Setting the Standard for Automation™

ISA Delhi Section

AMMONIA PROCESS OPTIMIZATION USING MASS SPECTROMETER

Sumeet Sarkar
Thermo Fisher Scientific

Standards
Certification
Education & Training
Publishing
Conferences & Exhibits

The International Society of Automation Delhi Section

Agenda

- Ammonia Process
- Why use Process MS for analysing process gases?
- Key Control Parameters
- Process Mass Spectrometer
  - *Multistream sampling*
  - *Ionization*
  - *Separation*
  - *Detection*
- Advantages of Mass Spectrometer
- Summary

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Ammonia

- Ammonia (NH_3) is produced in most countries as starting material for fertilizer production
- Also used to produce plastics, fibers and explosives
- Ammonia production costs tied to natural gas prices
- On-line gas analysis is well established as a means of process control in ammonia production
  - *In past, process GC and IR analyzers used extensively*
- Recent years, MS has increasingly become instrument of choice
  - *Faster analysis speed and flexibility*

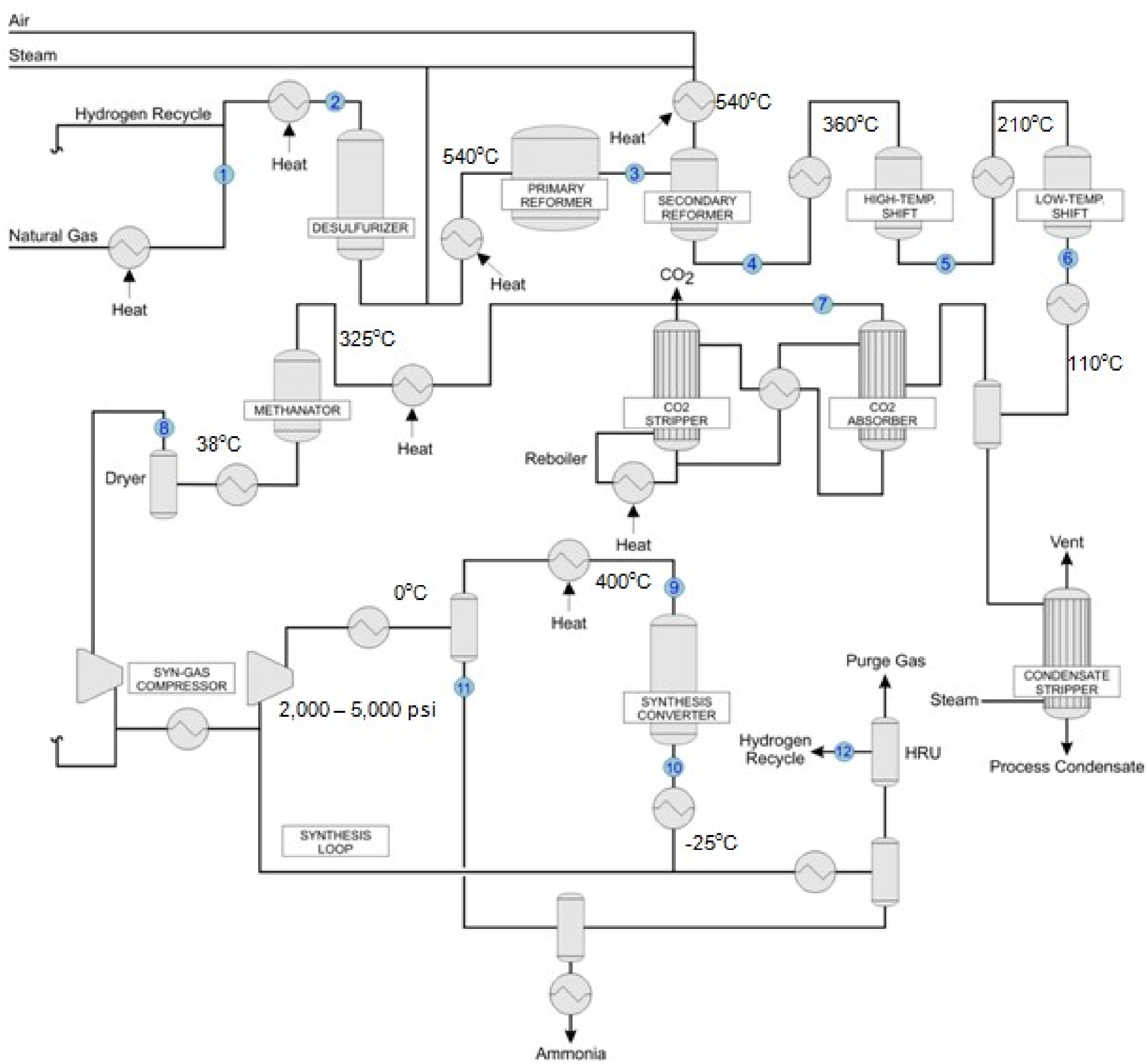
Ammonia Process

- Ammonia production can be summarized as:

  $3H_2 + N_2 \rightarrow 2NH_3$

- Hydrogen and nitrogen reacted over catalyst in strictly controlled 3:1 ratio
- This is the final step of the process - a number of other reactions take place first, to provide nitrogen and hydrogen in correct ratio

Ammonia Flow Diagram with MS Sample Points



1. Natural Gas
2. Primary Reformer Feed
3. Primary Reformer Effluent
4. Secondary Reformer Effluent
5. High Temp. Shift Outlet
6. Low Temp. Shift Outlet
7. CO_2 Absorber Outlet
8. Raw Synthesis Gas
9. Converter Inlet
10. Converter Outlet
11. High-Pressure Purge
12. Hydrogen Recovery

- Costs are minimized throughout process by using waste heat boilers and heat exchangers

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Why use Process MS?

- Fast analysis of process gases
  - *Seconds not minutes*
- Multi-component analysis
  - *Analyze inorganics & organics*
- Multi-stream analysis
  - *Up to 64 streams*
- Flexible analysis
  - *Analysis defined in software*
  - *Analyze different compounds in different streams*
- Precision, accuracy
  - *Between 0.1% and 1% relative*
- Dynamic range
  - *ppm to 100%*

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Key Control parameters

- Steam to Carbon ratio
  - Energy efficiency and efficient catalyst activity
- Air Requirement
  - Optimize the energy consumption
- Methane Slippage
  - Methane builds up in the synthesis loop requiring additional compression energy and reducing ammonia yield
- Shift Reaction
  - Very important to remove CO - it shifts back to CH_4, reaction is exothermic & can damage Methanator
  - Prevent Catalyst poisoning due to CO
- H/N Ratio
  - Hydrogen to Nitrogen ratio to be maintained at 3:1

