Analysis of Volatile Organic Compounds (VOCs) by Purge-and-Trap

Customer Training Course

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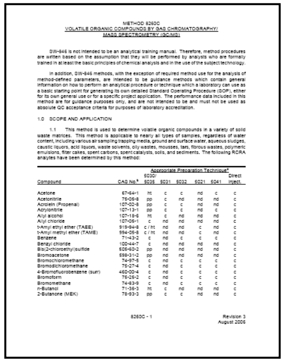
VOC Course Outline

- Introduction, history, and methodology
- Purge-and-Trap Theory
  - Principle of operation
  - The state machine
  - Flow paths
- Critical success factors to P&T
  - Purge efficiency
  - Sample Heating
  - Trapping efficiency
  - Desorb efficiency
  - Bake (reconditioning) efficiency
- Water management

Introduction, History, and Methodology

Overview



METHOD 8260C

VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/
MASS SPECTROMETRY (GC/MS)

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following RCRA analytes have been determined by this method:

		Appropriate Preparation Technique[a]					
Compound	CAS No.[b]	5030/ 5035	5031	5032	5021	5041	Direct Inject.
Acetone	67-64-1	ht	c	c	nd	c	c
Acetonitrile	75-05-8	pp	c	nd	nd	nd	c
Acrolein (Propenal)	107-02-8	pp	c	c	nd	nd	c
Acrylonitrile	107-13-1	pp	c	c	nd	c	c
Allyl alcohol	107-18-6	ht	c	nd	nd	nd	c
Allyl chloride	107-05-1	c	nd	nd	nd	nd	c
t-Amyl ethyl ether (TAEE)	919-94-8	c / ht	nd	nd	c	nd	c
t-Amyl methyl ether (TAME)	994-05-8	c / ht	nd	nd	c	nd	c
Benzene	71-43-2	c	nd	c	c	c	c
Benzyl chloride	100-44-7	c	nd	nd	nd	nd	c
Bis(2-chloroethyl)sulfide	505-60-2	pp	nd	nd	nd	nd	c
Bromoacetone	598-31-2	pp	nd	nd	nd	nd	c
Bromochloromethane	74-97-5	c	nd	c	c	c	c
Bromodichloromethane	75-27-4	c	nd	c	c	c	c
4-Bromofluorobenzene (surr)	460-00-4	c	nd	c	c	c	c
Bromoform	75-25-2	c	nd	c	c	c	c
Bromomethane	74-83-9	c	nd	c	c	c	c
n-Butanol	71-36-3	ht	c	nd	nd	nd	c
2-Butanone (MEK)	78-93-3	pp	c	c	nd	nd	c

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Revision 3
August 2006

Federal Regulation ⇄ VOC Methodology ⇄ Instrument Design

Regulation

- Water regulations
  - Federal Water Pollution Control Act (FWPCA) – 1948
  - Safe Drinking Water Act (SDWA) - 1974
  - Clean Water Act (CWA) – 1977, forms the basis for most monitoring programs today
- Waste regulations
  - Resource Conservation & Recovery Act (RCRA) – 1976
  - Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) – 1980
  - Superfund Amendments and Reauthorization Act (SARA) - 1986

Methodology

- EPA’s Priority Pollutant List (PPL) listed the compounds to be regulated and tested
  - 105 dangerous compounds
  - Analysis by GC methods
- Semi-volatile compounds
  - Extraction and concentration
  - Analysis by direct injection into GC
- Volatile compounds – no good analytical method available in the early 1970s
  - Extraction – lose volatiles
  - Direct injection – not sensitive enough
  - Needed a new technology

Methodology

- In 1974 and EPA chemist Tom Bellar developed a technique for concentrating volatile pollutants in water for low level detection
- Became known as “purge-and-trap”
- The 1st purge-and-trap instruments were “homemade” from ordinary materials available in most laboratories
- Commercial instrumentation came to market rapidly
- Instrument developments and improvements have been consistent ever since

Methodology

- Regulation drove method development, which in turn drove instrument design
- Multiple VOC methods written by different agencies
- Most of the VOC methods use same basic principle of operation for the P&T
- Differences in
  - Matrix
  - Target compound list
  - Detector
  - Concentration ranges
  - QA/QC

Water Methods

- 500 and 600 series methods developed by EPA Office of Water
- 500 series methods for drinking water
  - Analysis of raw source water and finished drinking water
  - Measures volatiles and semi-volatiles
  - 16 different methods
- Primary 500 series methods for VOCs in drinking water
  - Method 502.2: analysis of 60 volatile contaminants by P&T with PID/ELCD detection
  - Method 524.2, Rev. IV: analysis of 502.2 list plus 24 additional compounds by P&T with MS detection
  - As of June 2007 Method 524.2 currently being re-written

Water Methods

- 600 series methods for waste water
  - Municipal and industrial waste water
  - Measures volatiles and semi-volatiles
  - 18 different methods
- Primary 600 series methods for VOCs in waste water
  - Method 601: purgeable halocarbons by P&T with ELCD
  - Method 602: purgeable aromatics by P&T with PID
  - Method 624: purgeable VOCs by P&T with MS
  - Method 1624: purgeable VOCs by P&T with isotope dilution MS

Waste Methods

- SW846 5000 and 8000 series methods developed by EPA Office of Solid Waste
- 5000 series sample preparation methods
  - Method 5020: VOCs by headspace
  - Method 5030: VOCs by purge-and-trap
  - Method 5035: VOCs by closed-system purge-and-trap
- 8000 series determinative methods
  - Method 8015B: non-halogenated VOCs by FID
  - Method 8021B: aromatic and halogenated VOCs by PID/ELCD
  - Method 8260C: VOCs by MS

Other Methods

- Contract Laboratory Program (CLP)
  - Method OLM04.2
  - Method OLC03.2
- Massachusetts Volatile Petroleum Hydrocarbon (VPH) method
- State GRO methods
  - LUST program
- Air methods
  - TO9, TO15, etc.
- European and Asian methods
- More…

Evolution of Purge-and-Trap

- Forces that drive instrument development
  - Commercially available “off the shelf”
  - Automation and ease-of-use
  - Increase in sample load
  - Improvements in data accuracy and precision
  - New features to solve old problems (e.g. water)
  - Advances in technology
  - Changes in the methodology (e.g. addition of new compounds)

Evolution of Purge-and-Trap

1st Generation
Model 4460
Introduced 1986

2nd Generation
Model 4560
Introduced 1992

3rd Generation
The Eclipse
Introduced 2003

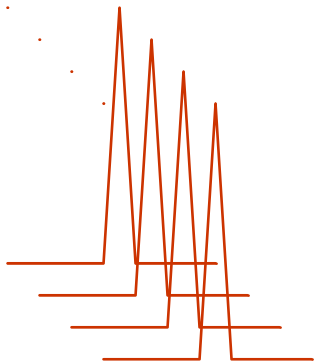
Purge-and-Trap Theory

VOC Techniques

- Direct injection
  - High ppb to high ppm
- Headspace
  - 20 ppb to low ppm
- Purge-and-trap
  - 10 ppt to 200 ppb
- Also depends to some extent on detector sensitivity

Purge-and-Trap Analysis

- To efficiently extract Volatile Organic Compounds (VOCs) from a matrix and concentrate them for transfer onto a GC analytical column
- Without sacrificing peak shape or resolution



P&T Advantages

- Extremely sensitive
  - Low ppt range possible
- Greatest extraction efficiency
  - Exhaustive for some analytes
- Large sample sizes
- Well understood methodology
- Covers a wide range of boiling points
  - -30°C to 220°C

P&T Limitations

- Complex compound lists with multiple chemistries
- More complex hardware than static headspace
- Water considerations
- Foaming samples
- Carry-over for samples with >200 ppb

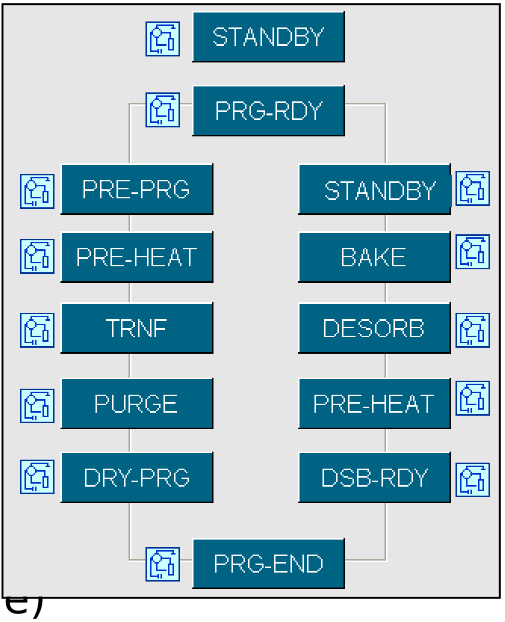
Principle of Operation

- Analytes are swept from the sample using an inert gas
  - Aka purging or extraction step
- Collected on a trap
  - Concentration step
- Trap is heated to release analytes and transfer to the GC column
  - Desorb step
- The entire system, including the trap, is baked (reconditioned) before running the next sample

Eclipse State Machine

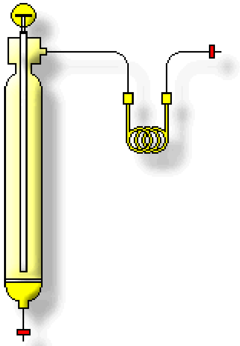
Eclipse State Machine

- The Eclipse uses 11 primary P&T states. A state is a set of trap temperature, water management temperature, and valve position combinations defined for P&T analyses:
    - Purge ready (with or without flow)
    - Prepurge
    - Preheat
    - Purge (adsorb)
    - Dry purge
    - Purge complete
    - Desorb ready
    - Desorb preheat
    - Desorb (with or without drain)
    - Backflush bake (with or without purge)
    - Standby

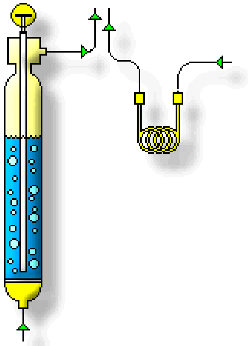


State Descriptions

Purge Ready



Pre-Purge

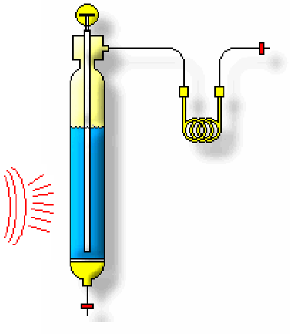


- PURGE READY: The Eclipse enters this state when all conditions are met to start the next analysis. The instrument sits at purge ready until a run initiates either by the operator or by an external device. The Eclipse can be configured to stop at purge ready after each sample run, waiting for the next sample and start command to be received.

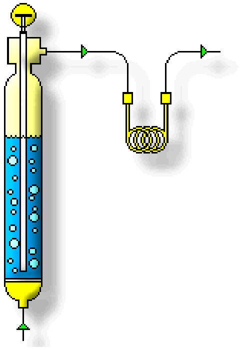
- PRE-PURGE: The Eclipse normally uses this optional state only for air analysis. Pre-purging an air tube removes oxygen and excess moisture accumulated in the tube during sample collection. Pre-purging a hydrophobic substrate (e.g., Tenax®) reduces the moisture transferred to the trap.

State Descriptions (cont.)

Pre Heat



Purge

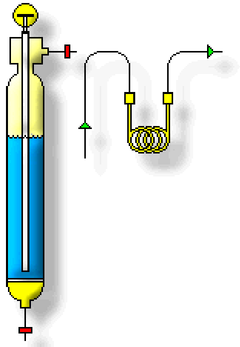


- PRE-HEAT: This state prior to purge allows a heated sample (e.g., air tube, soil, or water) to equilibrate to a preset temperature before purge begins. The Eclipse only uses this state when a sample heater or air-tube heater is present and sample heating is desired.

- PURGE: Sample extraction occurs during this state. Inert gas passes through the sample for a specified time and temperature, and volatiles adsorb onto the Eclipse’s trap for subsequent desorption to the GC column.

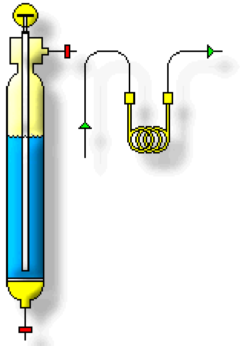
State Descriptions (cont.)

Dry Purge



- DRY PURGE: This optional state removes moisture from the hydrophobic substrates in the trap. During dry purge, the sample is bypassed and the trap purges with dry purge gas directly. Dry purge is usually not necessary with the Eclipse, which has an effective water management system.

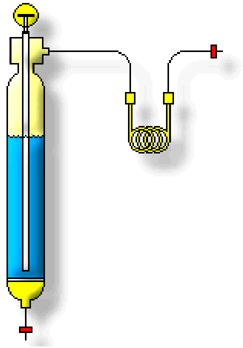
Purge End



- PURGE END: This pass-through state indicates the purge state completed. If the water management system is not ready, the Eclipse remains in purge end until the Cyclone Water Management™ system reaches the required set point for desorption.

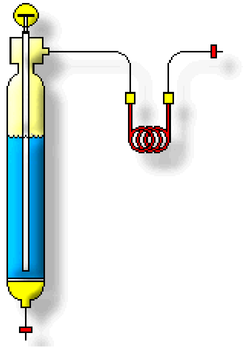
State Descriptions (cont.)

Desorb Ready



- DESORB READY: After completing all purging and the water management reaches its set point, the Eclipse advances to desorb ready. While in desorb ready, the Eclipse checks for ready signals from other components of the system (e.g., GC) before advancing to desorb.

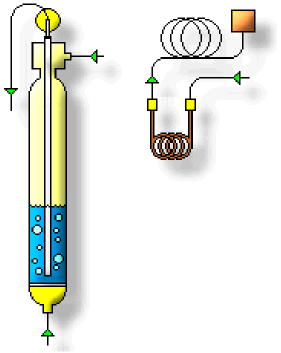
Desorb Preheat



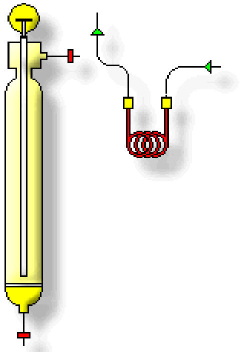
- DESORB PREHEAT: When desorb preheat is enabled, the Eclipse heats the trap to a desorb preheat set point without carrier gas flow (e.g., prior to valve rotation). Use this technique to achieve narrow desorption bandwidth when analyte release from the trap is slow.

State Descriptions (cont.)

Desorb



Backflush Bake

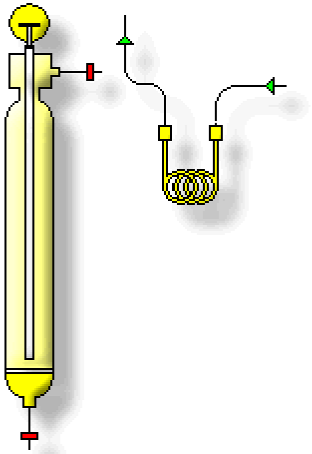


- DESORB: During desorb, the Eclipse’s trap heats rapidly to the set temperature, transferring volatile compounds through the Eclipse heated transfer line to the GC injector port. If using a needle sparger (draining is not possible), disable **Drain at Desorb.** Otherwise, an aqueous sample automatically drains during desorb (enable **Drain at Desorb**).

- BACKFLUSH BAKE: This cleanup state backflushes the trap under heat and reverse flow to remove and vent any components not transferred to the GC column. The water management also heats to remove and vent any compounds. Choose whether to purge or not purge the sample during bake.

State Descriptions (cont.)

