Sens.	Det Mass	RIF	RSD(F)
2	HYDROGEN	57.5%	0.25	002	<0.01	0.07912
3	NITROGEN	22.5%	1.0000	014	0.1215	0.2995
4	CARBON MONOXIDE	12%	1.0000	028	2.02	0.1505
5	CARBON DIOXIDE	8.5%	1.8600	044	<0.01	0.07545
6	ARGON	0.3%	1.5000	040	<0.01	0.4472
7	METHANE	0.4%	0.6980	015	0.01989	0.637

Second Stage: Streams are “cleaned up” and the production of H_2 is maximized



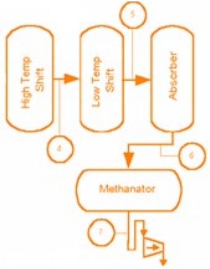
(4) High Temperature and (5) Low Temperature shifts remove the CO to increase the production of H_2.

$$CO + H_2O \longrightarrow CO_2 + H_2$$

(6) Absorber removes the CO_2 to levels less than 100ppm.
(7) Methanator converts the remainder of the CO and CO_2, which are poisons, to Methane.

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$
$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$

Temperature Shift: Typical



4. High Temperature Shift

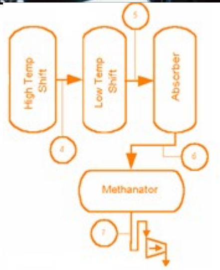
Component	Concentration
Hydrogen	52.70 %
Nitrogen	27.27 %
Carbon Monoxide	3.60 %
Carbon Dioxide	14.53 %
Argon	0.35 %
Methane	1.55 %

5. Low Temperature Shift

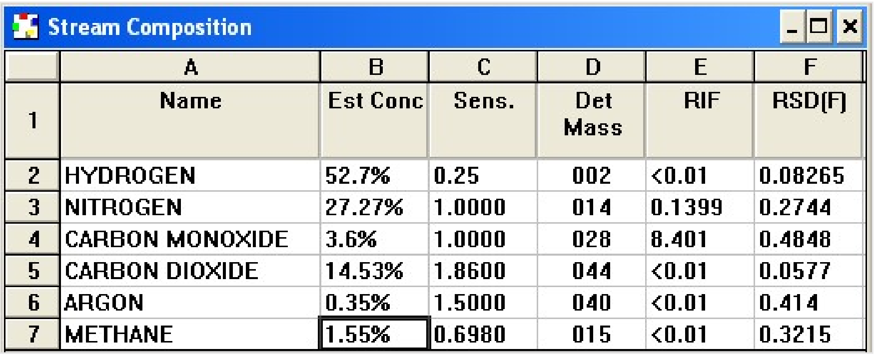
Component	Concentration
Hydrogen	54.20 %
Nitrogen	26.42 %
Carbon Monoxide	0.4 %
Carbon Dioxide	17.19 %
Argon	0.35 %
Methane	1.50 %

Analysis of CO, CO_2 and H_2 is desired to calculate the amount of additional steam required to convert CO to CO_2 and H_2

Temperature Shift: Results



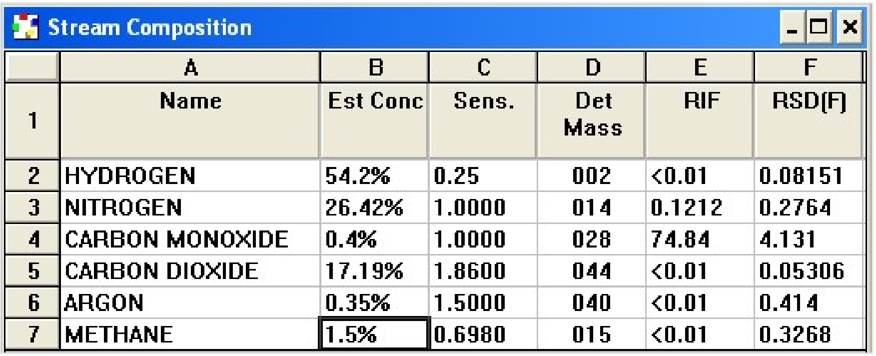
4. High Temperature Shift



	A	B	C	D	E	F
1	Name	Est Conc	Sens.	Det Mass	RIF	RSD(F)
2	HYDROGEN	52.7%	0.25	002	<0.01	0.08265
3	NITROGEN	27.27%	1.0000	014	0.1399	0.2744
4	CARBON MONOXIDE	3.6%	1.0000	028	8.401	0.4848
5	CARBON DIOXIDE	14.53%	1.8600	044	<0.01	0.0577
6	ARGON	0.35%	1.5000	040	<0.01	0.414
7	METHANE	1.55%	0.6980	015	<0.01	0.3215