Example of Process MS gas analysis

Component		Typical Composition %mol	Prima PRO precision of measurement (standard deviation) %mol
Methane	CH_4	93	0.02
Nitrogen	N_2	1	0.005
Ethane	C_2H_6	3	0.005
Carbon Dioxide	CO_2	1	0.002
Propane	C_3H_8	1	0.002
Isobutane	$i\text{-}C_4H_{10}$	0.2	0.002
n-Butane	$n\text{-}C_4H_{10}$	0.2	0.002
Isopentane	$i\text{-}C_5H_{12}$	0.1	0.002
n-Pentane	$n\text{-}C_5H_{12}$	0.1	0.002
n-Hexane	$n\text{-}C_6H_{14}$	0.1	0.002
Hydrogen Sulfide	H_2S	3 ppm	0.5 ppm
Methyl Mercaptan	CH_3SH	10 ppm	0.5 ppm
Ethyl Mercaptan	C_2H_5SH	10 ppm	0.5 ppm
n-Propyl Mercaptan	C_3H_7SH	10 ppm	0.5 ppm
n-Butyl Mercaptan	C_4H_9SH	10 ppm	0.5 ppm

Natural Gas: analysis time <30 seconds including stream switching

Primary Reformer Feed

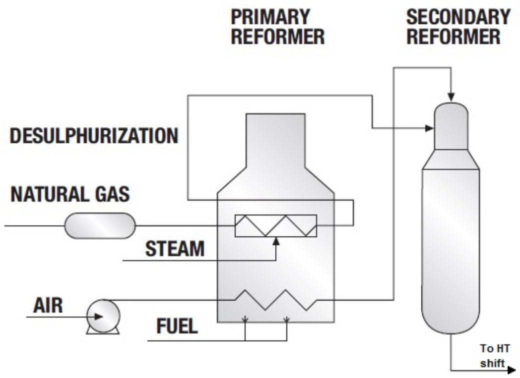
Typical Primary Reformer Feed			
Component	Minimum	Normal	Maximum
Methane	85.00	95.61	98.00
Ethane	0.50	1.04	4.00
Propane	0.00	0.09	1.80
Butane	0.00	0.02	0.80
Pentane	0.00	0.00	0.30
Carbon Dioxide	0.00	0.16	0.55
Nitrogen	0.00	1.06	3.00
Hydrogen	1.00	2.00	4.00
Argon	0.00	0.03	0.80
H_2S ppm	0.00	0.00	8.00

Primary Reformer Feed Specification		
Component	Concentration Vol.%	Precision* Absolute %
Methane	85.00 - 98.00	0.02
Ethane	0.50 - 5.00	0.005
Propane	1.00 - 3.00	0.005
n-Butane	1.00 - 2.00	0.005
Carbon Dioxide	1.00 - 3.00	0.003
Nitrogen	1.00 - 5.00	0.01
Argon	0.01 - 0.5	0.001
Hydrogen	1.00 - 5.00	0.005

* 8-Hour analysis precision (single standard deviation) for analysis time 15 seconds

- Steam is then added to Natural Gas at Primary Reformer
- $CH_4 + H_2O \rightarrow CO + 3H_2$
  $CO + H_2O \rightarrow CO_2 + H_2$
- Need to determine amount of steam required to react with methane and other hydrocarbons -
- **Steam to Carbon ratio**

Primary Reformer Effluent



- Two reformers are used since only 30-40% of methane is reformed in first reactor
- Air is added at reformer stage as source of N_2

Primary Reformer Effluent			
Component	Minimum	Normal	Maximum
Hydrogen	60.00	65.38	70.00
Methane	12.00	15.91	18.00
Carbon Monoxide	6.00	7.97	10.00
Carbon Dioxide	9.00	10.36	12.00
Nitrogen	0.00	0.37	1.00
Argon	0.00	0.01	0.10

Primary Reformer Specification		
Component	Concentration Vol.%	Precision* Absolute %
Hydrogen	60.00 - 70.00	0.03
Methane	12.00 - 18.00	0.01
Carbon Monoxide	6.00 - 10.00	0.03
Carbon Dioxide	9.00 - 12.00	0.01
Nitrogen	0.10 - 3.00	0.02
Argon	0.10 - 0.50	0.001

* 8-Hour analysis precision (single standard deviation) for analysis time 15 seconds

Secondary Reformer

- Methane reforming reaction is continued in secondary reformer by introducing air into reactor
- Air is the nitrogen source; combustion produces temperatures around 1250˚C (2300˚F) which result in further methane reforming
- Methane Slippage (unreacted CH_4) is an important parameter to monitor here
- Methane builds up in the synthesis loop requiring additional compression energy and reducing ammonia yield

Secondary Reformer Effluent

Component	Minimum	Normal	Maximum
Hydrogen	53.00	54.08	58.00
Methane	0.30	0.41	0.70
Carbon Monoxide	11.00	12.55	15.00
Carbon Dioxide	5.00	7.47	10.00
Nitrogen	20.00	25.18	26.00
Argon	0.20	0.31	0.40

Secondary Reformer Specification

Component	Concentration Vol.%	Precision* Absolute %
Hydrogen	50.00 - 65.00	0.03
Methane	0.30 - 2.00	0.002
Carbon Monoxide	10.00 - 14.00	0.03
Carbon Dioxide	5.00 - 10.00	0.01
Nitrogen	20.00 - 26.00	0.02
Argon	0.10 - 0.50	0.001

* 8-Hour analysis precision (single standard deviation) for analysis time 15 seconds

Shift Reaction

$CO + H_2O \rightarrow CO_2 + H_2$

- For maximum conversion, shift reaction is done in two stages, one at high temperature, one at lower temperature
- Very important to remove CO - it shifts back to CH_4, reaction is exothermic & can damage Methanator
- Aim to convert 99+% of CO to CO_2

High Temperature Shift Reactor Outlet		
Component	Typical Concentration Vol.%	Precision Absolute %
Hydrogen	55.00 - 70.00	0.03
Methane	0.10 - 0.50	0.001
Carbon Monoxide	1.00 - 3.00	0.03
Carbon Dioxide	12.00 - 17.00	0.01
Nitrogen	15.00 - 21.00	0.02
Argon	0.10 - 0.50	0.001

Low Temperature Shift Reactor Outlet		
Component	Concentration Vol.%	Precision Absolute %
Hydrogen	70.00 - 75.00	0.02
Methane	0.10 - 0.50	0.001
Carbon Monoxide	0.10 - 0.50	0.002*
Carbon Dioxide	9.00 - 12.00	0.01
Nitrogen	9.00 - 15.00	0.01
Argon	0.10 - 0.50	0.001

* Not measurable with necessary precision by MS so NDIR analyzer is recommended. However Prima PRO can be used to provide backup alarm for CO break-through

Methanator

$CO + 3H_2 \rightarrow CH_4 + H_2O$

$-\Delta H_{25℃} = 49.3\ kcal/mol$*

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

$-\Delta H_{25℃} = 39.4\ kcal/mol$

- Methanation is highly exothermic - temperature rise for converting 1% CO is ~ 75℃, for 1% CO_2 is ~ 60℃. Normal methanator operating temperature is 325℃ with Ni/Al_2O_3 catalyst. So if CO or CO_2 is too high this can damage Methanator.
- Output from Methanator is Synthesis Gas (Syn-Gas)
- Ideal composition is 75% H_2, 25%N_2