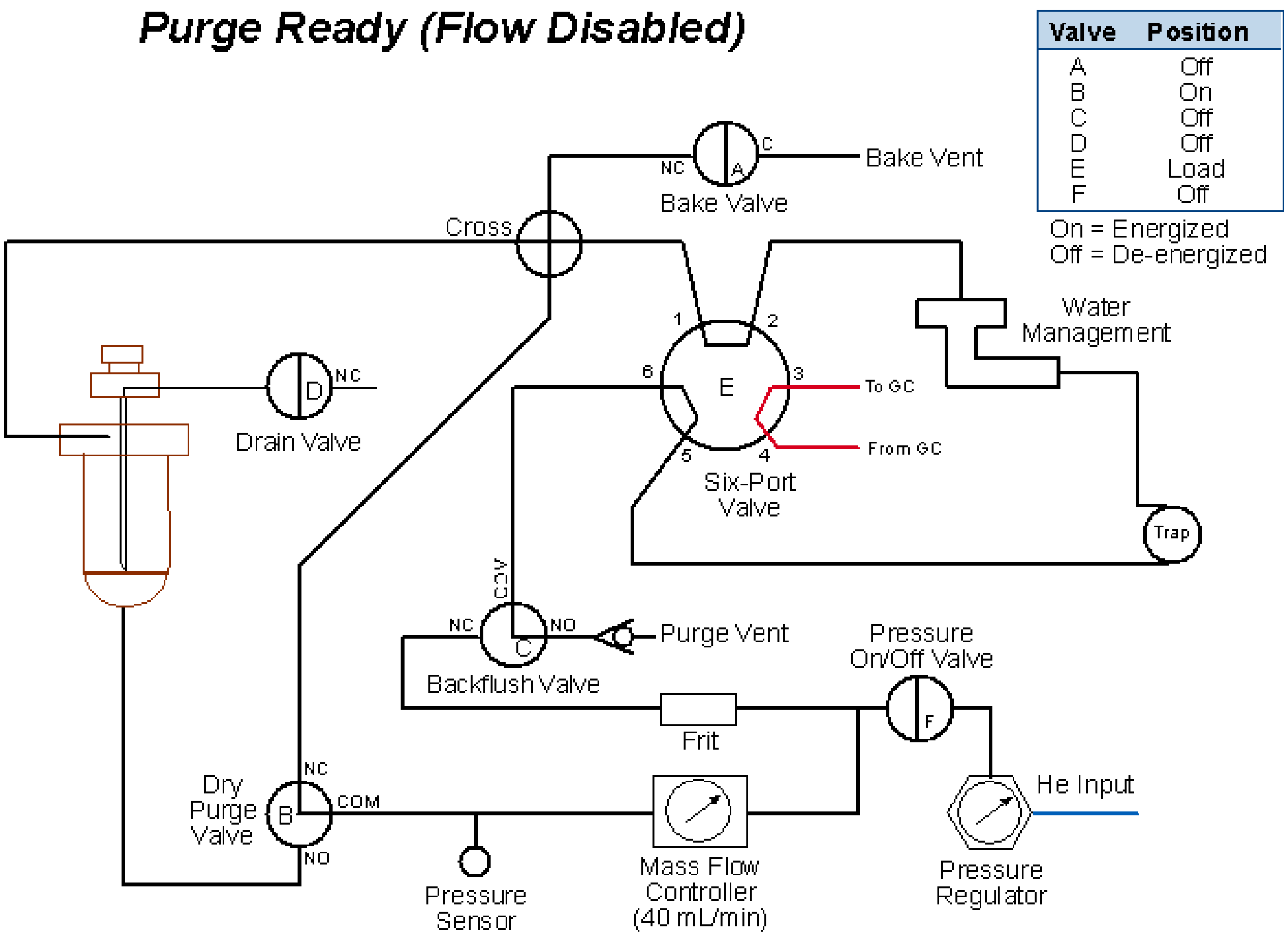
Standby



- STANDBY: The Eclipse remains in this pass-through state until attaining all temperature set points. When all heated zones are ready and the trap cools to the purge temperature set point, the Eclipse advances to purge ready.
- Standby is one of a few states not indicated on the cycle state indicator on the Status screen and is only seen on the status bar since no parameter entry is possible.

Eclipse Flow Diagrams

Purge Ready (Flow Disabled)

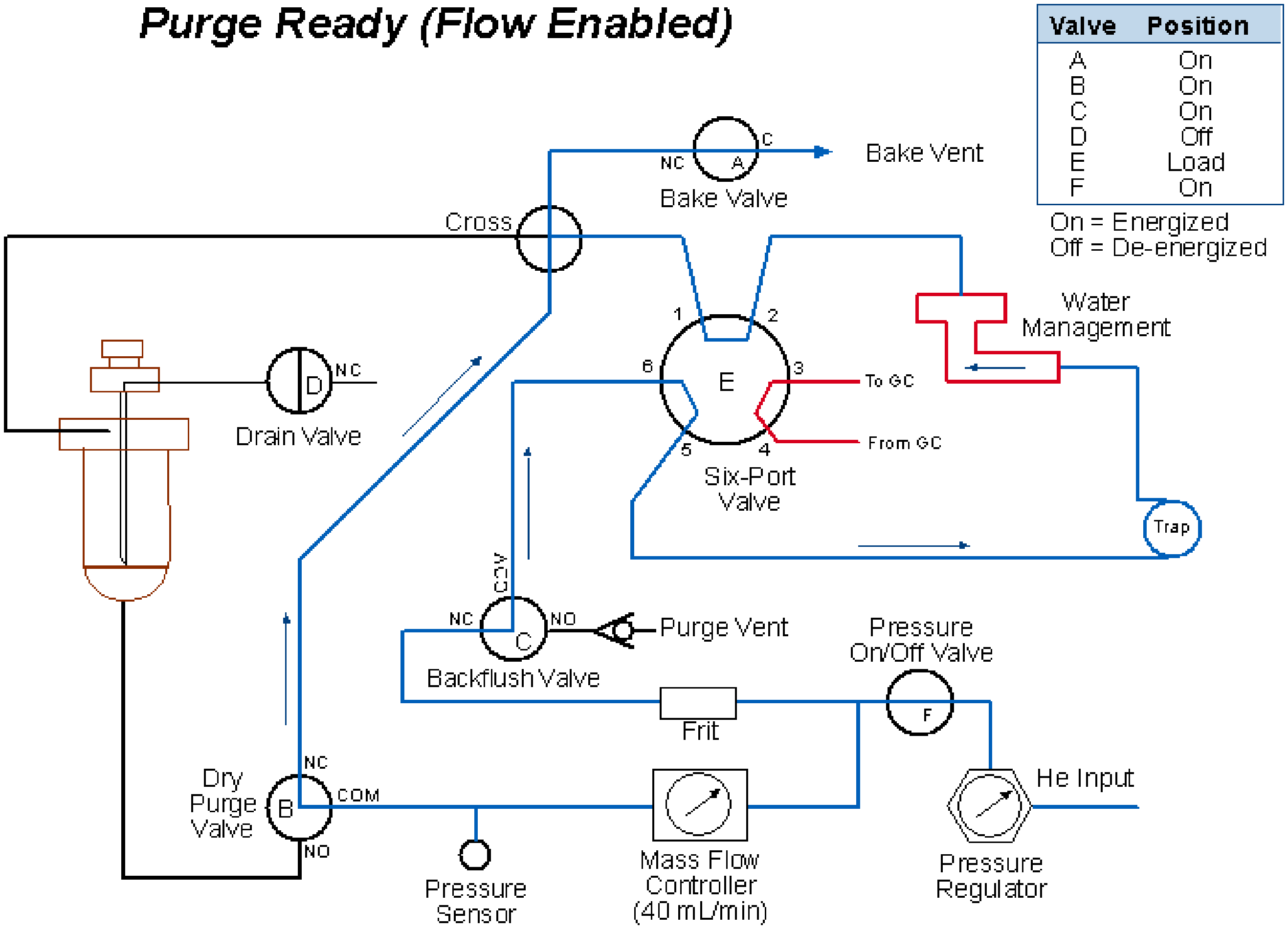


Purge Ready (Flow Disabled)

Valve	Position
A	Off
B	On
C	Off
D	Off
E	Load
F	Off

On = Energized
Off = De-energized

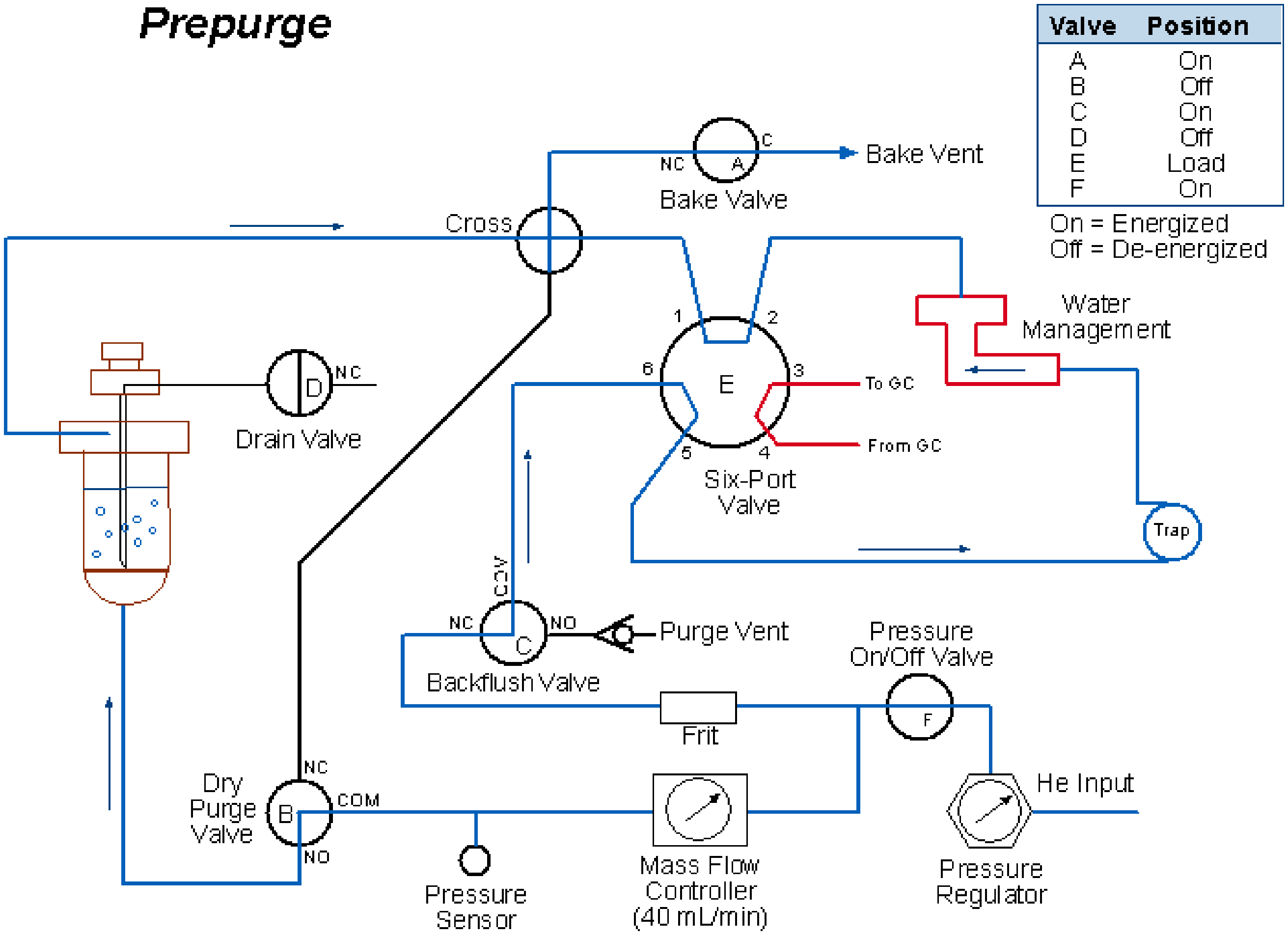
Purge Ready (Flow Enabled)



Valve	Position
A	On
B	On
C	On
D	Off
E	Load
F	On

On = Energized
Off = De-energized

Prepurge



Valve	Position
A	On
B	Off
C	On
D	Off
E	Load
F	On

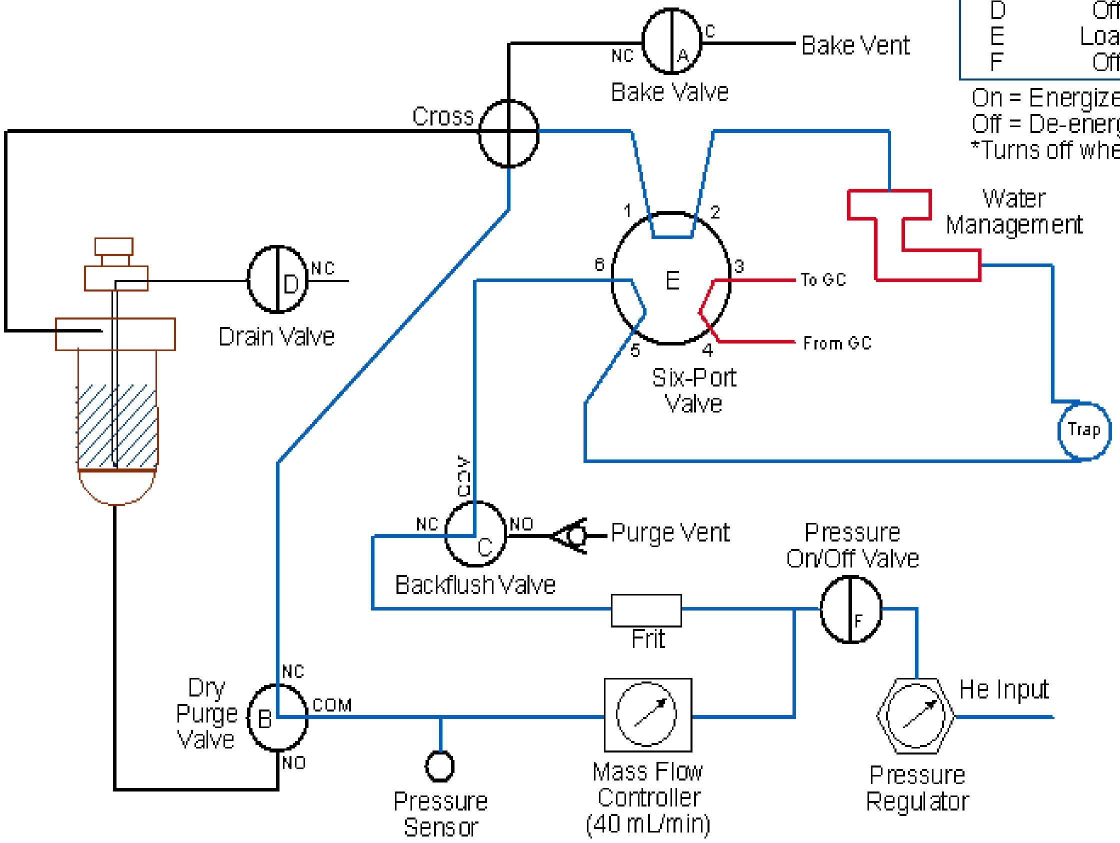
On = Energized
Off = De-energized

Sample Preheat (No Flow)

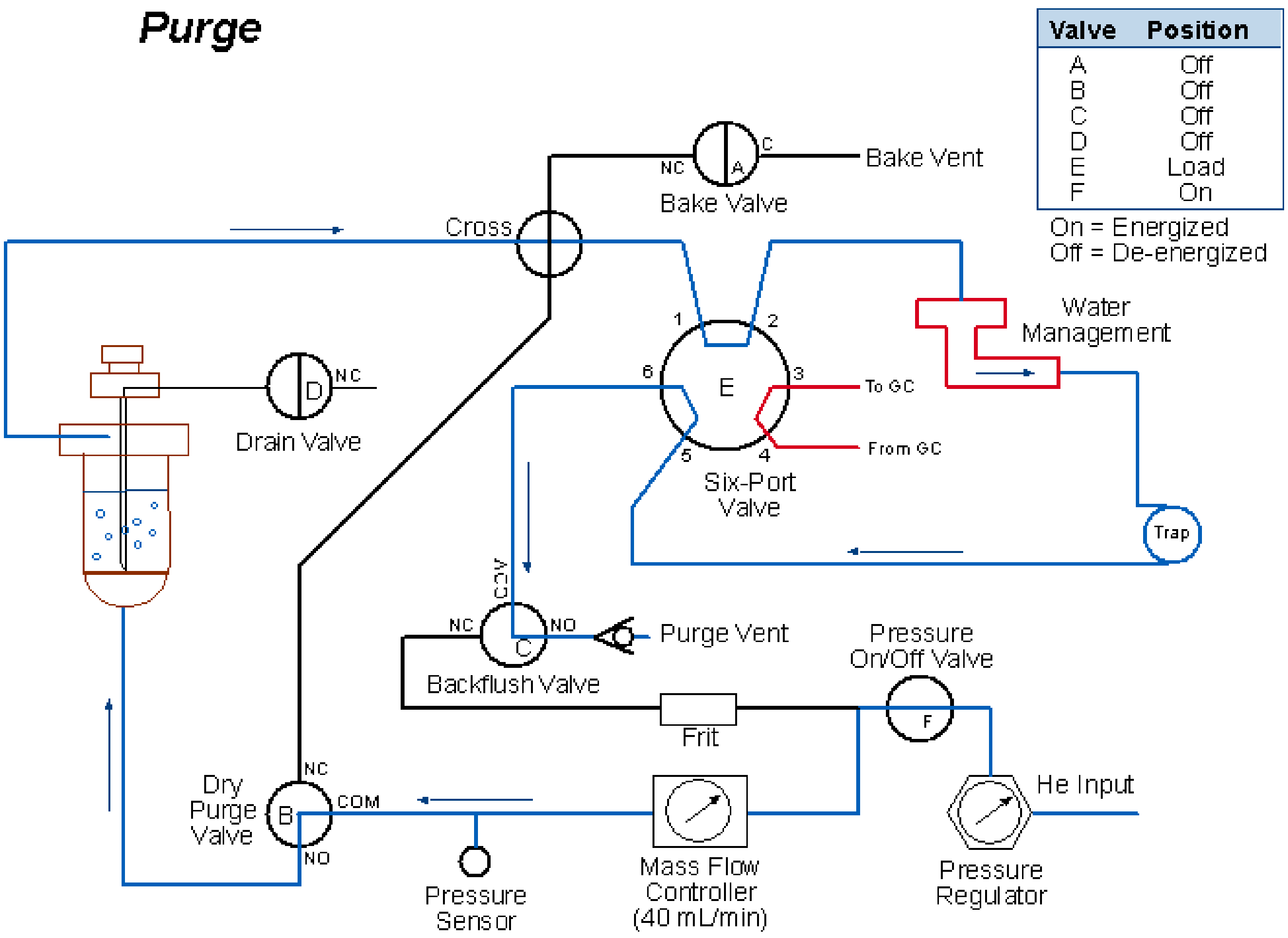
Sample Preheat (No Flow)

Valve	Position
A	On → Off*
B	On
C	On
D	Off
E	Load
F	Off

On = Energized
Off = De-energized
*Turns off when pressure is ≤2psi.