Calculation of Relative Interference Factor and RSD

5. Low Temperature Shift



	A	B	C	D	E	F
1	Name	Est Conc	Sens.	Det Mass	RIF	RSD(F)
2	HYDROGEN	54.2%	0.25	002	<0.01	0.08151
3	NITROGEN	26.42%	1.0000	014	0.1212	0.2764
4	CARBON MONOXIDE	0.4%	1.0000	028	74.84	4.131
5	CARBON DIOXIDE	17.19%	1.8600	044	<0.01	0.05306
6	ARGON	0.35%	1.5000	040	<0.01	0.414
7	METHANE	1.5%	0.6980	015	<0.01	0.3268

CO measurement is limited by interference form N_2

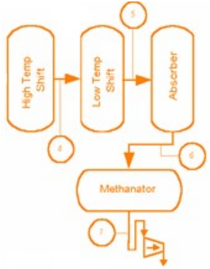
Outlets: Typical

6. Absorber Outlet

Component	Concentration
Hydrogen	65.33 %
Nitrogen	31.80 %
Carbon Monoxide	0.48 %
Carbon Dioxide	0.08 %
Argon	0.41 %
Methane	1.81 %

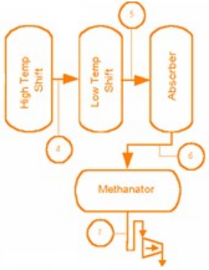
7. Methanator Outlet

Component	Concentration
Hydrogen	69.80 %
Nitrogen	28.00 %
Carbon Monoxide	< 5 ppm
Carbon Dioxide	< 5 ppm
Argon	0.30%
Methane	1.70 %

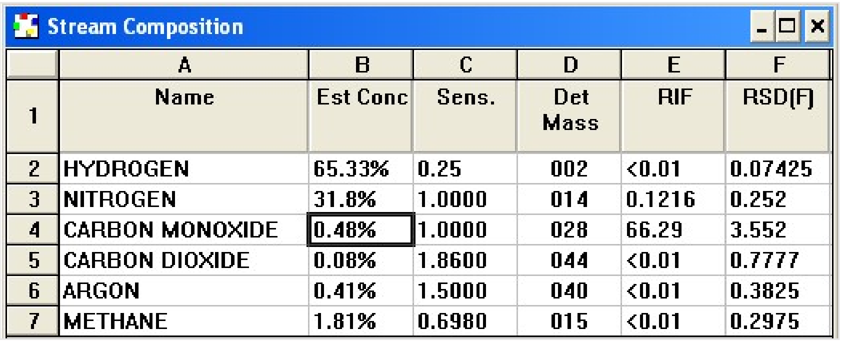


The analysis of the oxides, CO and CO2 are important to prevent poisoning of catalysts in converter

Outlet: Results



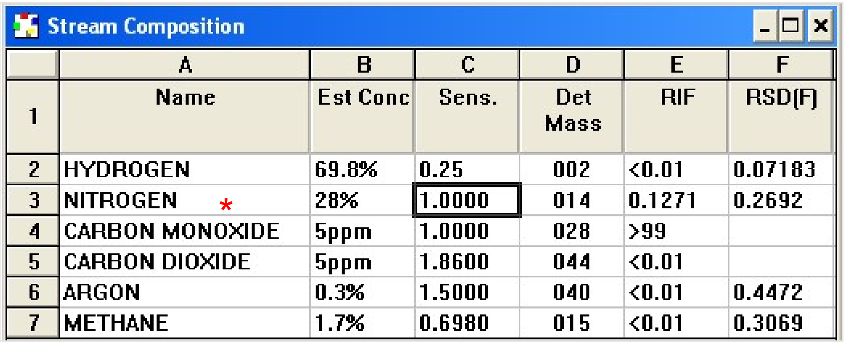
6. Absorber Outlet



	A	B	C	D	E	F
1	Name	Est Conc	Sens.	Det Mass	RIF	RSD(F)
2	HYDROGEN	65.33%	0.25	002	<0.01	0.07425
3	NITROGEN	31.8%	1.0000	014	0.1216	0.252
4	CARBON MONOXIDE	0.48%	1.0000	028	66.29	3.552
5	CARBON DIOXIDE	0.08%	1.8600	044	<0.01	0.7777
6	ARGON	0.41%	1.5000	040	<0.01	0.3825
7	METHANE	1.81%	0.6980	015	<0.01	0.2975