Raw Synthesis Gas

Component	Minimum	Normal	Maximum
Hydrogen	69.00	71.15	75.00
Methane	0.50	0.92	1.50
Carbon Monoxide	0.00	0.0005	0.0020
Carbon Dioxide	0.00	0.0005	0.0010
Nitrogen	23.00	27.59	28.00
Argon	0.20	0.34	0.40

Raw Synthesis Gas Specification

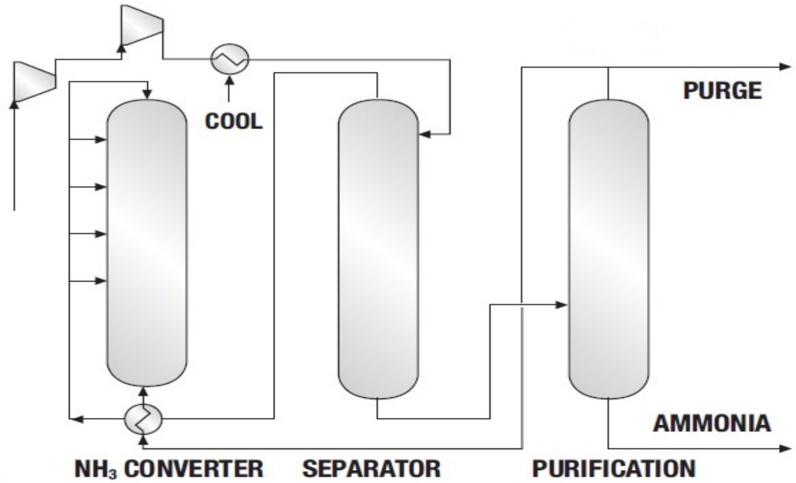
Component	Concentration Vol.%	Precision Absolute %
Hydrogen	65.00 - 75.00	0.02
Methane	0.30 - 1.50	0.001
Nitrogen	20.00 - 28.00	0.01
Argon	0.10 - 0.50	0.002
Helium	0.10 - 0.50	0.001

* Enthalpy change ΔH = energy used in bond breaking reactions – energy released in bond making products

Synthesis Loop

$3H_2 + N_2 \rightarrow 2NH_3$

Need to keep HN ratio close to 3:1



- Syn-gas from methanator is compressed at high pressure (2,000 to 5,000 psi), mixed with recycled gas and cooled to 0˚C. Stream then enters final reactor to produce NH_3 using FeO catalyst
- Condensed ammonia is separated from unconverted synthesis gas
- Only ~30% of syn-gas is converted on each pass so large recycle stream returns effluent to compressor for re-processing
- Small portion of overhead gas is purged to prevent buildup of inert gases (Ar, He) in circulating gas system.

Synthesis Loop Performance Specifications

Synthesis Gas Feed to Converter

Component	Minimum	Normal	Maximum
Hydrogen	55.00	59.15	70.00
Methane	2.00	3.76	8.00*
Ammonia	1.00	2.49	3.00
Argon	1.00	1.74	4.00*
Nitrogen	20.00	32.86	35.00

Converter Effluent

Component	Minimum	Normal	Maximum
Hydrogen	40.00	44.99	50.00
Methane	2.00	4.34	5.00
Ammonia	14.00	18.46	21.00
Argon	1.00	2.01	5.00
Nitrogen	20.00	30.19	35.00

Converter Feed Specification

Component	Concentration Vol.%	Precision Absolute %
Hydrogen	55.00 - 70.00	0.03
Methane	1.00 - 8.00	0.002
Ammonia	1.00 - 3.00	0.002
Helium*	0.50 - 1.00	0.001
Nitrogen	20.00 - 35.00	0.01
Argon*	0.50 - 4.00	0.002

Converter Effluent Specification

Component	Concentration Vol.%	Precision Absolute %
Hydrogen	40.00 - 60.00	0.02
Methane	1.00 - 5.00	0.002
Ammonia	10.00 - 21.00	0.01
Nitrogen	15.00 - 35.00	0.01
Argon*	1.00 - 5.00	0.002

* Inerts increase due to recycling, if they get too high energy used for compression is wasted and NH_3 yield is reduced

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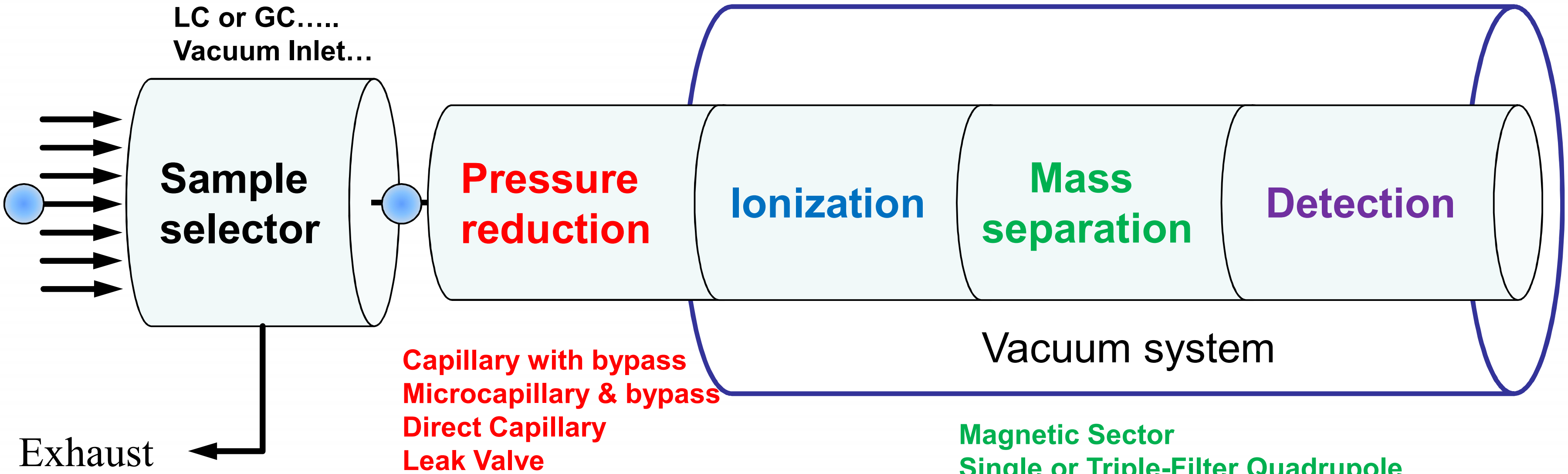
Basic components of a mass spectrometer

- A mass spectrometer separates and quantifies atoms and molecules according to their mass

Auto-Sampler
Batch Inlet
Solenoid Valves
Rapid Multi-Stream Sampler
LC or GC…..
Vacuum Inlet…