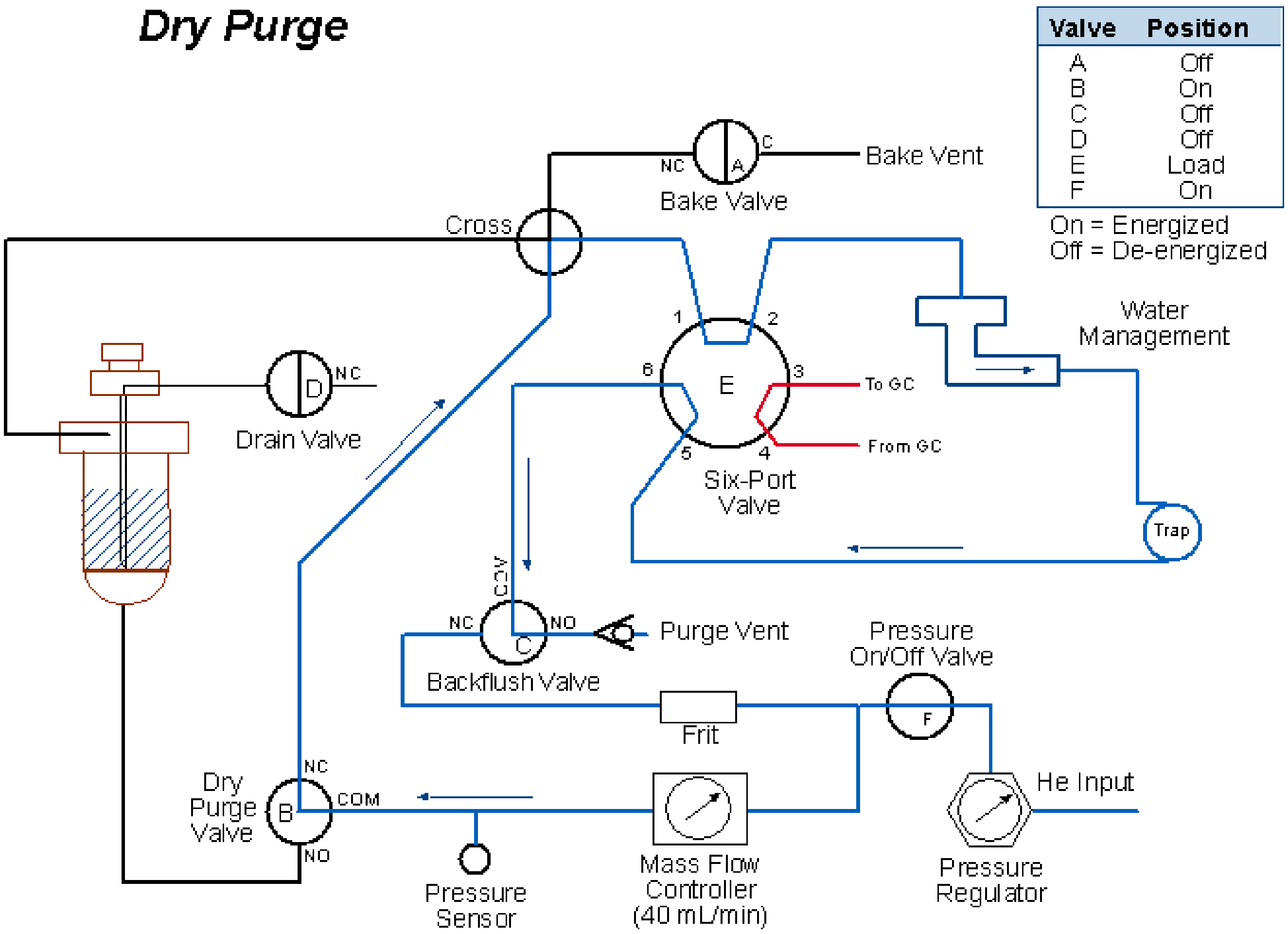
Purge



Valve	Position
A	Off
B	Off
C	Off
D	Off
E	Load
F	On

On = Energized
Off = De-energized

Dry Purge



Valve	Position
A	Off
B	On
C	Off
D	Off
E	Load
F	On

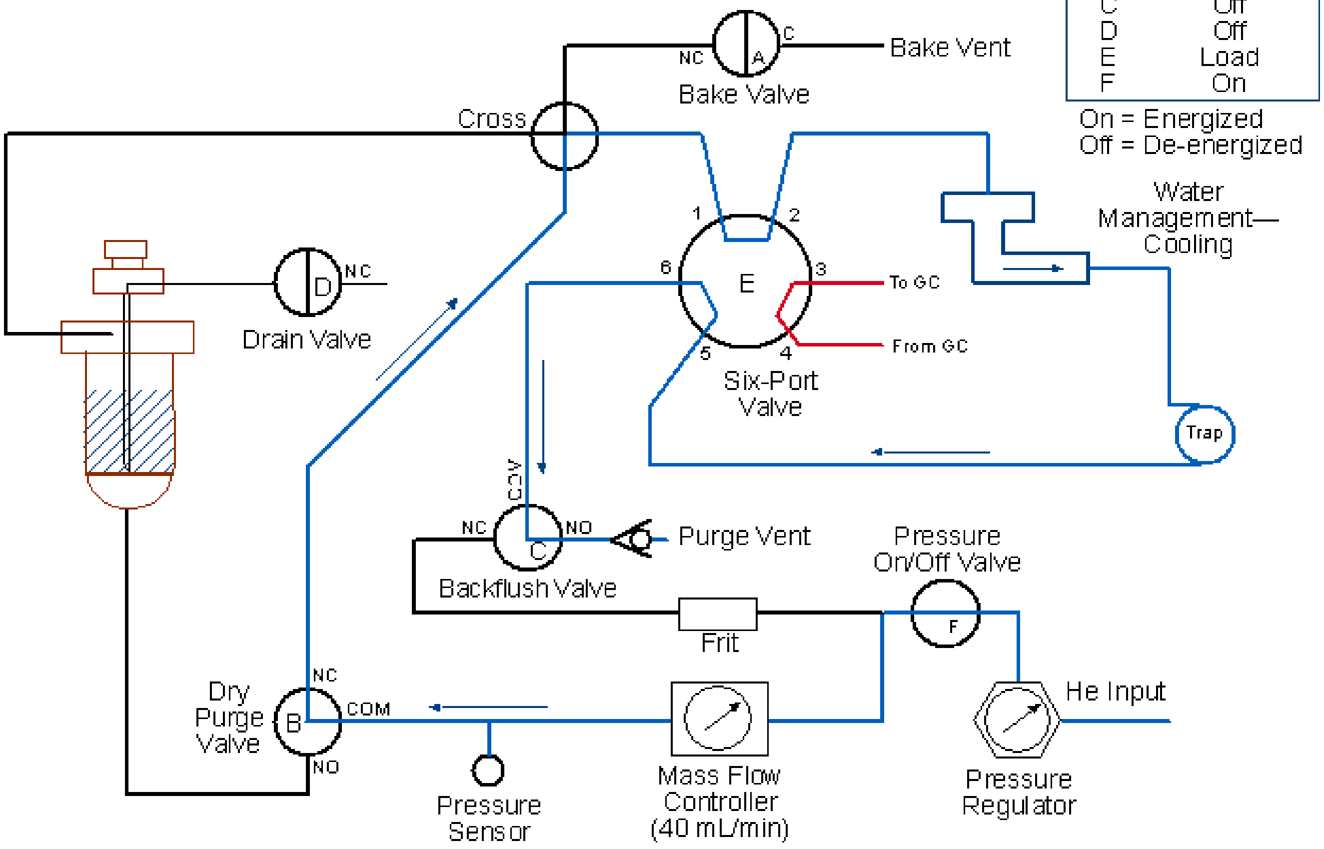
On = Energized
Off = De-energized

Purge Complete

Purge Complete

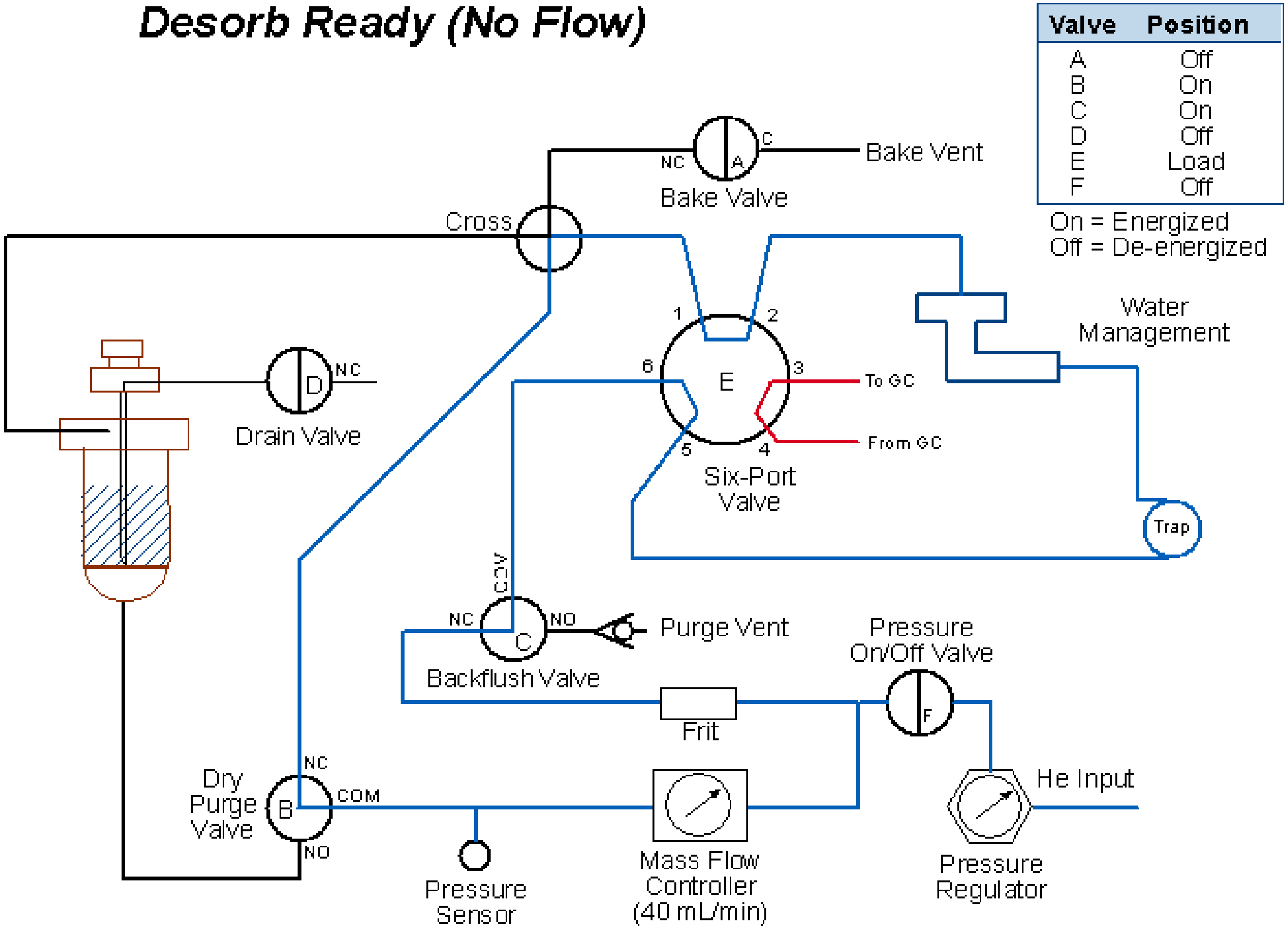
Valve	Position
A	Off
B	On
C	Off
D	Off
E	Load
F	On

On = Energized
Off = De-energized



Desorb Ready (No Flow)

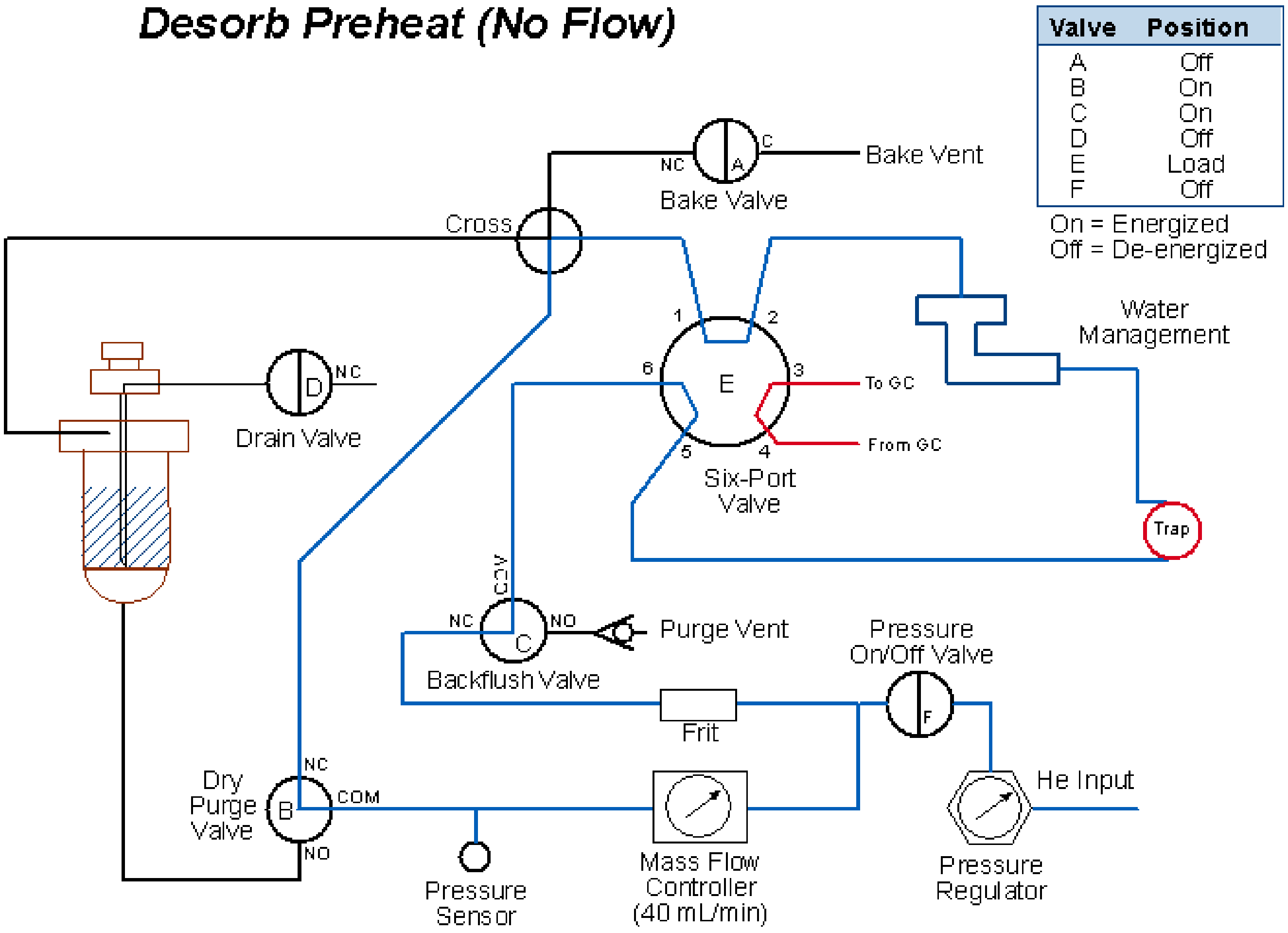
Desorb Ready (No Flow)



Valve	Position
A	Off
B	On
C	On
D	Off
E	Load
F	Off

On = Energized
Off = De-energized

Desorb Preheat (No Flow)