Calculation of Relative Interference Factor and RSD

7. Methanator Outlet



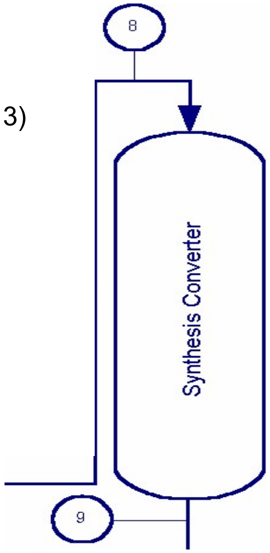
	A	B	C	D	E	F
1	Name	Est Conc	Sens.	Det Mass	RIF	RSD(F)
2	HYDROGEN	69.8%	0.25	002	<0.01	0.07183
3	NITROGEN *	28%	1.0000	014	0.1271	0.2692
4	CARBON MONOXIDE	5ppm	1.0000	028	>99	
5	CARBON DIOXIDE	5ppm	1.8600	044	<0.01	
6	ARGON	0.3%	1.5000	040	<0.01	0.4472
7	METHANE	1.7%	0.6980	015	<0.01	0.3069

- CO at 5ppm can not be measured in the presence of N_2

Third stage: Converter Produces Ammonia

The (8) Synthesis Converter “converts” the nitrogen and the hydrogen to (9) Ammonia (NH_3)

$$N_2 + 3H_2 \longrightarrow 2NH_3$$



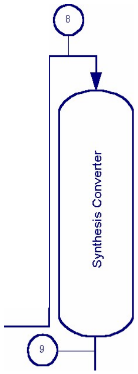
Converter: Typical

8. Converter Inlet

Component	Concentration
Hydrogen	65.00 %
Nitrogen	22.50 %
Argon	2.50 %
Helium	0.50 %
Methane	7.00 %
Ammonia	2.00 %

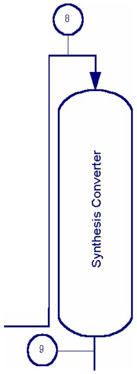
9. Converter Outlet

Component	Concentration
Hydrogen	54.00 %
Nitrogen	19.50 %
Argon	3.50 %
Helium	0.50 %
Methane	7.50 %
Ammonia	15.00 %

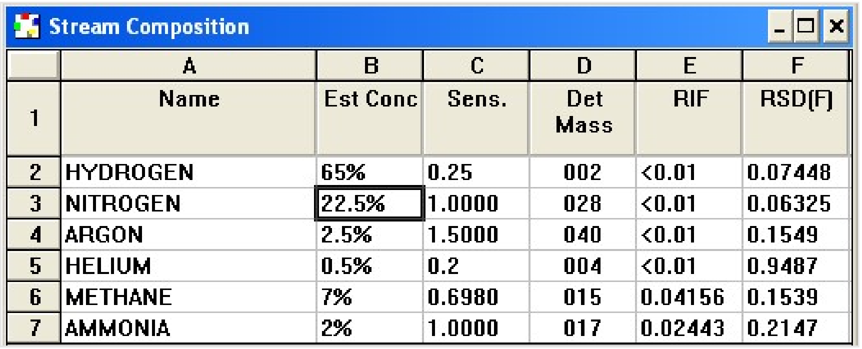


Efficient production of ammonia through the control of the Feed to Air (H_2:N_2) ratio within +- 0.01%

Converter: Results

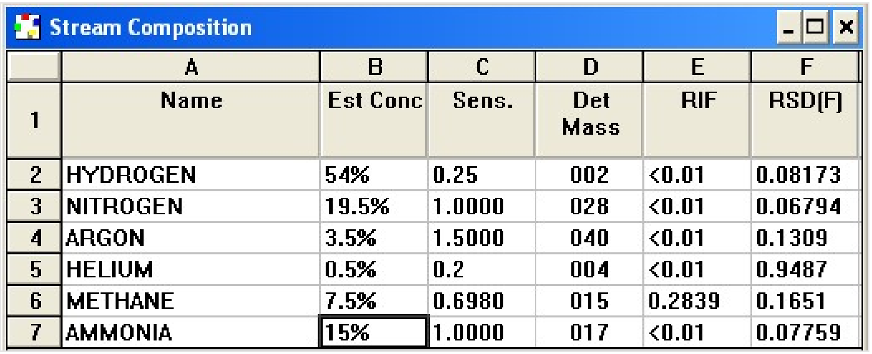


8. Converter Inlet



	A	B	C	D	E	F
1	Name	Est Conc	Sens.	Det Mass	RIF	RSD(F)
2	HYDROGEN	65%	0.25	002	<0.01	0.07448
3	NITROGEN	22.5%	1.0000	028	<0.01	0.06325
4	ARGON	2.5%	1.5000	040	<0.01	0.1549
5	HELIUM	0.5%	0.2	004	<0.01	0.9487
6	METHANE	7%	0.6980	015	0.04156	0.1539
7	AMMONIA	2%	1.0000	017	0.02443	0.2147