Electron Ionization (EI)
Chemical Ionization (CI)
Inductively-Coupled Plasma (ICP)
Laser Desorption…

Faraday
Multiplier (SEM)
Ion Trap…



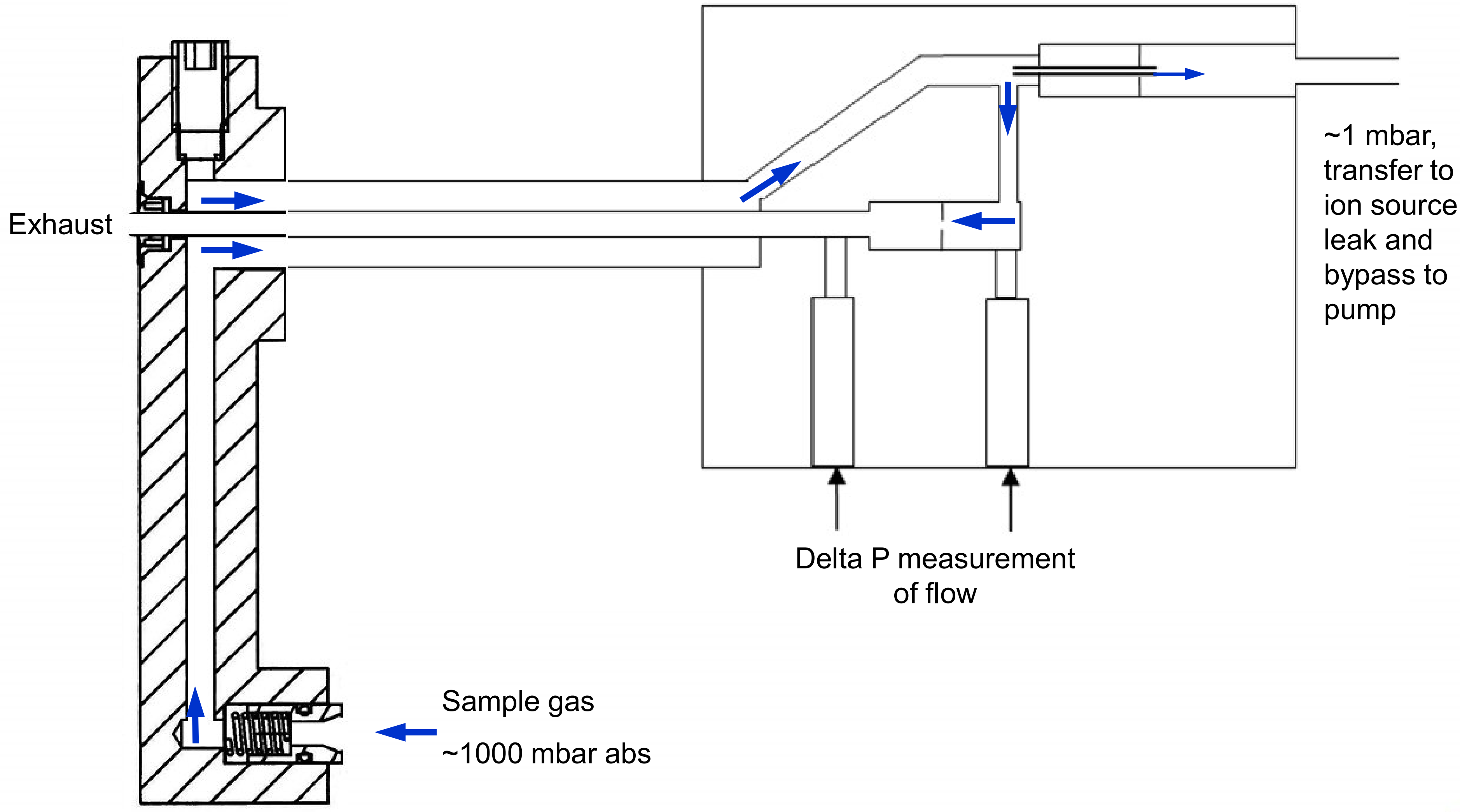
Capillary with bypass
Microcapillary & bypass
Direct Capillary
Leak Valve
Membrane…

Magnetic Sector
Single or Triple-Filter Quadrupole
Triple Quadrupole
Hexapole/Octopole
Sector/Electrostatic Double Focusing
Quad/Sector MS/MS
Ion Cycloidal Resonance (ICR)
Time-of-Flight (TOF)…