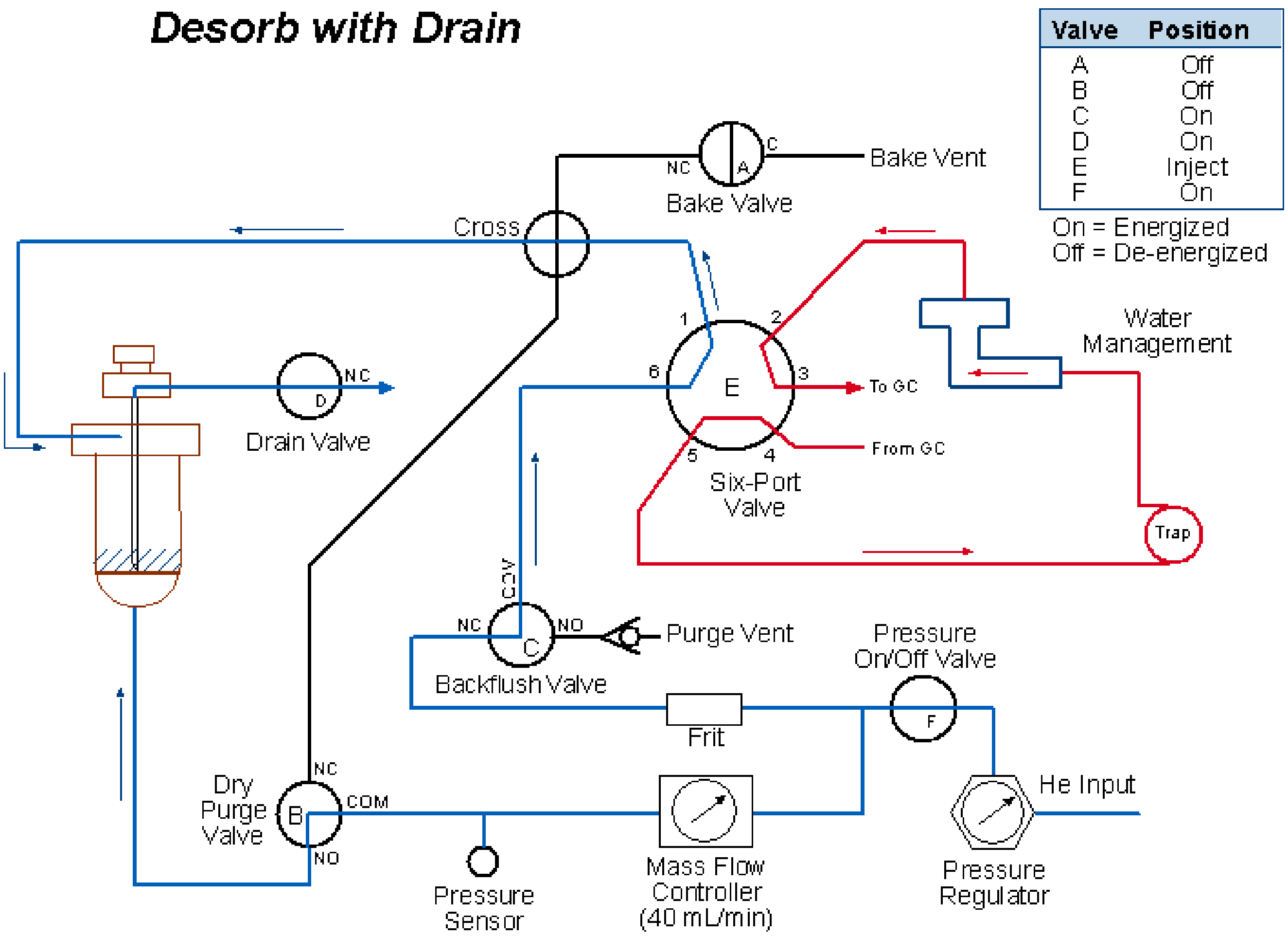


Desorb Preheat (No Flow)