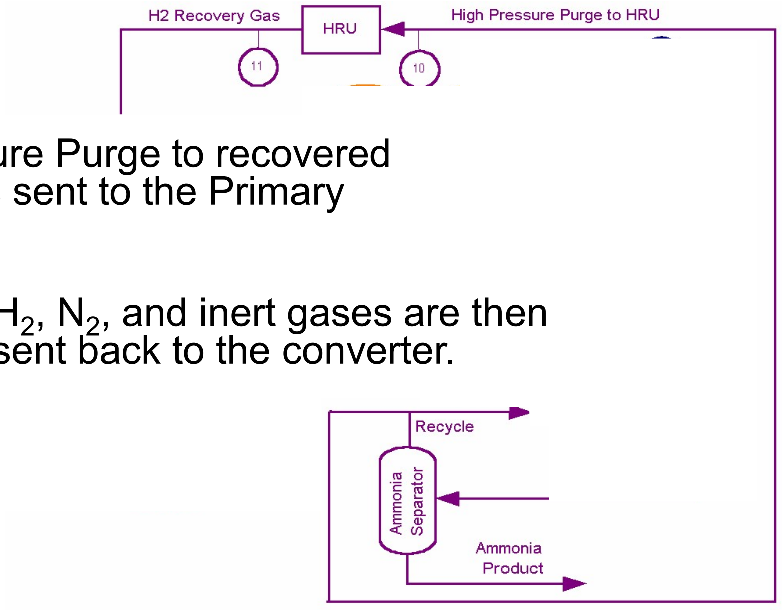
9. Converter Outlet



	A	B	C	D	E	F
1	Name	Est Conc	Sens.	Det Mass	RIF	RSD(F)
2	HYDROGEN	54%	0.25	002	<0.01	0.08173
3	NITROGEN	19.5%	1.0000	028	<0.01	0.06794
4	ARGON	3.5%	1.5000	040	<0.01	0.1309
5	HELIUM	0.5%	0.2	004	<0.01	0.9487
6	METHANE	7.5%	0.6980	015	0.2839	0.1651
7	AMMONIA	15%	1.0000	017	<0.01	0.07759

Calculation of Relative Interference Factor and RSD

Final Stage: Collects Ammonia Product, Recycles Inert Gases and Hydrogen Recovery

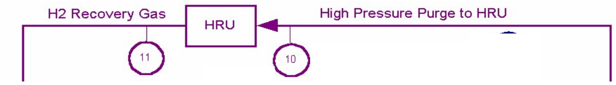


(10) High Pressure Purge to recovered
(11) Hydrogen is sent to the Primary reformer.

H_2, N_2, and inert gases are then sent back to the converter.

The ammonia Product stream is separated from the other gases.

Hydrogen Recovery: Typical



10. Purge Gas

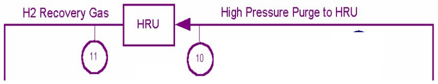
Component	Concentration
Hydrogen	62.00 %
Nitrogen	22.50 %
Argon	3.50 %
Helium	0.50 %
Methane	11.00 %
Ammonia	2.00 %

11. H_2 Recovery Gas

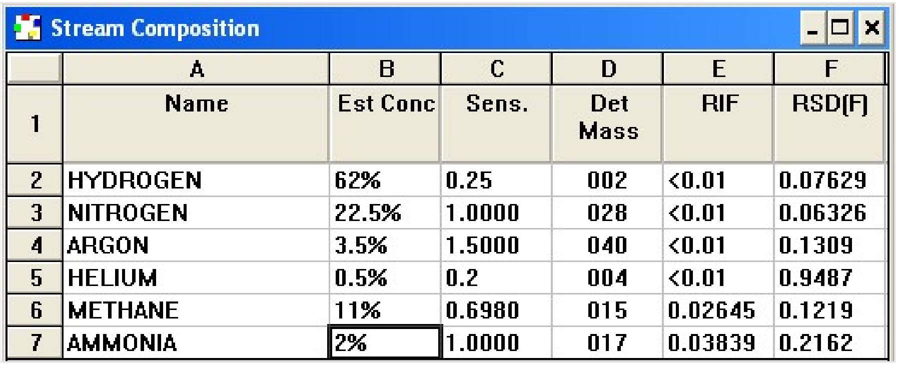
Component	Concentration
Hydrogen	50.00 %
Nitrogen	10.00 %
Argon	1.75 %
Helium	0.60 %
Methane	37.50 %