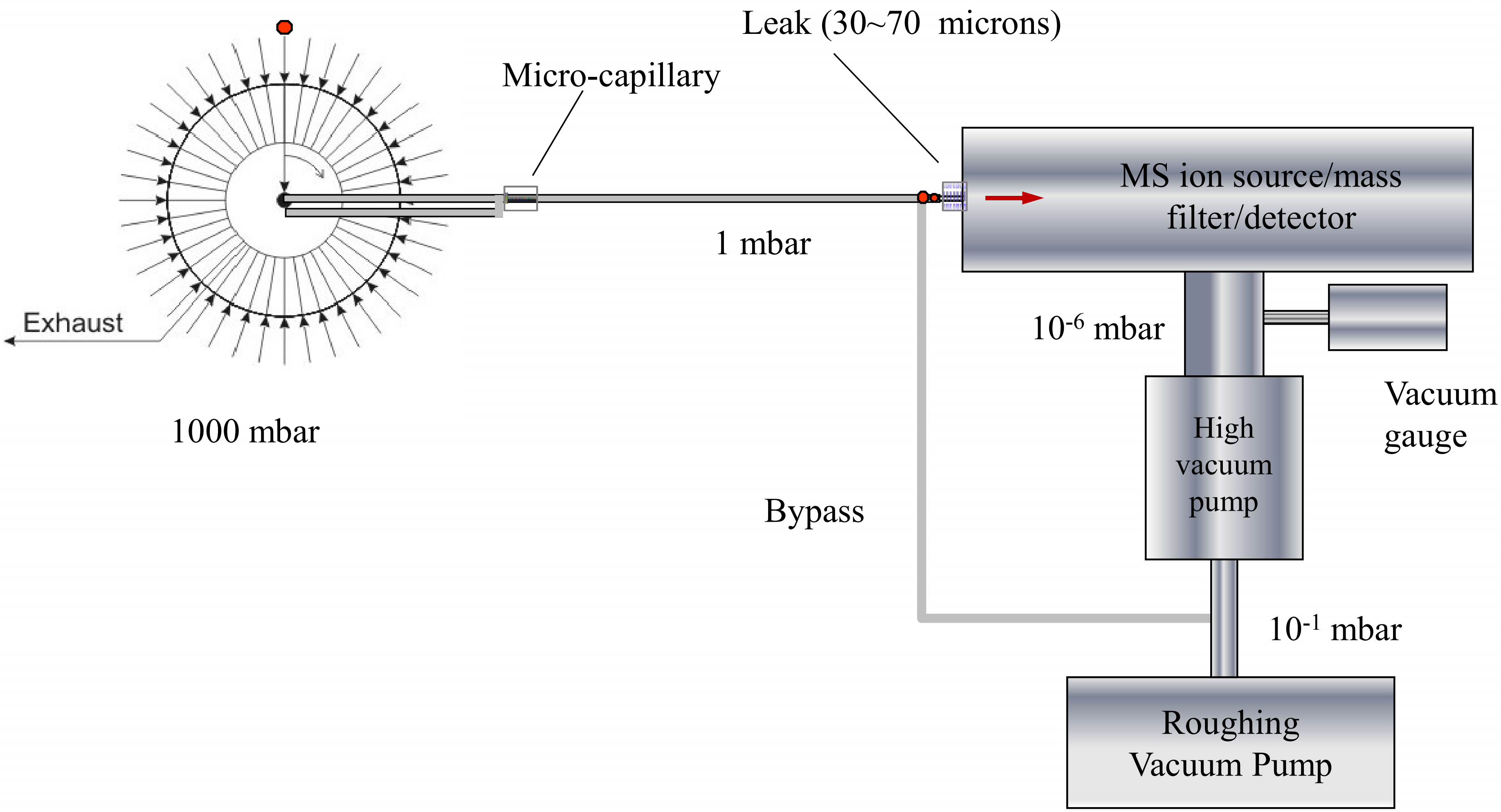
RMS Rapid Multistream Sampler operation

- Engineered to be extremely reliable and virtually maintenance-free
- RMS is not a rotary valve
- All sample gases flow all the time from their inlet port to corresponding port in stator face
- Stepper motor drives rotating arm over the port in the stator face corresponding to the selected sample
- Position of rotating arm is optically encoded for reliable, computer controlled stream selection
- 3 years warranty
- Uses coaxial bypass flow design, creating internal fast loop to minimize response times and avoid cross-contamination

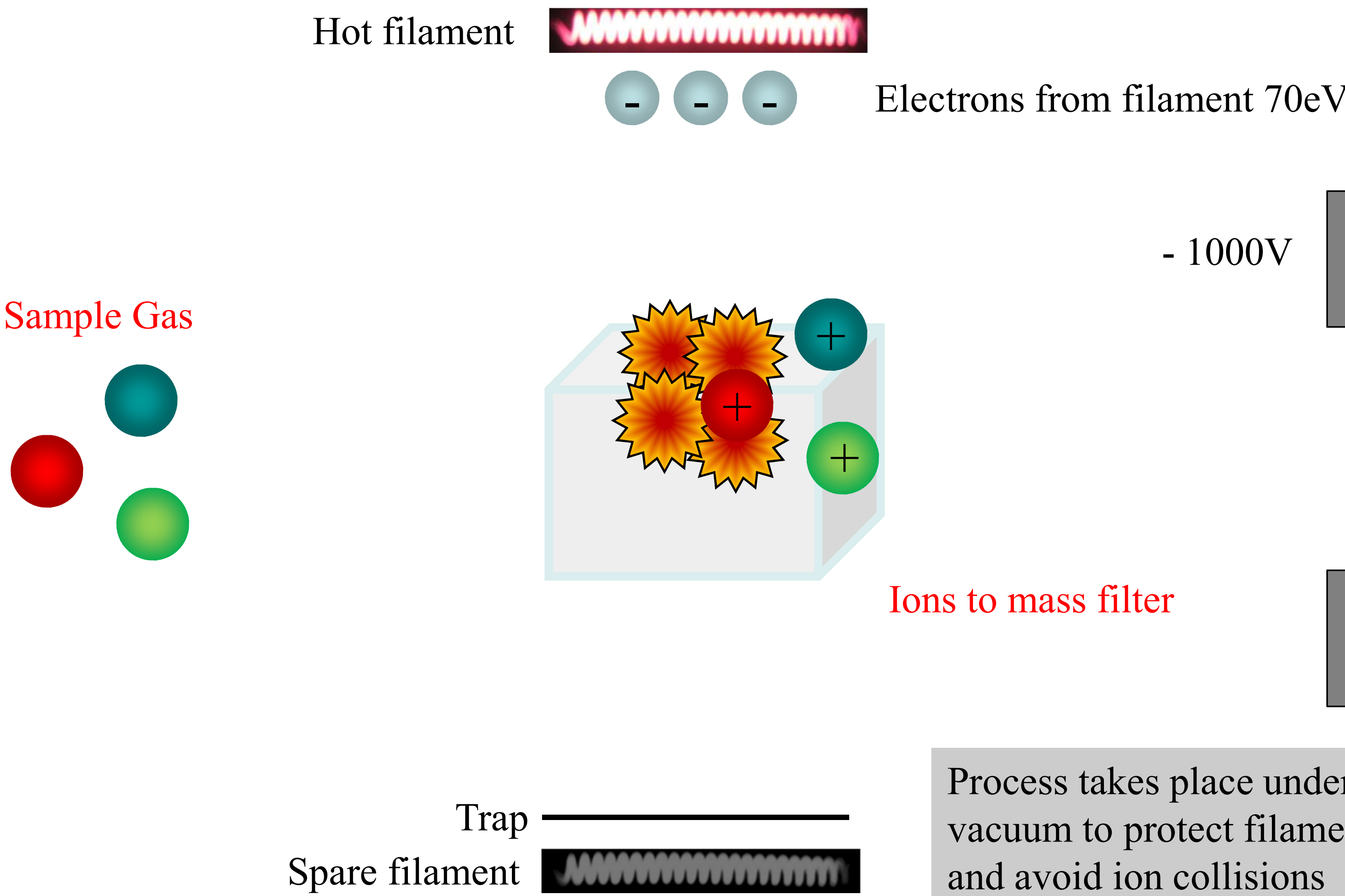
Pressure Reduction at Micro-capillary inlet