Valve	Position
A	Off
B	On
C	On
D	Off
E	Load
F	Off

On = Energized
Off = De-energized

Desorb With Drain

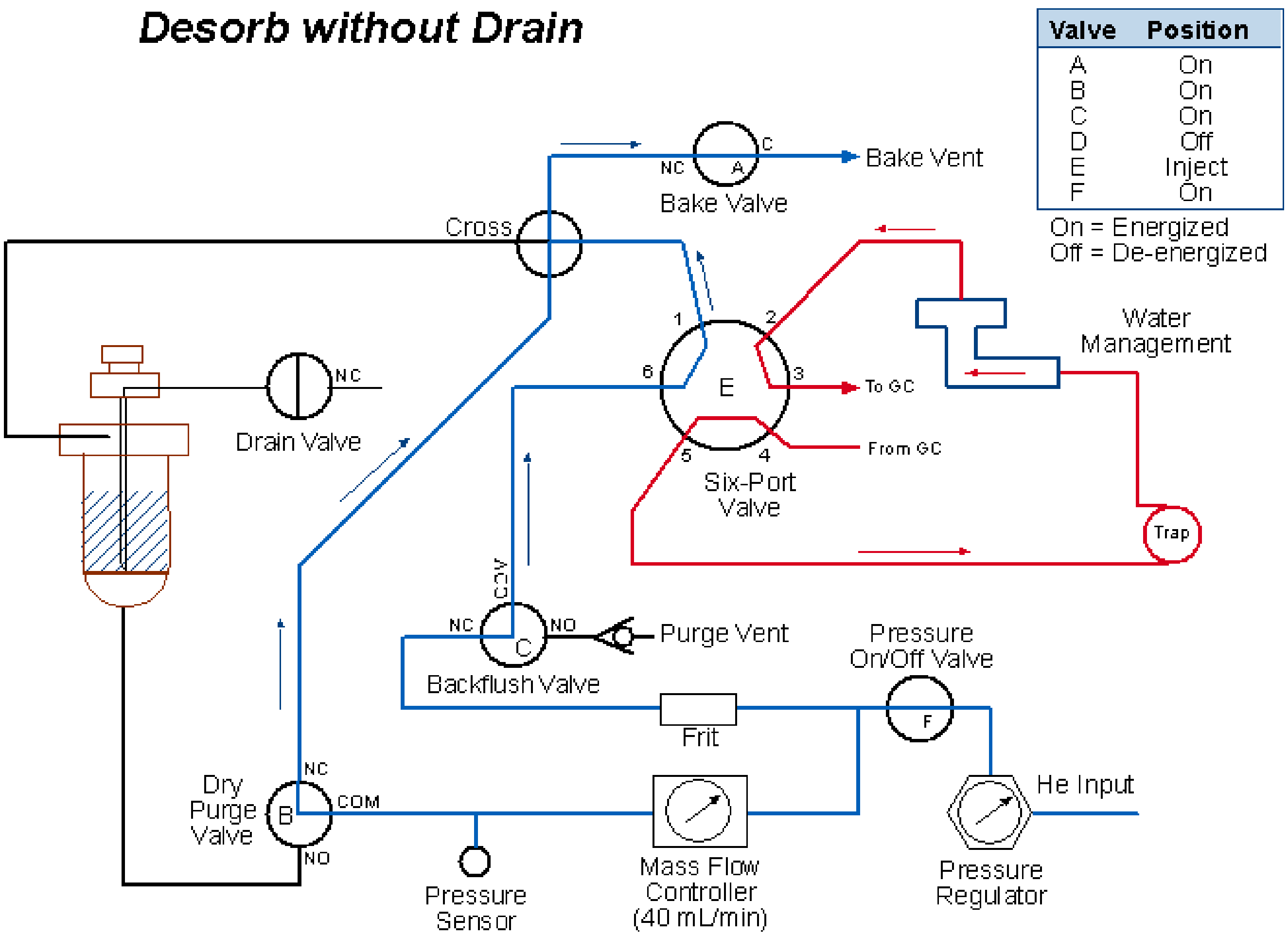


Desorb with Drain

Valve	Position
A	Off
B	Off
C	On
D	On
E	Inject
F	On

On = Energized
Off = De-energized

Desorb Without Drain

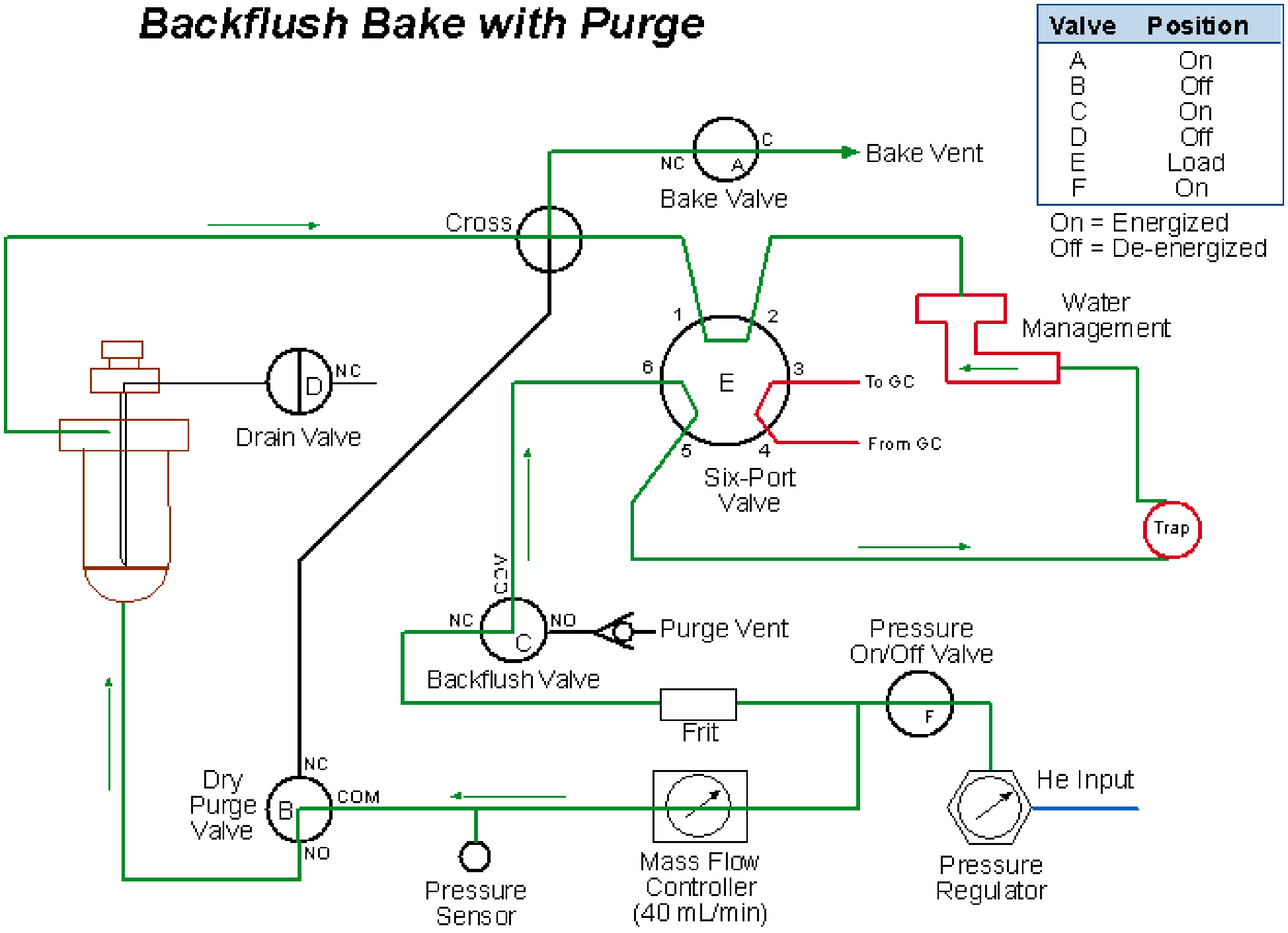


Desorb without Drain

Valve	Position
A	On
B	On
C	On
D	Off
E	Inject
F	On

On = Energized
Off = De-energized

Backflush Bake With Purge

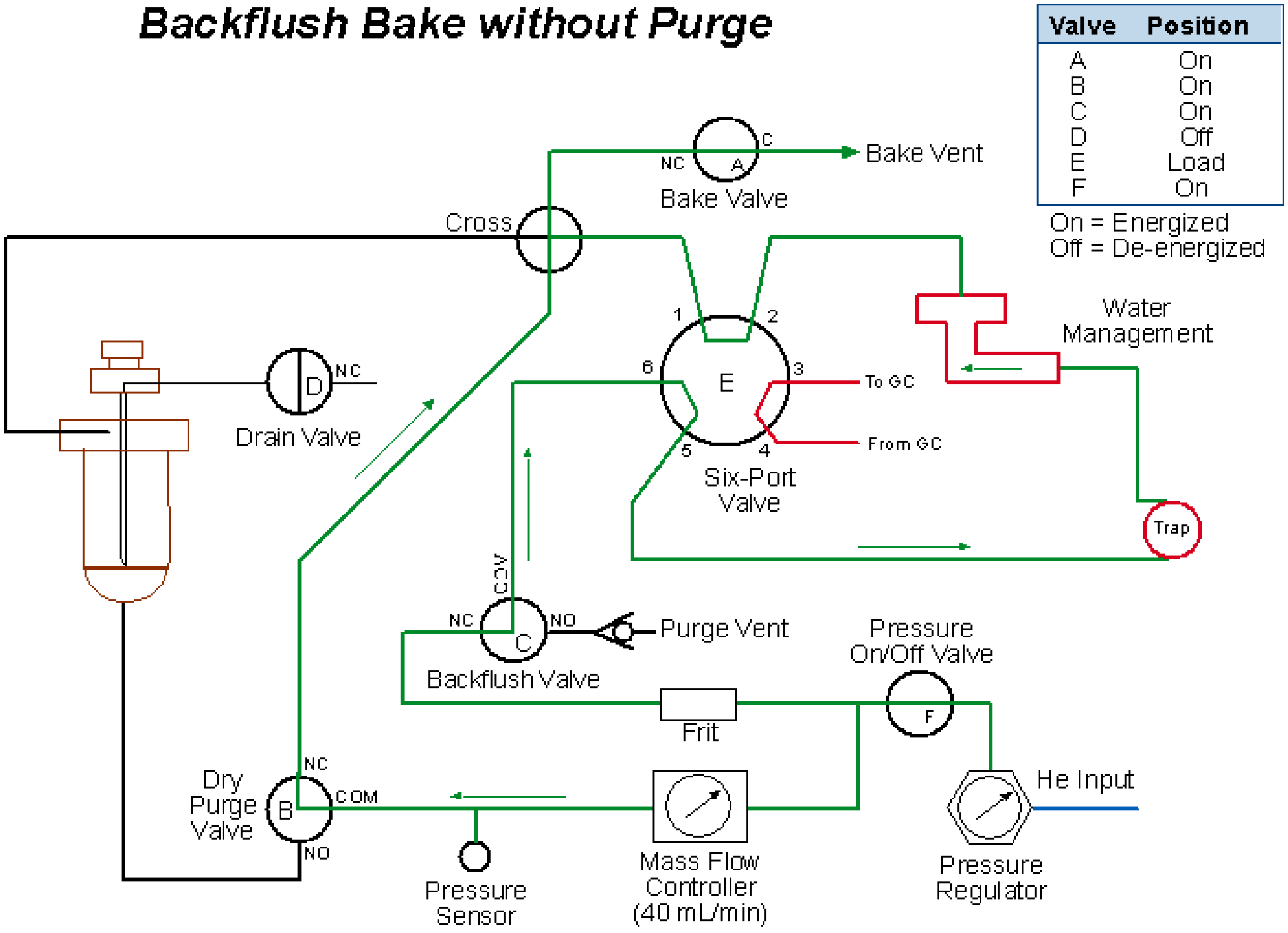


Backflush Bake with Purge

Valve	Position
A	On
B	Off
C	On
D	Off
E	Load
F	On

On = Energized
Off = De-energized

Backflush Bake Without Purge

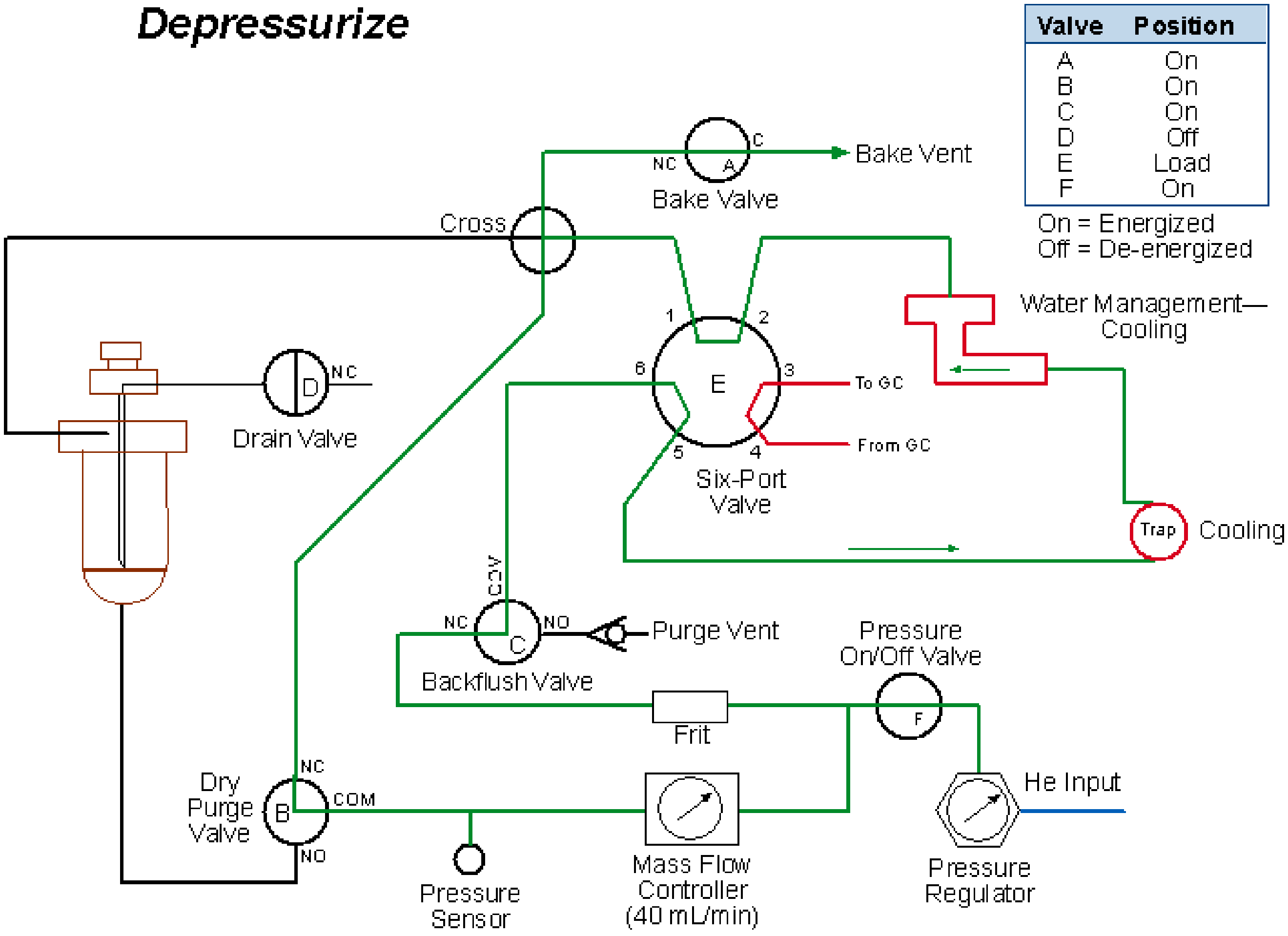


Backflush Bake without Purge

Valve	Position
A	On
B	On
C	On
D	Off
E	Load
F	On

On = Energized
Off = De-energized

Depressurize



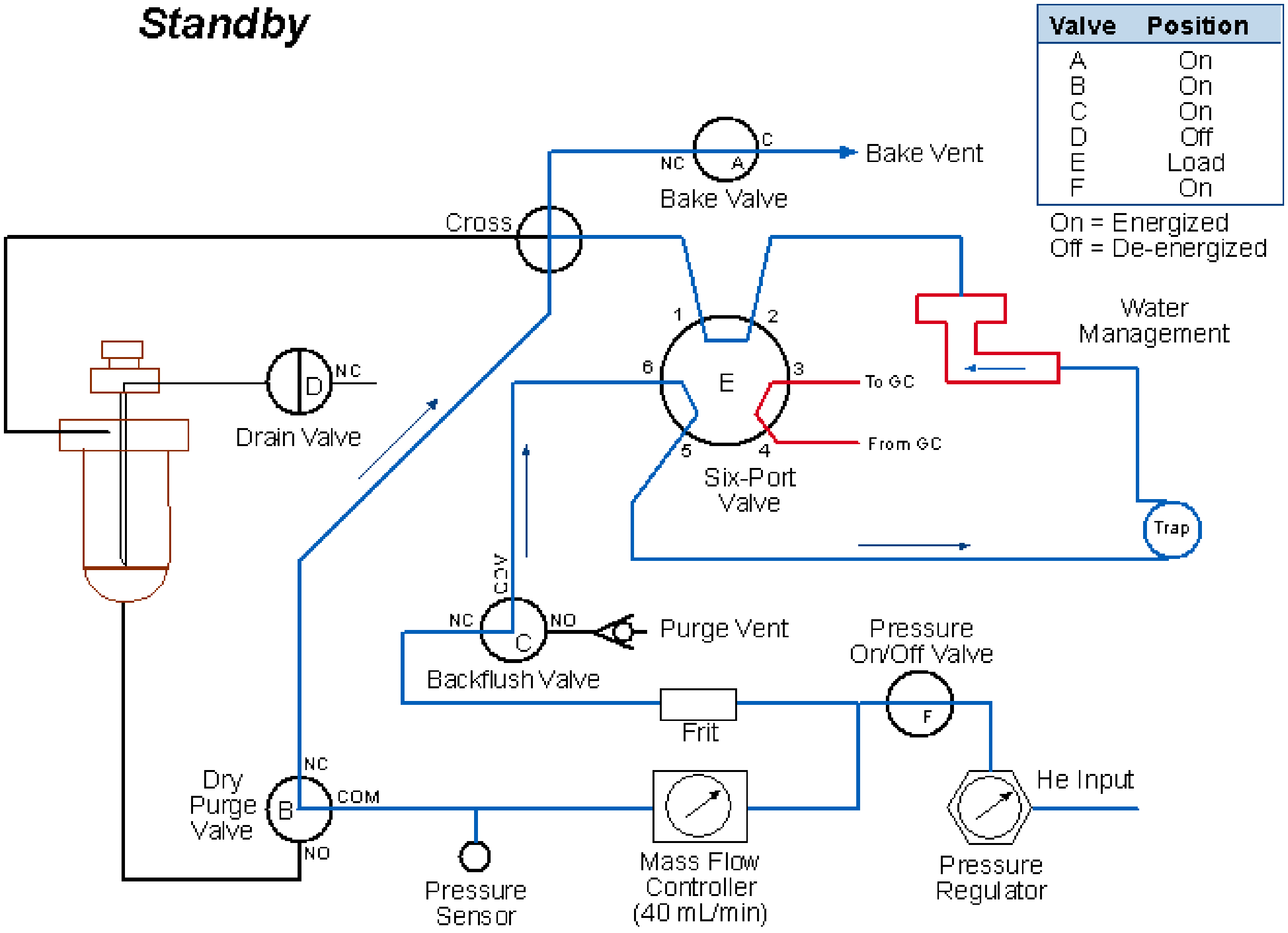
Depressurize

Valve	Position
A	On
B	On
C	On
D	Off
E	Load
F	On

On = Energized
Off = De-energized

Opportunity through Innovation™

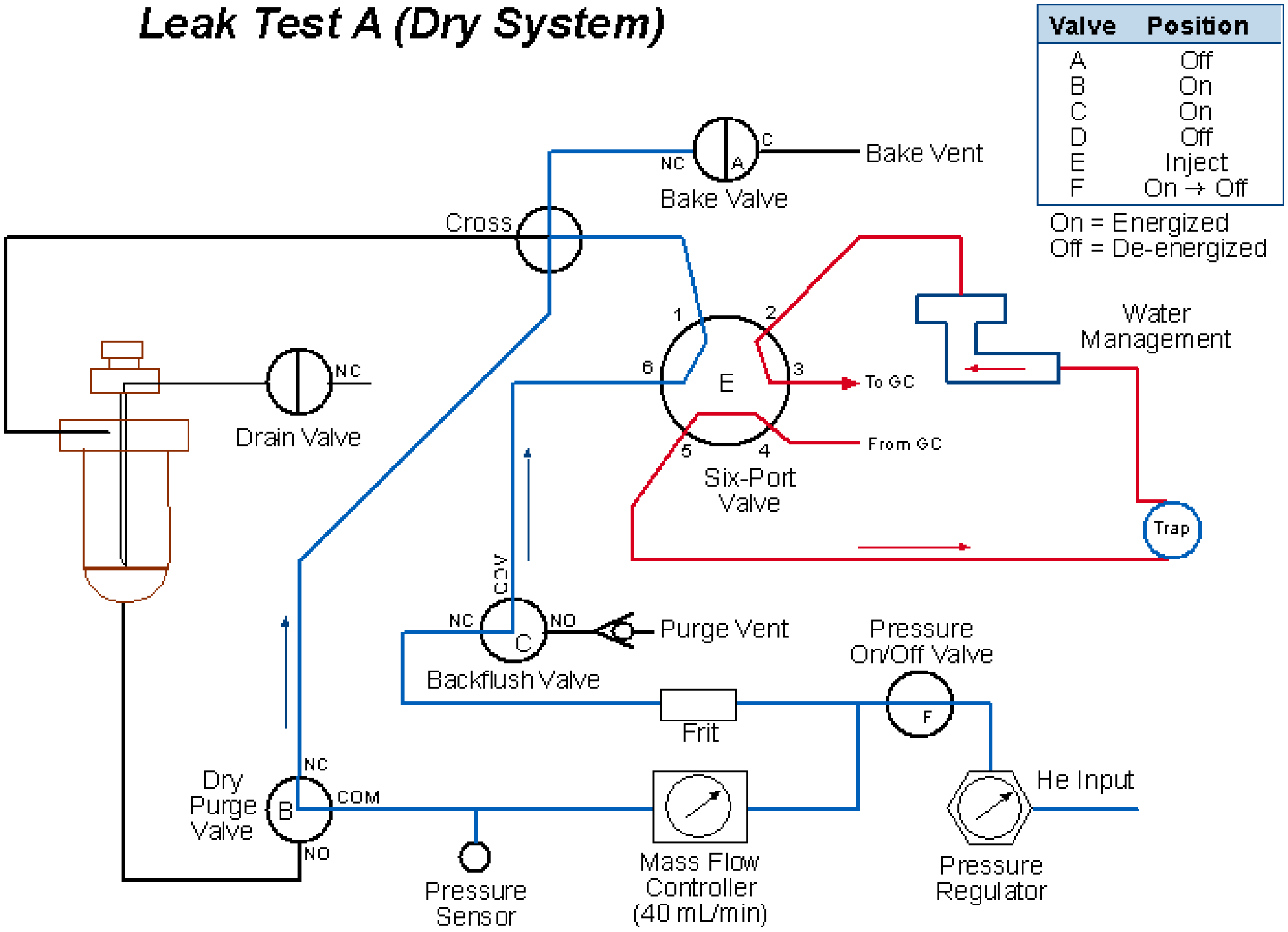
Standby



Valve	Position
A	On
B	On
C	On
D	Off
E	Load
F	On

On = Energized
Off = De-energized

Leak Test A (Dry System)

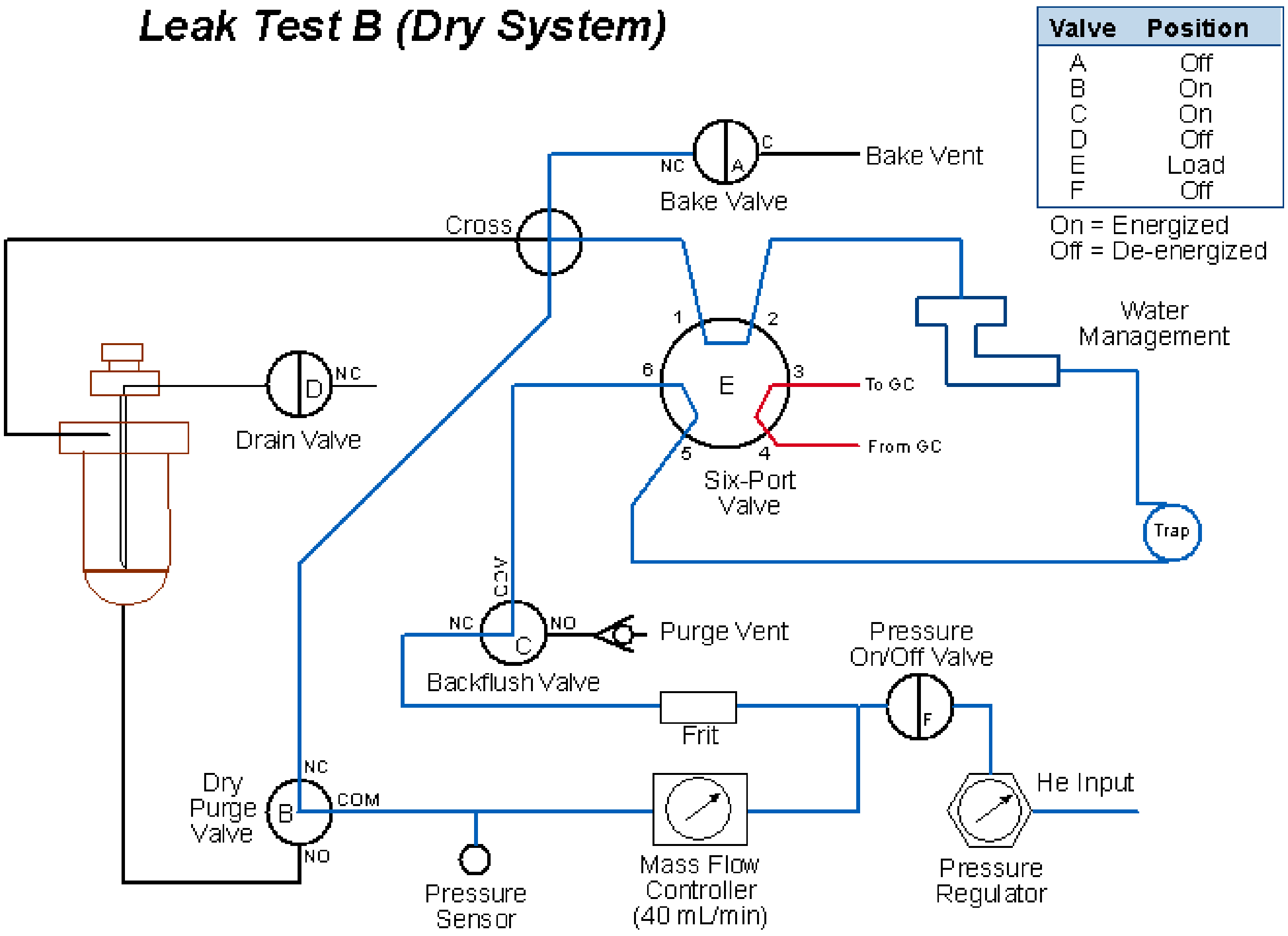


Leak Test A (Dry System)

Valve	Position
A	Off
B	On
C	On
D	Off
E	Inject
F	On → Off

On = Energized
Off = De-energized

Leak Test B (Dry System)

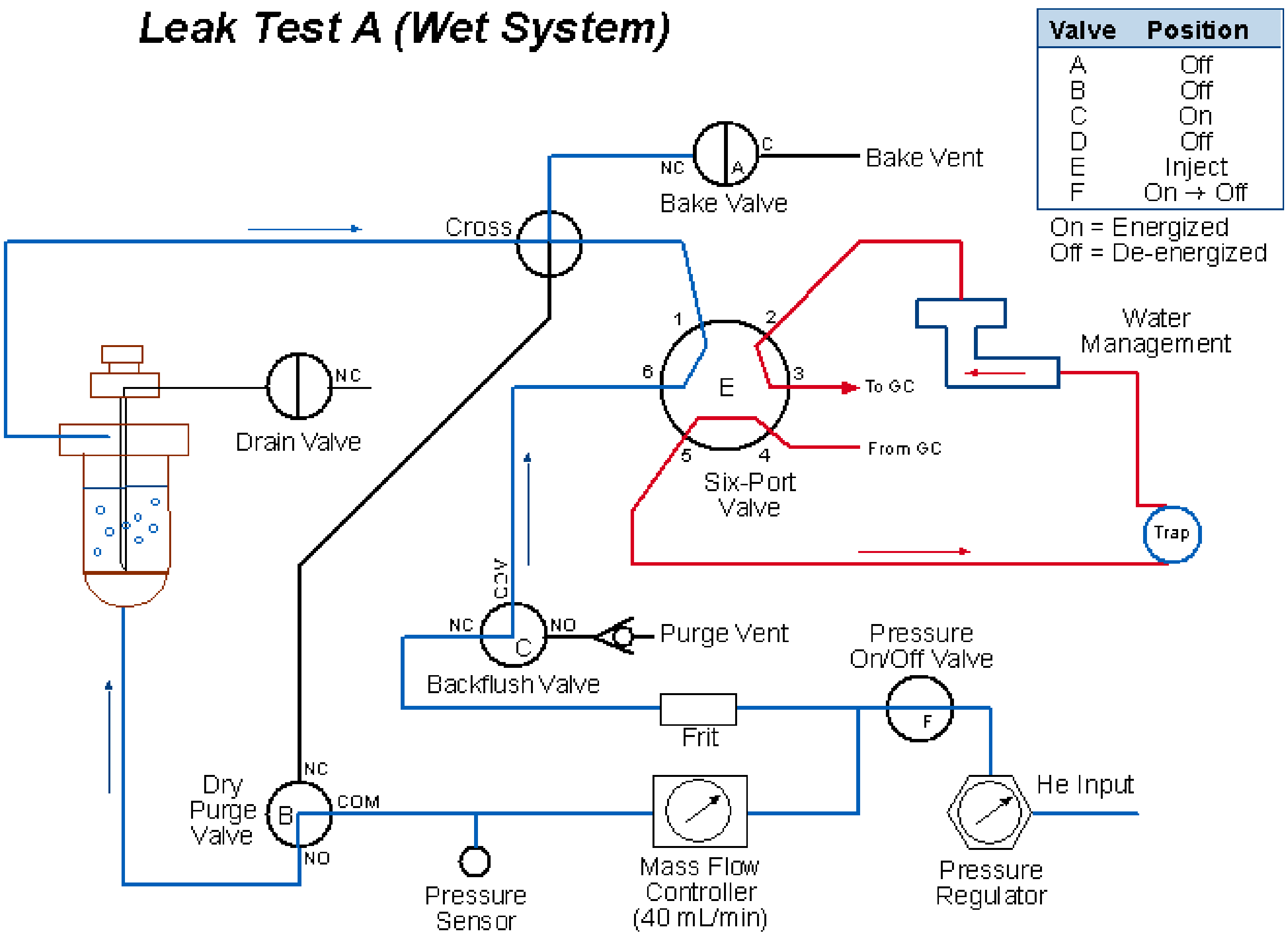


Leak Test B (Dry System)