- Much of the converter inlet is made up of recycled gases
- Control of the inert gases helps maintain the control for feed gases

Hydrogen Recovery: Results

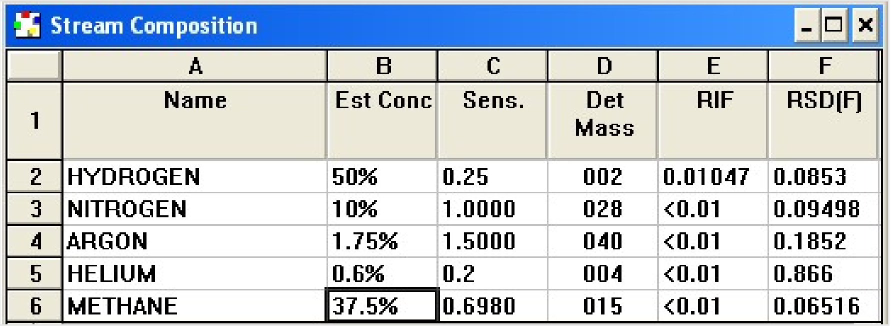


10. Purge Gas



	A	B	C	D	E	F
1	Name	Est Conc	Sens.	Det Mass	RIF	RSD(F)
2	HYDROGEN	62%	0.25	002	<0.01	0.07629
3	NITROGEN	22.5%	1.0000	028	<0.01	0.06326
4	ARGON	3.5%	1.5000	040	<0.01	0.1309
5	HELIUM	0.5%	0.2	004	<0.01	0.9487
6	METHANE	11%	0.6980	015	0.02645	0.1219
7	AMMONIA	2%	1.0000	017	0.03839	0.2162

11. H_2 Recovery Gas



	A	B	C	D	E	F
1	Name	Est Conc	Sens.	Det Mass	RIF	RSD(F)
2	HYDROGEN	50%	0.25	002	0.01047	0.0853
3	NITROGEN	10%	1.0000	028	<0.01	0.09498
4	ARGON	1.75%	1.5000	040	<0.01	0.1852
5	HELIUM	0.6%	0.2	004	<0.01	0.866
6	METHANE	37.5%	0.6980	015	<0.01	0.06516

Calculation of Relative Interference Factor and RSD

Calibration and Validation

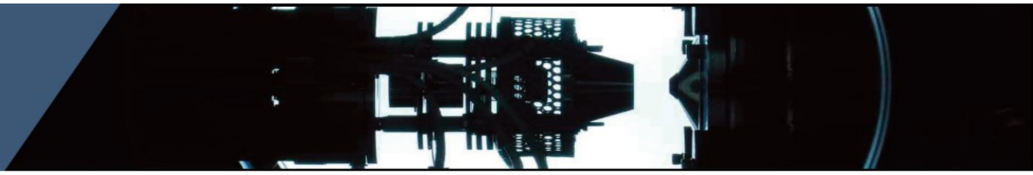
- Validation Gases (if required):
  - Daily, Weekly or Monthly depending on company policy or local regulation
  - Each validation requires <500 atm cc of gas
  - Small gas bottle will allow for biweekly validation for 3+ years

- Calibration Gases:
  - Required:
    - Any time instrument does not accurately validate
    - Following maintenance that involves venting the vacuum chamber
    - Typically once every 1-6 months
  - Each calibration step requires <500 atm cc of gas
  - Small gas bottle will allow for biweekly calibration for 3+ years

Customer Feedback

Comment	Estimate
Optimizing Purge Gas Recovery	$100,000 to $120,000/year
Energy saving equal to 0.6 GJ per ton NH3	$1,500 per day
Plants run smoothly and stable	Daily production variations were +/- 25 tons/day, now +/- 1-2 tons/day
H/N ratio	With GC's 3.1+/- 0.1. With MS 3.1 +/- 0.007
Stable steam-to-carbon ratio and H/N ratio	1 million $ per plant in 3 years
Yield and Catalyst	Increased yield over time and increased catalyst life
Startup	It takes only hours to reach set point instead of days

Ammonia Production



Real-time Gas Analysis

Thank you for your attention

- Any Questions?