Pressure Reduction



Ionisation

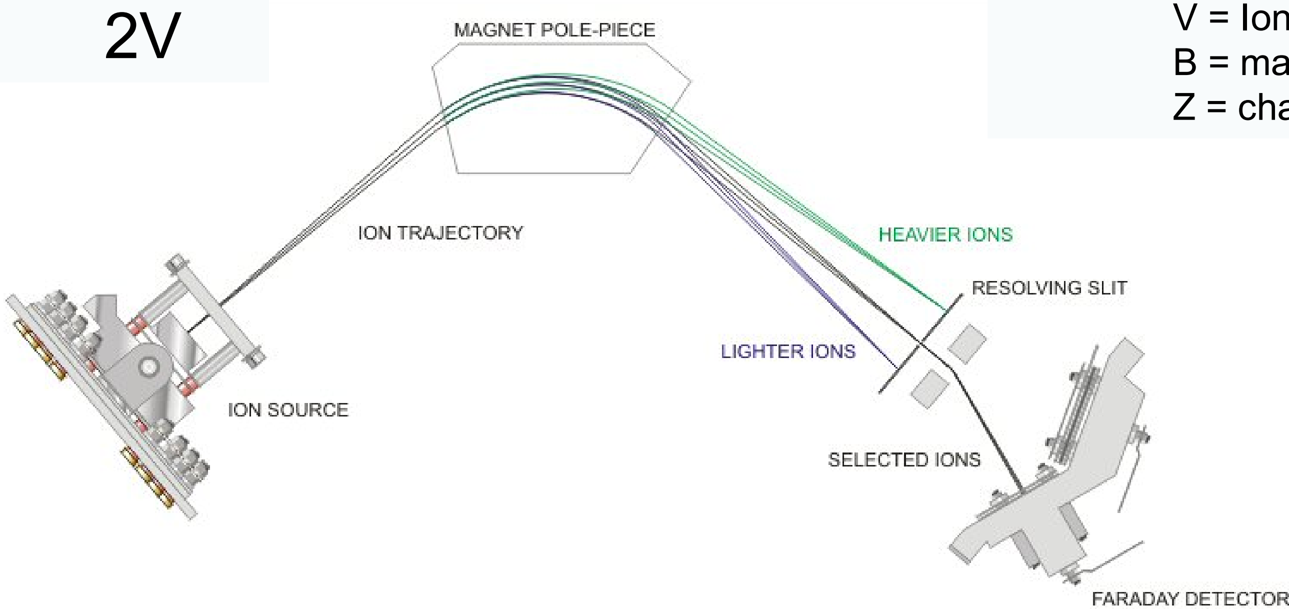


Process takes place under vacuum to protect filaments and avoid ion collisions

Magnetic sector

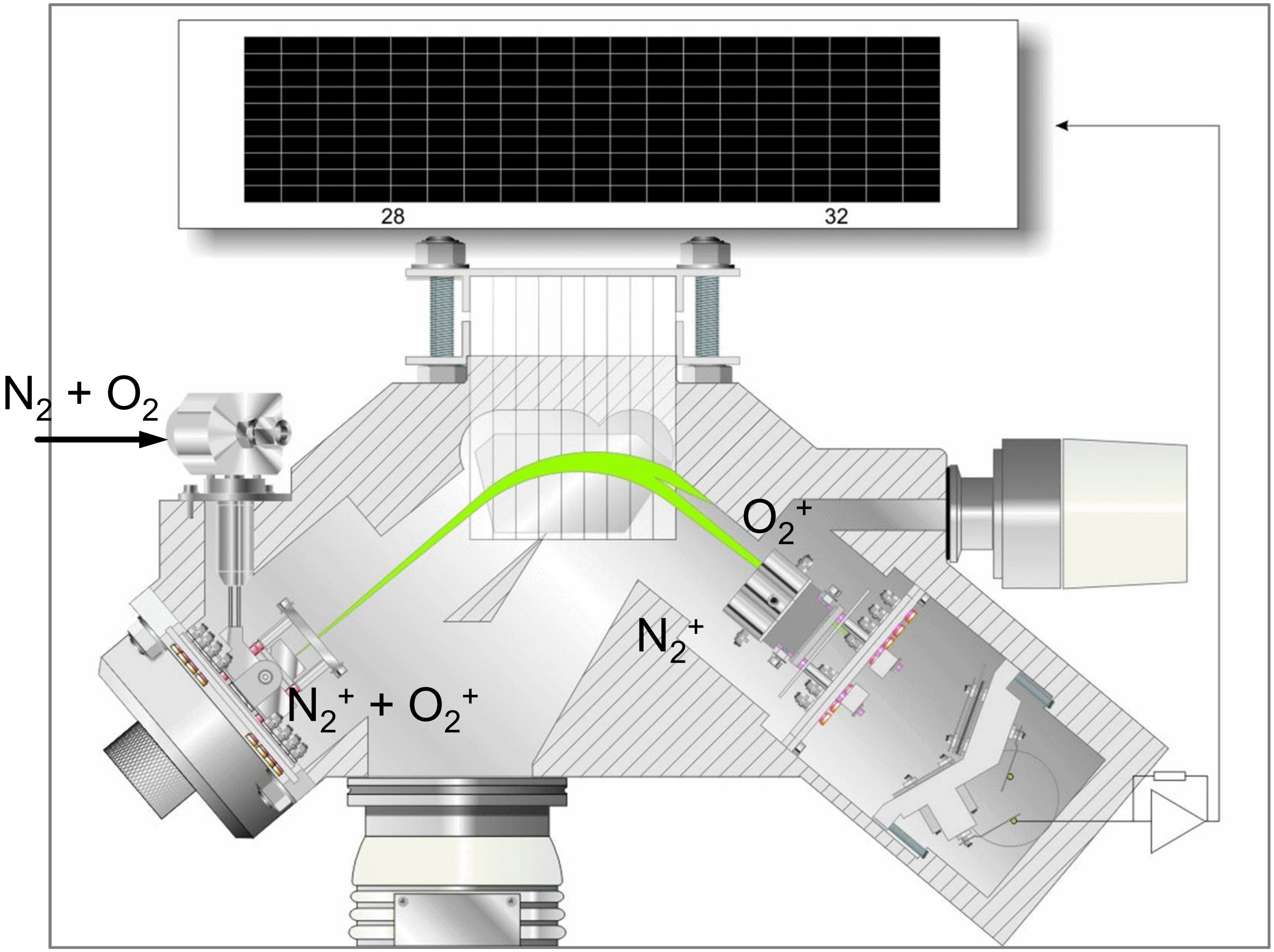
$$\frac{m}{z} = \frac{B^2 \times r^2}{2V}$$

Where: r = radius of orbit
M = mass of particle
V = Ion Energy (1kV)
B = magnetic field strength
Z = charge of particle