Valve	Position
A	Off
B	On
C	On
D	Off
E	Load
F	Off

On = Energized
Off = De-energized

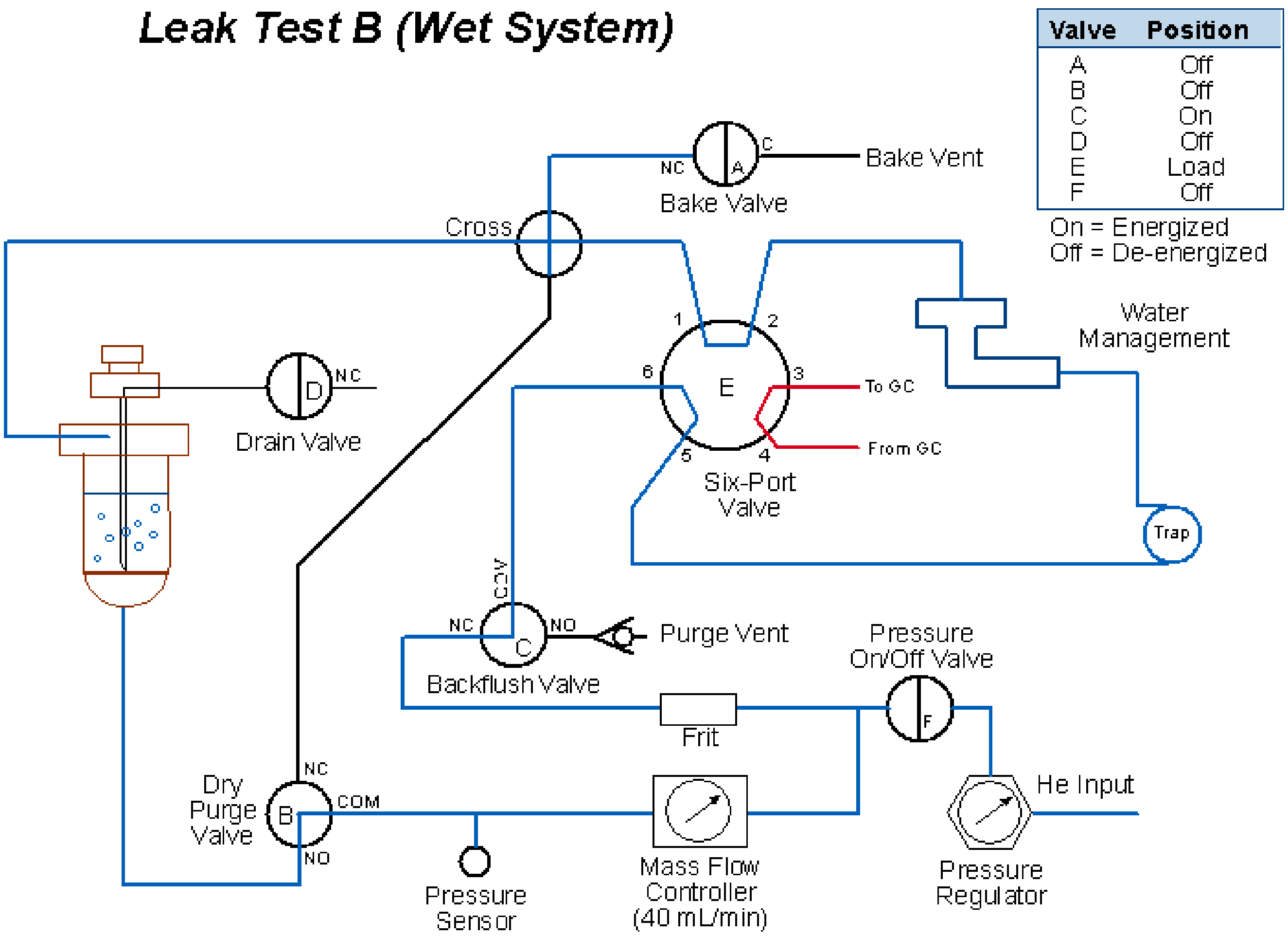
Leak Test A (Wet System)



Valve	Position
A	Off
B	Off
C	On
D	Off
E	Inject
F	On → Off

On = Energized
Off = De-energized

Leak Test B (Wet System)



Valve	Position
A	Off
B	Off
C	On
D	Off
E	Load
F	Off

On = Energized
Off = De-energized

Critical Success Factors in Purge-and-Trap

Critical Success Factors

- Purge (extraction) efficiency
- Trapping efficiency
- Rapid desorption
- Effective water management
  - Especially important for MS
- Minimize carryover
- Automation
- Cycle time

Purge Efficiency

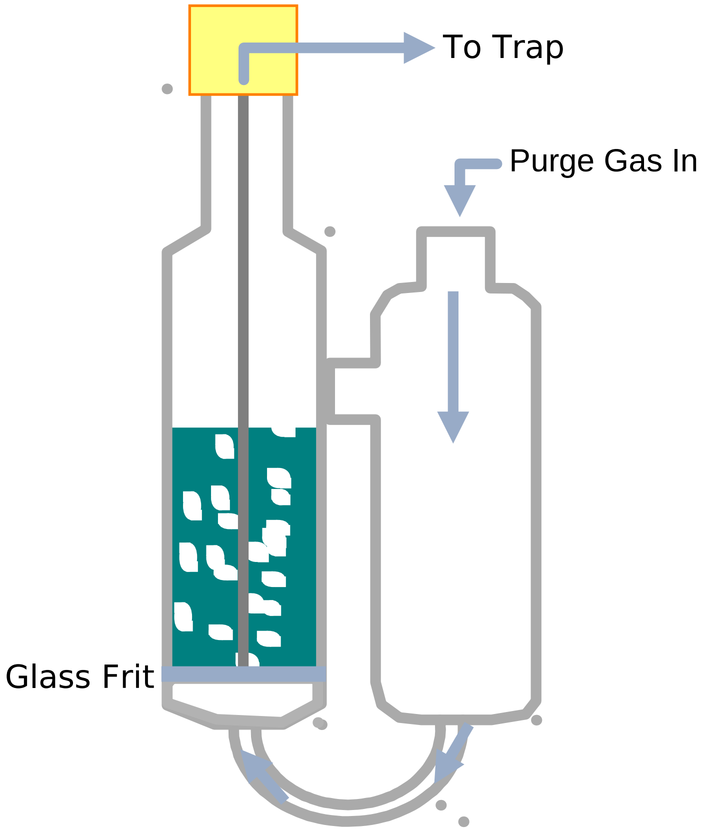
Purge Goal

- Purge (extract) volatile analytes from a sample matrix for concentration on a trap sorbent material with 100% recovery
  - Wide range of VOC compound chemistries
  - Wide range of sample matrix types

Factors Affecting Purge Efficiency

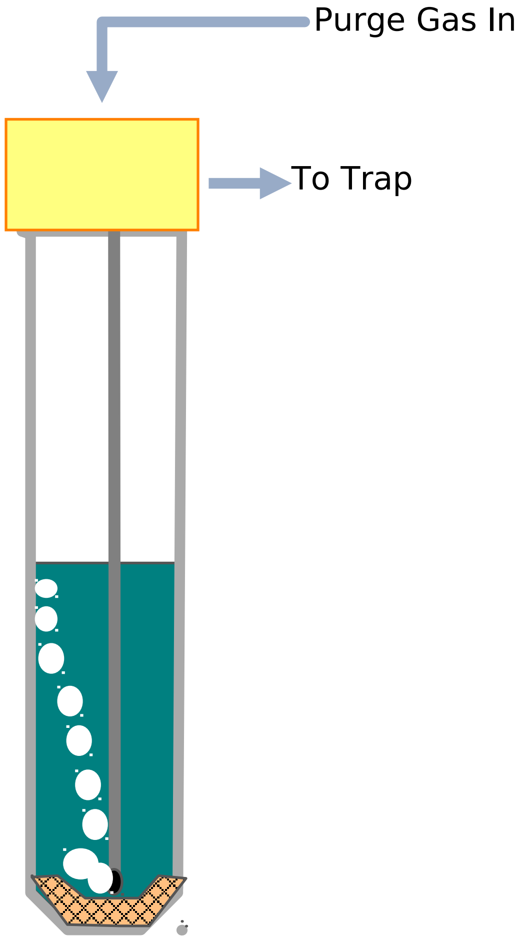
- Extraction volume of the purge gas (usually He)
  - Flow rate and purge time
  - 35-40 mL/min x 11 minutes = 440 mL
  - Too little volume = low recovery of heavies
  - Too much volume = breakthrough of gases
- Type of sparger
  - Needle sparger v. frit sparger
- Sample temperature
  - Ambient adequate for most compounds
  - Heating will improve purge efficiency
  - Some matrices may need more heating

Sparge Option #1



- Fritted sparger – purge gas passes through glass frit
- Advantage
  - Finely divided bubbles
  - Higher purge efficiency
- Disadvantage
  - Difficult to clean

Sparge Option #2



- Needle sparger – purge gas exits from tip of needle
- Advantage
  - Disposable glassware, good for complex or “dirty” samples
- Disadvantage
  - Lower purge efficiency (10-15%)

Sample Heating

Sample Heating Considerations

- Pro: Heating the sample improves purge efficiency for polar, water-soluble compounds
- Con: Heating the sample may transfer additional water to the trap
  - Requires good water management
- Heating techniques vary
  - Sleeve or jacket style heater (Tekmar and EST)
    - Slow
    - Inconsistent heating
  - Infrasparge heater (OI patent)
    - Fast
    - Accurate

To Heat or Not To Heat?

- Heating the sample increases purge efficiency and response of the polar compounds
  - Ketones, ethers, alcohols, nitriles, etc.
  - Method 524 Rev. 4 and 8260 long list
- Whether or not to heat the sample varies from lab to lab
  - Depends on method and interpretation of method
  - Most agencies permit heating the sample

To Heat or Not To Heat? (cont.)

- If sample is not heated, sample temperature can vary significantly with ambient laboratory temperature
  - Especially true if samples are sub-ambient prior to purging
- Gentle heating can assure that all standards and samples are purged at the same temperature
  - Avoids variation in ambient laboratory temperatures
  - Improves calibration %RSD
  - Recommended sample temperature is 40-45°C

Patented Infrasparge™ Sample Heater

- The Eclipse patented sample heater uses infrared light
  - Extremely rapid heating
- The thermocouple is submerged in the sample for precise control
- Jacket-type heaters are slow to heat, poor control of actual sample temperature, and obscure view of the sample during purge

Patented Infrasparge™ Sample Heater

- When in operation the front cover allows an unobstructed view of the sample
- When cover is removed the safety switch opens and heater is disabled
  - Safety feature
- Capable of heating water sample to boiling point
  - (Not recommended)

Trapping Efficiency

Trapping Goal

- Concentrate and focus the VOCs on to an adsorbent material as they are purged from the sample
  - Chromatographic properties of absorption and release

Factors Affecting Trap Efficiency

- Selection of the proper adsorbent for the application
  - Match adsorbent to compound list and concentration
  - Multiple layer traps common
  - Most designed to work with 440 mL purge volume
- Hydrophobic or hydrophilic?
- Operational temperature range
  - Effective at ambient temperatures? Sub-ambient?
  - Analyte release during heating
  - Stable through multiple heating/cooling cycles

Trap Selection

- Some of the original USEPA methods specified Tenax as the trap packing material
  - Dry-purge used to remove water
  - Still used for methods that don’t include the gases
  - E.g. BTEX, THM, VPH, geosmin, etc.
- When the list was expanded to include the light gases silica gel and charcoal were added to the trap
  - Charcoal (or carbon mole sieve) traps only Cl2F2C
  - Silica gel traps chloromethane through Cl3FC
  - Tenax traps everything else
- Cannot remove water from silica gel with a dry-purge
- Because of the hydrophilic nature of silica gel it became necessary to develop a hydrophobic trapping material
  - Supelco VOCARB trap
  - Requires a dry purge step to remove water prior to DESORB

Trap Selection (cont.)

- The VOCARB trap is usually the trap of choice for use with Tekmar and EST concentrators because of its hydrophobic character
- Because OI concentrators employ active water management during DESORB, either the 3-layer trap or the VOCARB trap can be used
- Three traps most commonly used with the OI concentrators are:
  - #7: Tenax only
  - #10: Tenax, silica gel, carbon mole sieve
  - #11: VOCARB

Trap Selection (cont.)

- The #10 and #11 traps each have advantages and disadvantages
- Both traps will work very well in the Eclipse and both are supported by OI
- Individual users may have a preference for one or the other

The #10 (3-Layer) Trap

Advantages	Disadvantages
Longer lifetime	Peak shape of 1st 6 gases is slightly broader than on the #11 trap
Lower temperatures • 20°C at purge • 180°C at desorb preheat • 190°C at desorb • 210°C at bake	First peak may tail slightly
Faster cool-down and shorter cycle time	NOTE: Even though the peak shape is slightly broader on the #10 trap, the peaks are very symmetric and extremely reproducible. This results in reliable, long-lasting calibrations.
Consistent response	
Higher response in 2nd ½ of the chromatogram	
Good trap-to-trap reproducibility	

The #11 (VOCARB) Trap

Advantages	Disadvantages
Hydrophobic character aids water management	Shorter overall lifetime
Excellent peak shape and baseline resolution of 6 early eluting gases	Higher temperatures* •20°C at purge • 230°C at desorb preheat • 240°C at desorb • 250°C at bake
	Longer cool down and longer cycle times
	Need to use dry purge can lead to longer cycle times
	Lower response in 2nd ½ of the chromatogram
	Poor trap-to-trap reproducibility

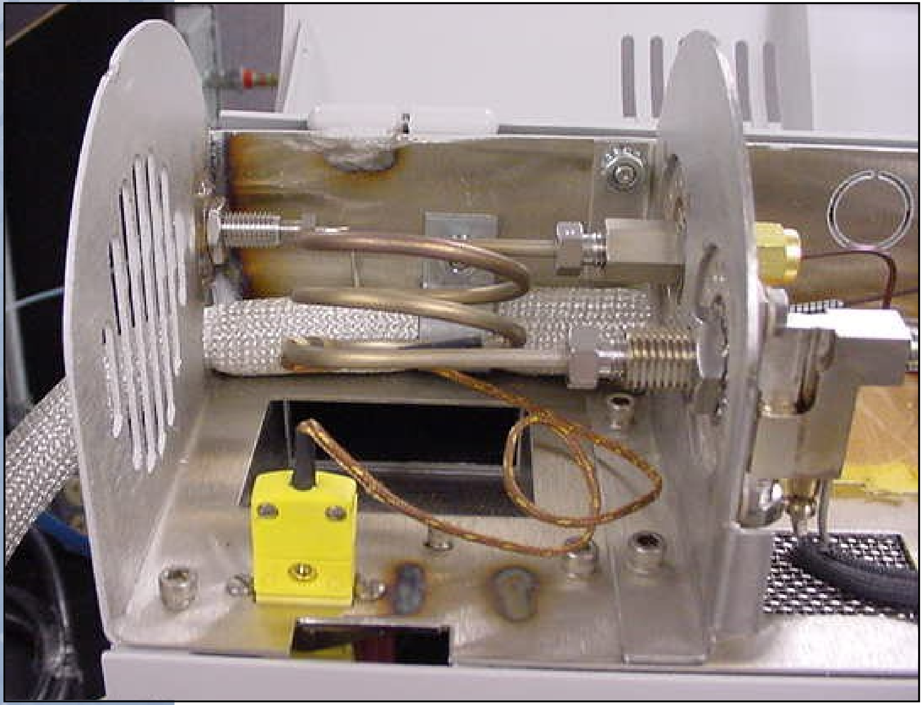
*Temperatures shown here are recommended for the Eclipse.
Other sample concentrators may require higher settings.

Indirect Trap Heating

- Some P&T instruments employ indirect trap heating
  - Sleeve or jacket
- Several drawbacks
  - Inconsistent heating, TC is in the sleeve, not at the trap
  - Slow heating rate of ~300-400°C/minute
  - Longer cool-down times due to the insulation (sleeve) around the trap

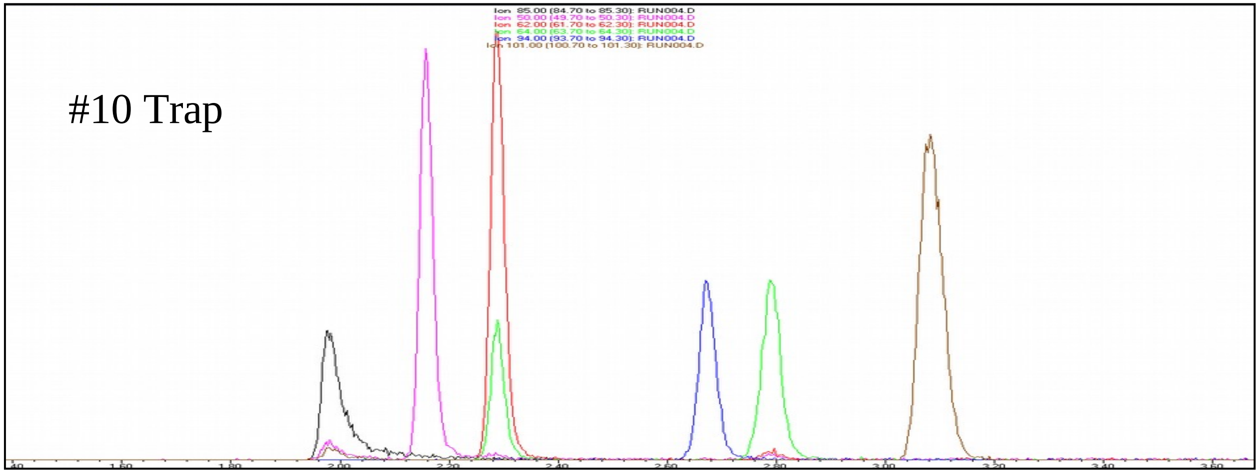
Direct Resistive Trap Heating

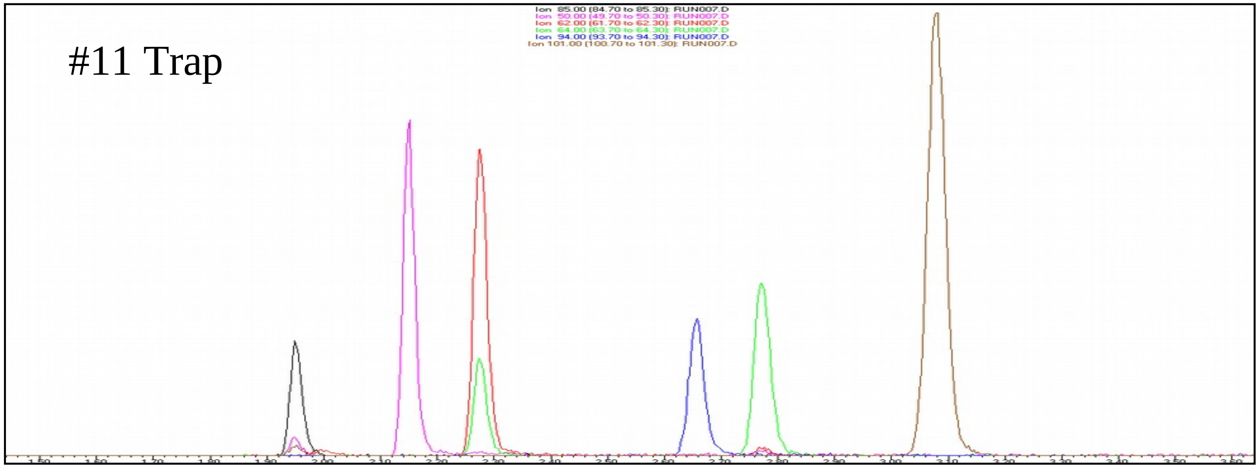
- ~20 years ago, OI introduced patented direct resistive trap heating
- Switch turns off power when cover is open



- SS trap electrically isolated
- Current applied directly to the trap
- Thermocouple controls temperature of the trap (not the sleeve)
- Fast heating rate, 900-1100°C/ minute
- Accurate, reproducible heating
- Faster cool down
- Shorter desorb times

Chromatography of the Gases


#10 Trap


#11 Trap

Why Are Some Peaks Broader?

Purge Flow → #10 Trap ← Desorb Flow

Tenax®

Silica Gel

Charcoal

Most VOCs trapped on Tenax layer

5 gases trapped on silica gel

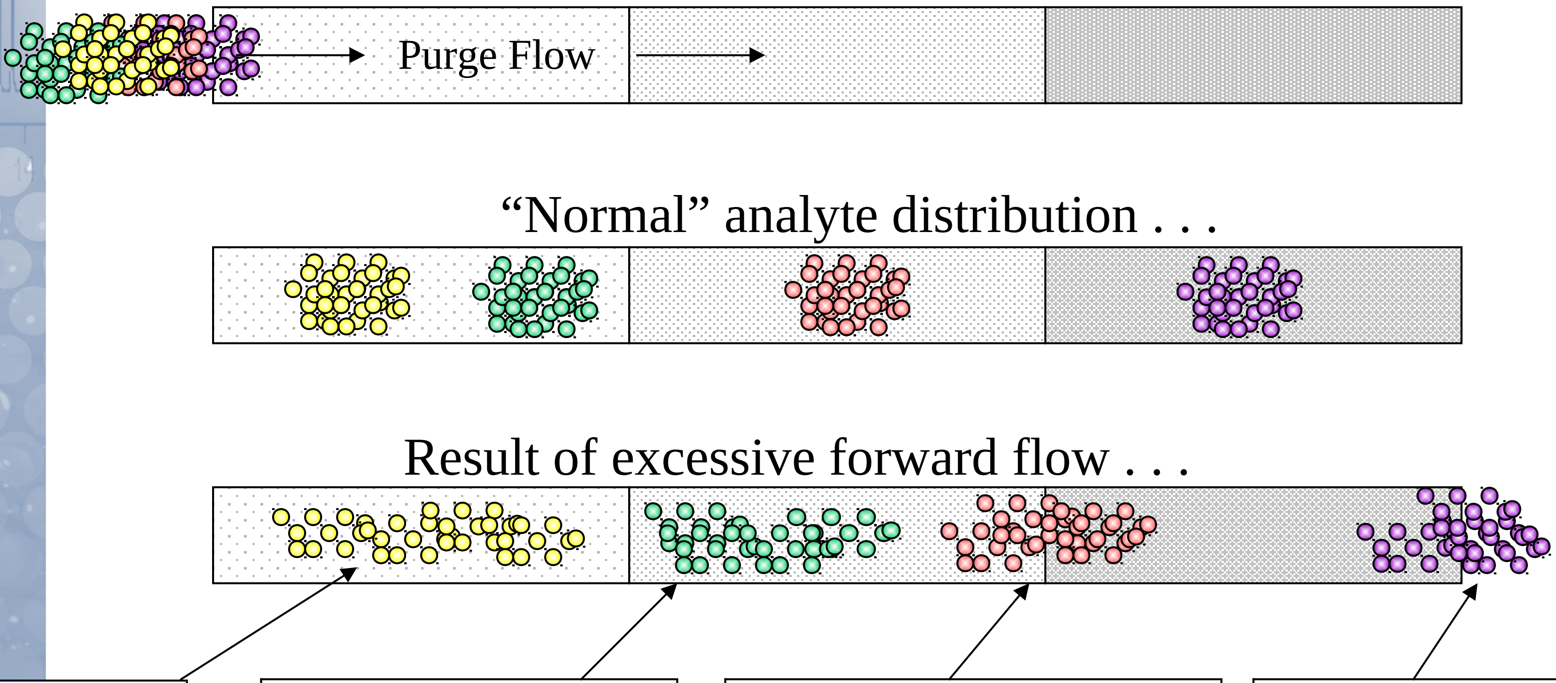
Freon 12 trapped on charcoal

- Most compounds are trapped on the Tenax and always have very sharp chromatography
- Five gases are trapped on the silica gel (with the H2O) and one is trapped on the charcoal
- During desorb the gases must pass through multiple layers, and this causes them to broaden slightly
- It can also cause the Freon 12 to develop a tail

Additional Trap Considerations

- All commercially prepared traps are designed to work with a fixed volume of purge gas
  - 40 mL/min x 11 minutes = 440 mL purge gas
- Hydrophobic materials use dry-purge to remove water
  - Tenax, VOCARB, etc.
- When using the dry-purge step the additional forward flow volume through the trap can cause problems
- High flow rates or elevated trap temperatures during the dry-purge step will magnify this problem
  - Even moderate heating of the trap during dry-purge to assist with water removal will cause the volatile components to migrate forward through the trap packing material
- Best overall performance is achieved when no dry-purge is used

Common Trap Problems



"Normal" analyte distribution . . .

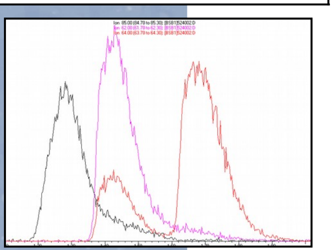
Result of excessive forward flow . . .

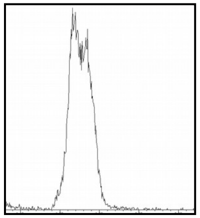
Band-broadening = poor peak shape

Stronger adsorbent = carryover

Straddling 2 adsorbents = split peaks

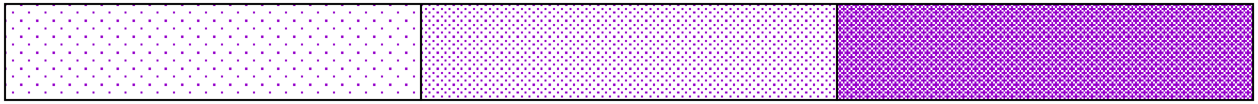
Breakthrough = low recovery





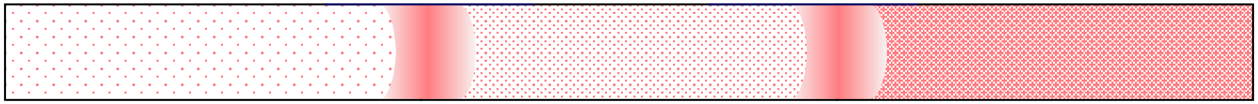
Additional Trap Considerations

“Normal” adsorbent packing . . .

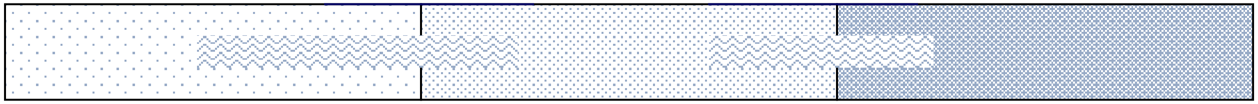


High flows or pressure pulses in opposite directions
can cause additional trap degradation, such as . . .

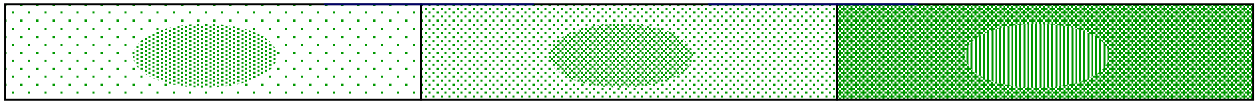
1. “Blurring” of the adsorbent interface



2. Channeling



3. Inconsistent or too tight packing in spots



Trap Performance Factors

- The VOCARB trap requires a dry-purge step to remove water
  - May push analytes onto more adsorbent packing
  - Harder to remove during desorb & bake = carryover
- Instrument designs, such as the Tekmar Velocity, that use high flow rates and/or elevated trap temperatures during dry-purge will tend to magnify this problem
- OI 4560 & Eclipse do not require dry-purge or elevated flow rates

Water Considerations For The Trap

- During purge, water from the sample passes onto the trap (hydrophobic or hydrophilic)
  - Unavoidable, common to all purge-and-trap
  - Requires effective approach to water management
- Disadvantages
  - Populates sites potentially excluding analytes
  - Can cause poor focusing of water-soluble compounds
  - Can interfere with chromatography
- Advantage
  - Flash vaporization can aid transfer to GC column

Desorb Efficiency

Desorption Goal

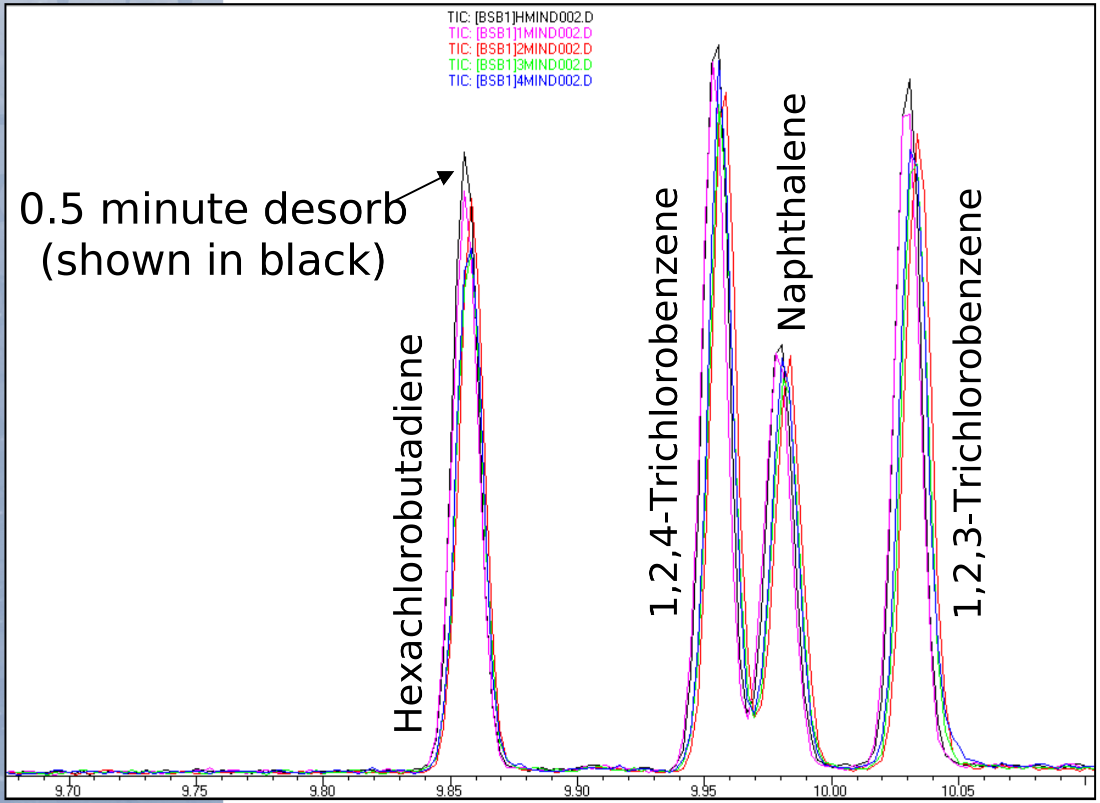
- Rapid release of analytes from the adsorbent material and transfer to the head of the GC column in a tightly focused band

Factors Affecting Desorption Efficiency

- Trap heating technique
  - Direct v. indirect heating
- Trap heating rate
  - Narrow, focused bandwidth
- Release of analytes from adsorbent
  - 100% recovery, minimize memory effect
- Desorb flow rate
  - Controlled by column flow rate and split ratio
- Water management

High Recovery With Short Desorb Times

- Overlaid chromatograms of the 4 heaviest peaks using desorb times of 4, 3, 2, 1, and 0.5 minutes.



The 4 heaviest compounds had ~100% recovery with a ½-minute desorb

#10 Trap

45 mL/min flow

½-min desorb

Additional Desorb Considerations

- Any P&T will transfer some H_2O to the GC during the entire length of the desorb period
- Depending on the GC column and detector used, excess water can affect peak shape, resolution, and sensitivity
- It is important to use the shortest desorb time possible to minimize H_2O transfer
  - Desorb time of ½ minute can be used with the Eclipse due to direct trap heating
  - All analytes are desorbed in the first 10-15 seconds
  - After all analytes are desorbed, the only thing transferred to the column is WATER!