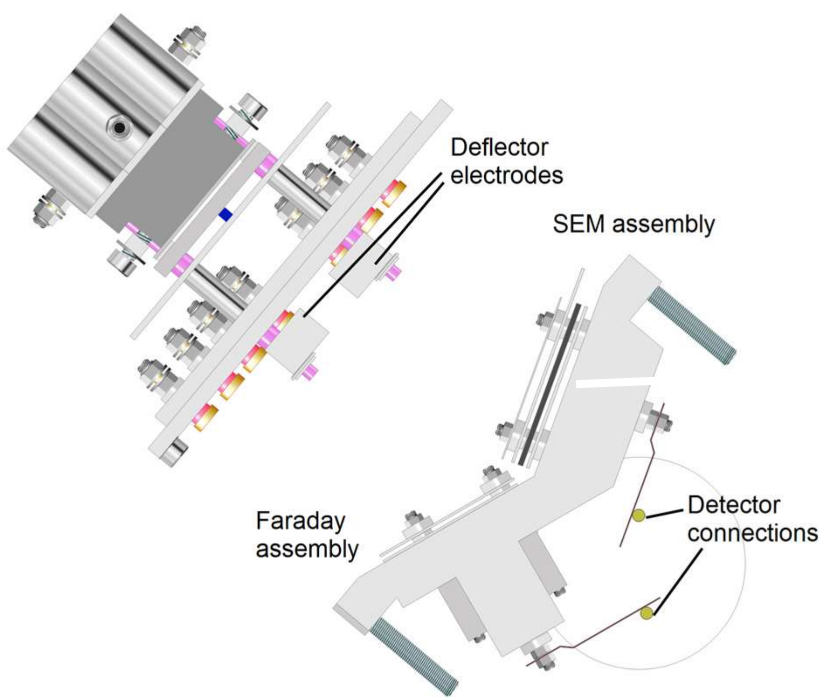


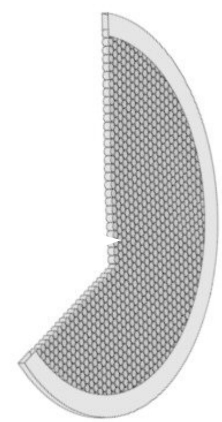
- If a charged particle is injected into a magnetic field with constant velocity, then the Lorentz force will act on the particle, causing it to move in a circular orbit of constant radius
- Radius depends on particle's mass, charge & velocity and the magnetic field strength

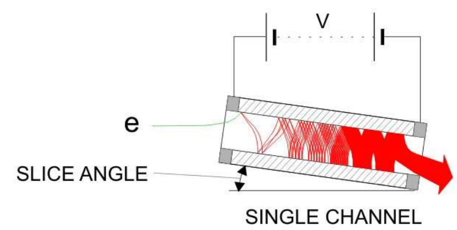
Magnetic sector



Dual detector assembly



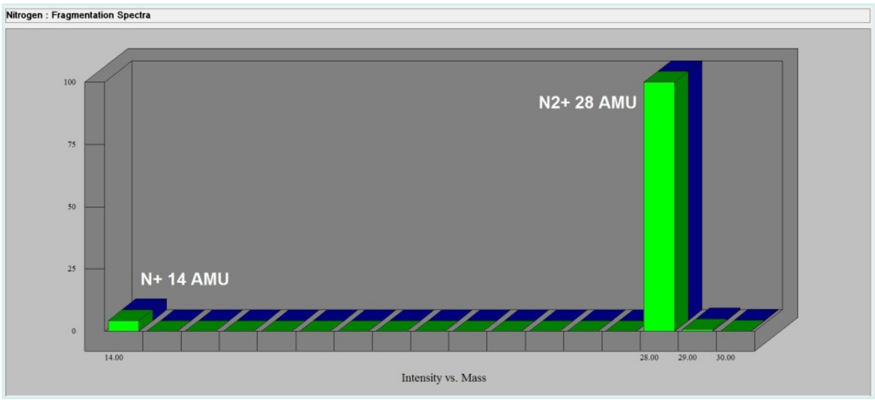




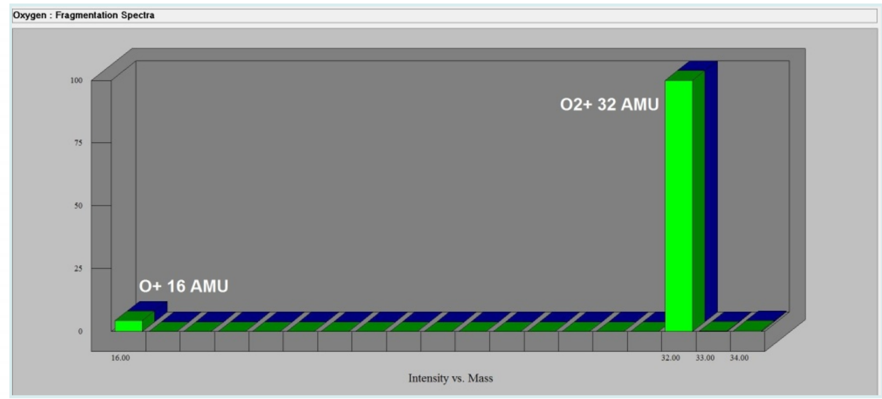
- Standard Faraday detector used in the range 10ppm – 100%*
- Optional Secondary Electron Multiplier (SEM) used in the range 10 ppb-100ppm*
- Ion beam is directed to appropriate detector by applying deflecting voltage under software control