Bake Efficiency

Bake (Reconditioning) Goal

- Complete release of remaining analytes or matrix contaminants from the trap prior to analysis of the next sample
  - Other system components also cleaned (rinsed or flushed) during this step

Factors Affecting Bake Efficiency

- Rapid, accurate heating of the trap to a given temperature
  - Temperature depends on adsorbent type
- Time held at that temperature
  - Complete release of contaminants
- Minimum gas flow
  - Flush contaminants from the sample pathway as they are released

Water Management

Traditional Water Management

- Some traditional approaches to water management include:
    - Don’t heat the sample
        - Can lead to poor recoveries for water soluble compounds and higher %RSDs
    - Hydrophobic trap material (e.g. VOCARB or Tenax)
    - Dry-purge to blow the H_2O off of the trap
        - Additional gas volume can cause poor trap performance
        - Increases cycle time
    - Short desorb time
    - High split ratio
    - Adsorbent trapping of the H_2O during purge
        - E.g. Velocity’s dry flow moisture trap
        - Poor performance of polar compounds
    - Cold trap H_2O during desorb
        - OI’s patented water management fitting (WMF)
- Most P&T designs use a combination

OI’s Approach to Water Management

- Use a short desorb time to minimize amount of H2O transferred to the GC column
  - ½-minute is all that is needed
  - Also shortens cycle time
- Use a high split ratio with a short column
  - 30-meter column and 35:1 split
  - 20-meter column and 100:1 split
- Heat the sample for best recovery of all analytes, especially the polar compounds
  - Calibration %RSDs usually <10%
  - Best temperature is 40-45°C
- Don’t use a trap that requires dry-purge, as that will just lengthen the cycle time
- OI patented water management fitting (WMF)

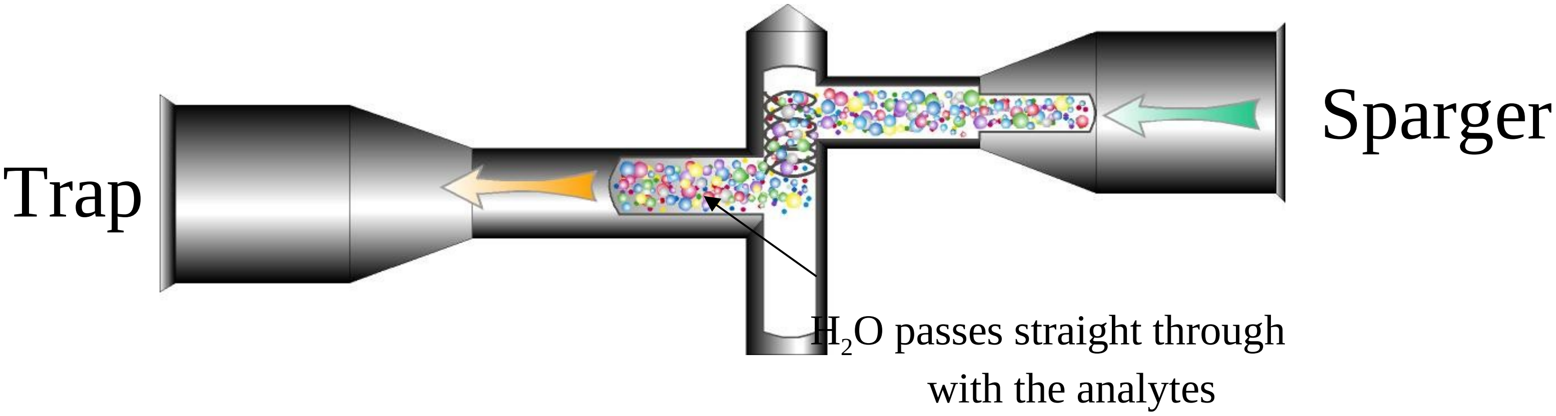
Cyclone Water Management

Patented Water management Fitting

Heater and thermocouple

Cyclone Water Management - PURGE

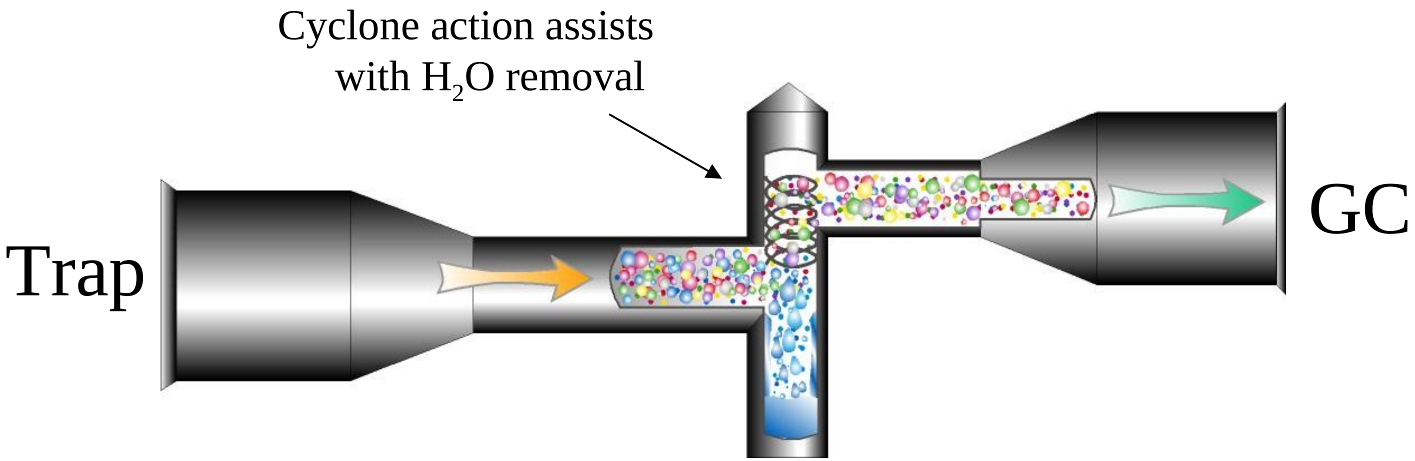
- WMF is in line before the trap
- The WMF is held at 110°C and H2O passes through it, onto the trap, along with the analytes



H_2O passes straight through with the analytes

Cyclone Water Management - DESORB

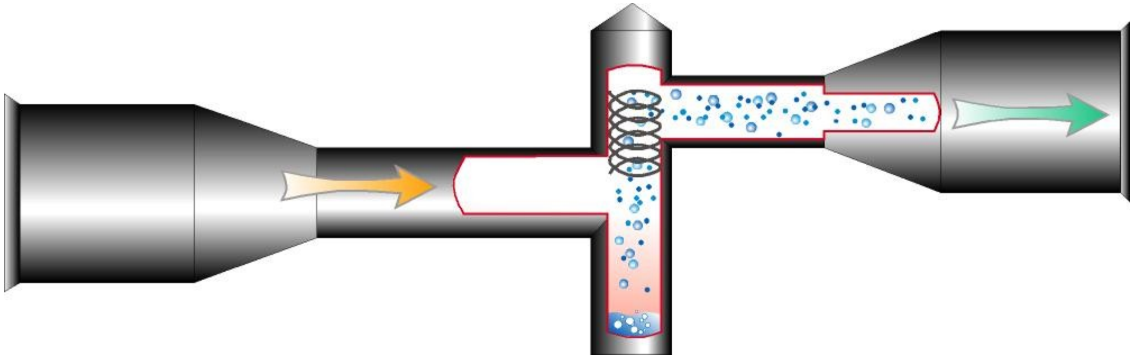
- The WMF is cooled to ambient laboratory temperature and the H2O is “cold trapped” as the analytes are transferred to the GC column



Cyclone Water Management - BAKE

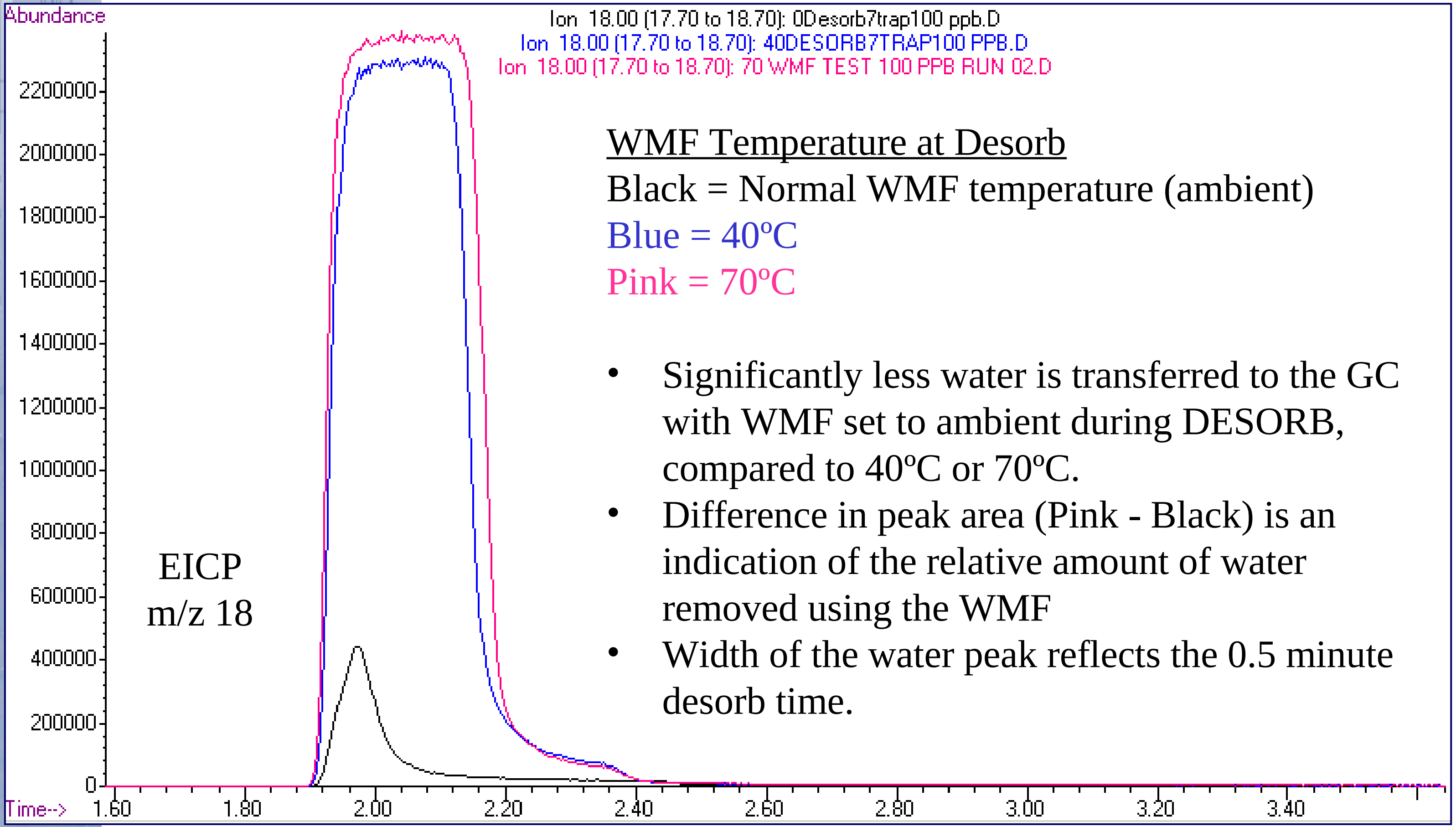
- The WMF is heated to 240°C and the trapped H2O is vaporized and removed through the vent

During bake the WMF is prepared for the next sample



To Vent

Water Removed During DESORB



<u>WMF Temperature at Desorb</u>

Black = Normal WMF temperature (ambient)

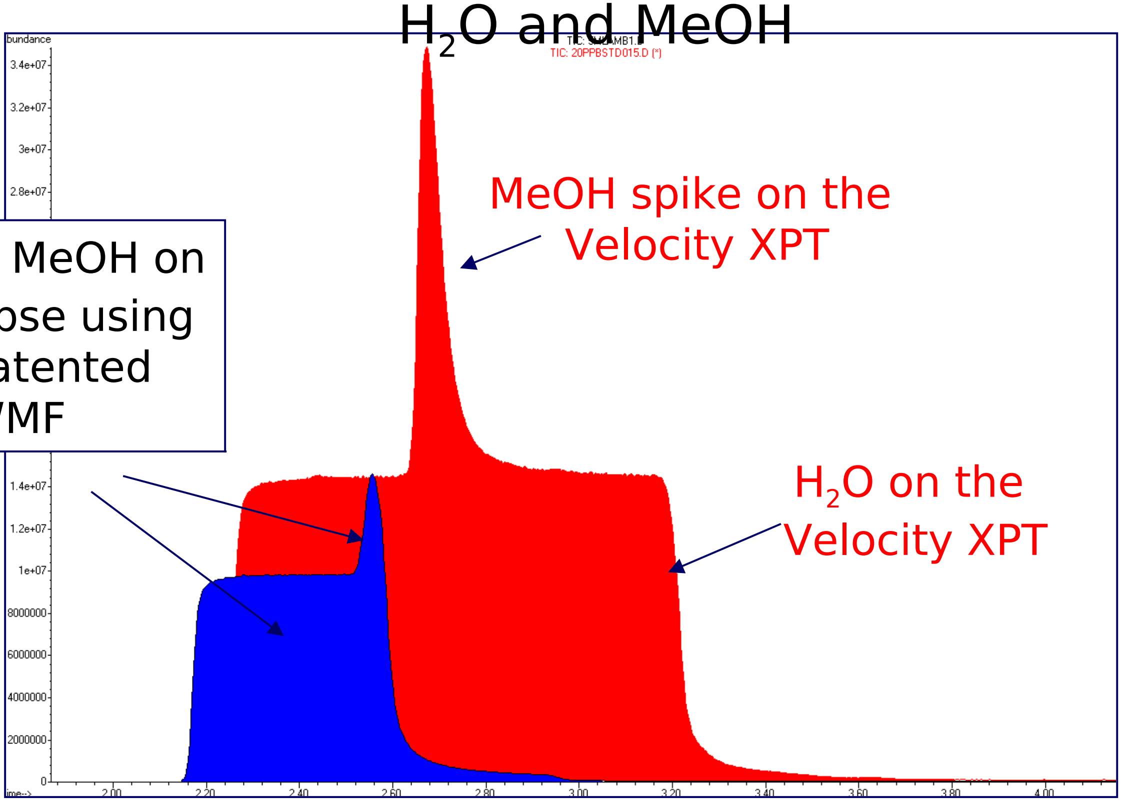
Blue = 40ºC

Pink = 70ºC

- Significantly less water is transferred to the GC with WMF set to ambient during DESORB, compared to 40ºC or 70ºC.
- Difference in peak area (Pink - Black) is an indication of the relative amount of water removed using the WMF
- Width of the water peak reflects the 0.5 minute desorb time.

H_2O on the Eclipse & Velocity

5 mL of a mid-point standard purged at ambient temperature and scanned to monitor H_2O and MeOH

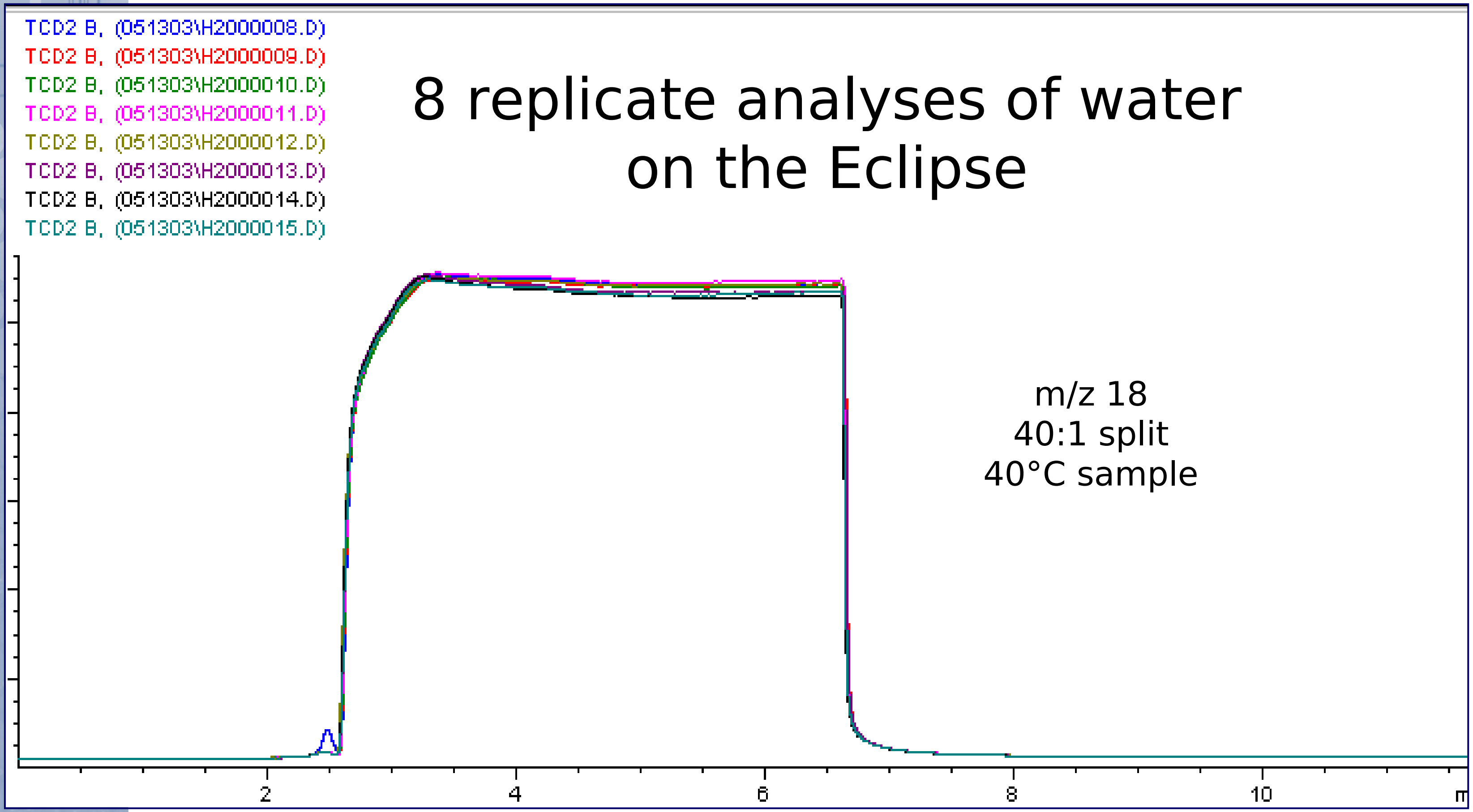


MeOH spike on the Velocity XPT

H_2O and MeOH on the Eclipse using the patented WMF

H_2O on the Velocity XPT

Repeatability



8 replicate analyses of water
on the Eclipse

m/z 18
40:1 split
40°C sample

References

- “Optimizing the Analysis of Volatile Organic Compounds”, Chris English, available from Restek
- “Helpful Hints for Analyzing Volatile Organics”, Chris English, available from Restek
- “A Guide to Environmental Analytical Methods”, Genium Publishing Corporation

Thank you for your attention.
Q&A