* Application dependent

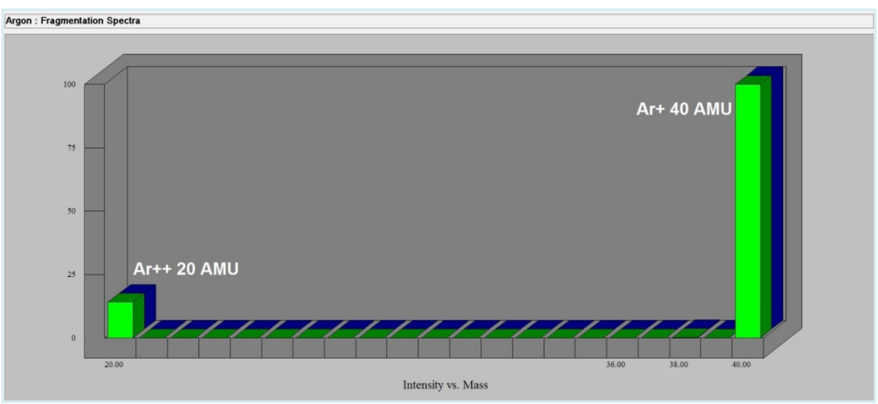
Mass spectra: molecular fingerprints



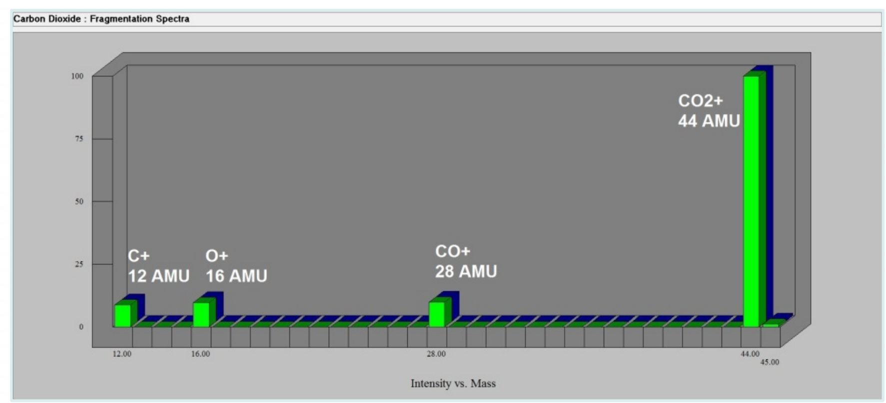
Nitrogen



Oxygen



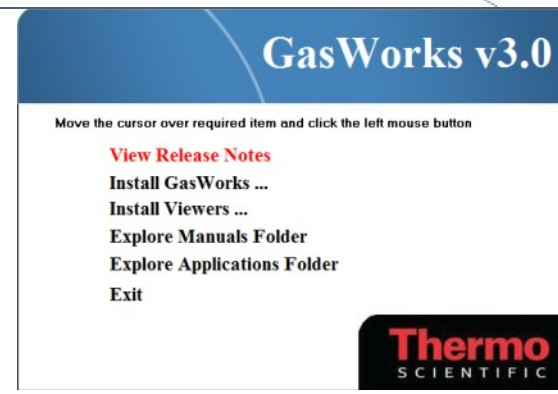
Argon

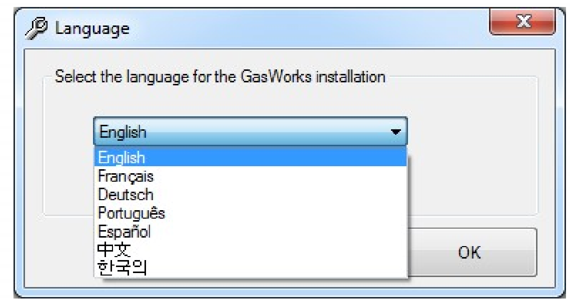


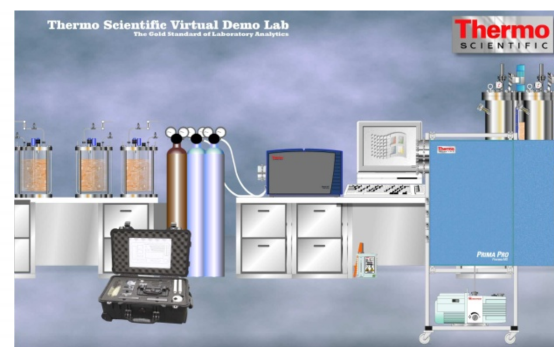
Carbon dioxide

GasWorks Process MS software

- For Prima PRO, Prima BT & Sentinel PRO
- Multi-point, multi-component process gas analysis
- Supports stand-alone analyzer operation
- Sets no limits to the number of sample streams or analytical methods
- Includes rigorous mathematical engine to deconvolute complex mixtures
- Multi-language support for all HMI screens
- Multi-layered security with expiring passwords and audit trail (21CFR p11)
- Industry best diagnostics and equipment support package
- Includes System Wizard specifically configured to fully document the analyzer hardware







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Advantages of Mass Spectrometer over other technologies

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  - *Seconds not minutes*
- Multi-component analysis
  - *Analyze inorganics & organics*
- Multi-stream analysis
  - *Up to 64 streams*
- Flexible analysis
  - *Analysis defined in software*
  - *Analyze different compounds in different streams*
- Precision, accuracy
  - *Between 0.1% and 1% relative*
- Dynamic range
  - *ppm to 100%*
- Utilities
  - *Power and Instrument Air*
- **Three Years Warranty**

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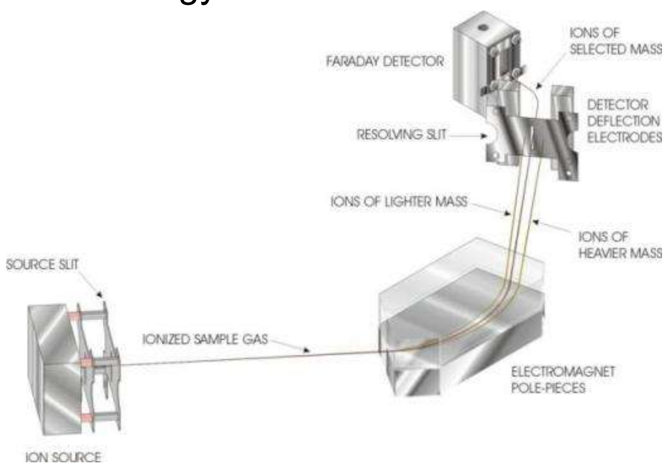
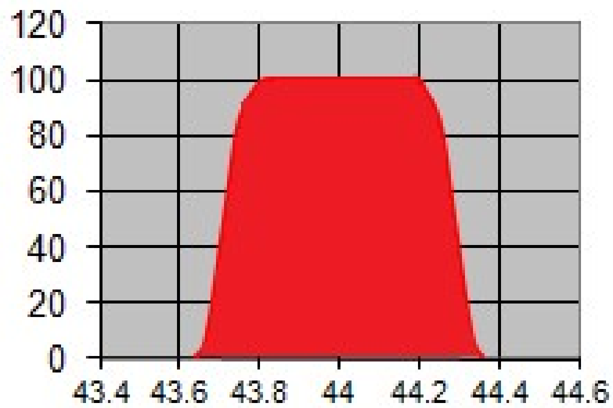
Special Features of Magnetic Sector technology

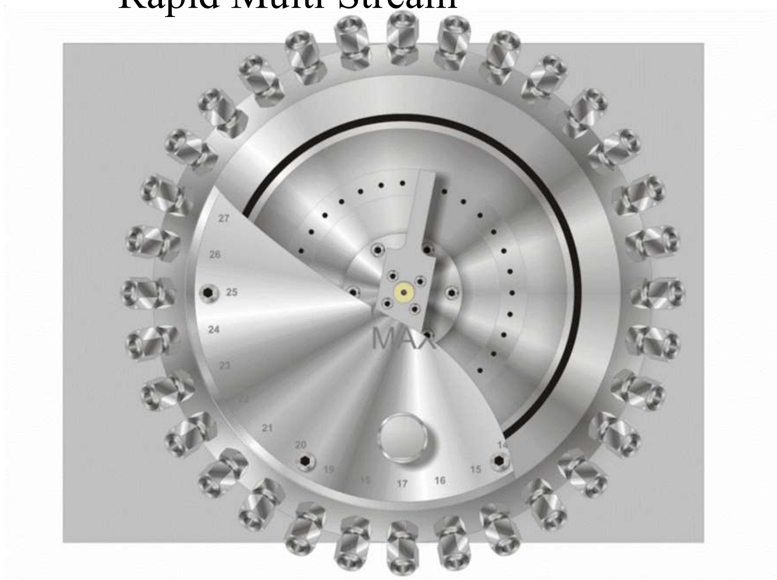
Ion energy 1000 eV



Flat topped Peak : Fault Tolerant



Rapid Multi Stream



3 Years Warrantee

Mass Spectrometer Value Summary

- Prima PRO provides most precise measurements to optimize control of ammonia production process
  - *Gas Mixing and Burner Control in Reformer*
  - *H_2S in Natural Gas feed*
  - *Hydrogen/Nitrogen ratio (0.05% RSD)*
  - *Steam/Carbon ratio*
  - *Methane slippage (± 20 ppm accuracy)*
  - *Inert gas build-up in synthesis Loop*
  - *Monitor catalyst activity to schedule plant outages*

- Provides lowest true cost of ownership and best guaranteed performance specifications of any available process analyzer on the market

QUESTIONS?

The world leader in serving science