Alloway
Your Resource for Defensible Data

Advanced Instrumentation

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Total Organic Carbon (TOC)
Dissolved Organic Carbon (DOC)

- TOC – carbon bound in organic compounds
- Non-specific indicator of water quality
- Comes from natural organic matter (NOM)
  - Humic acid
  - Fulvic acid
  - Amines
  - Urea
- Comes from synthetic sources
  - Detergents
  - Pesticides and Herbicides
  - Fertilizers
  - Chlorinated Organics

Total Organic Carbon (TOC)
Dissolved Organic Carbon (DOC)

- TOC provides estimate of NOM in source water
- Chlorinated Disinfection Byproducts (DBP's)
  - Created when active chlorine compounds react with NOM in source water
- Higher levels of NOM = Higher level of carcinogens in processed drinking water

Total Organic Carbon (TOC)
Dissolved Organic Carbon (DOC)

- TOC Analysis
  - Measures Total Carbon (TC)
  - Measures Inorganic Carbon (IC)
  - TOC = Difference
    - TC-IC = TOC
- Non-purgeable Organic Carbon (NPOC)
  - Purge acidified sample
    - Nitrogen or carbonless air
  - Remove IC first
  - Measure remaining carbon

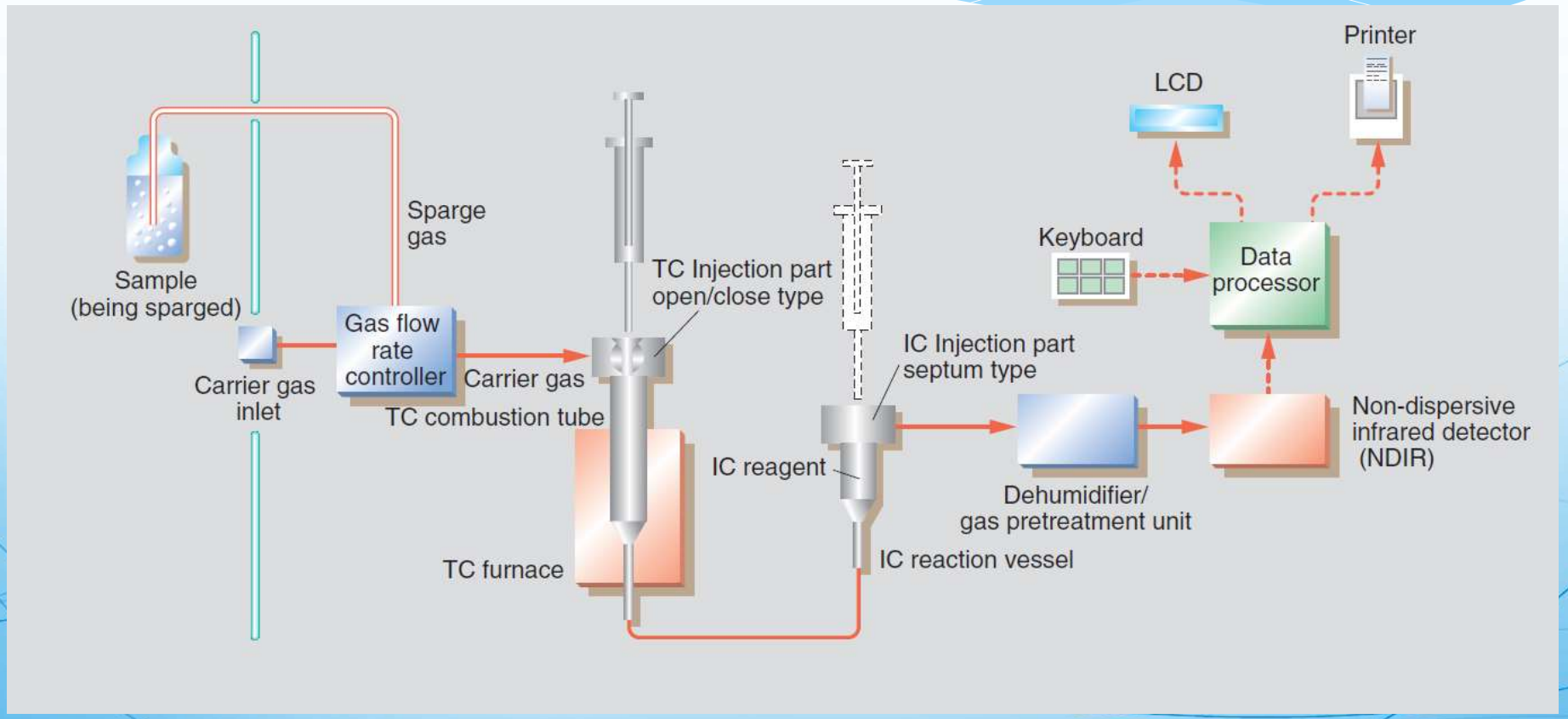
Total Organic Carbon (TOC)
Dissolved Organic Carbon (DOC)

- 5310B is a method of detecting organic carbons in both drinking and waste waters
- TOC and DOC have a PQL of 0.7 mg/L
- A MDL of ~0.1 mg/L

TOC and DOC: How it Works

- TOC and DOC are analyzed by injecting the sample into a heated chamber with a catalyst.
  - 680 ˚C combustion chamber
- The catalyst causes the water to be vaporized
- The organic carbon is oxidized into CO_2 and H_2O.
- The CO_2 is transported by carrier gas to detector
- CO_2 is measured by a non-dispersive infrared analyzer.

TOC and DOC: How it Works



TOC and DOC: Sample Preparation

- Sample preparation is fairly straight forward for this method
  - All samples must be preserved with 50% H_2SO_4 to reach a pH <2
  - Samples for DOC come to the lab unpreserved and are filtered by the analyst then preserved with 50% H_2SO_4 to reach a pH <2
  - Sample pH is checked at log in and again bench side by the analyst to insure the pH is <2. The pH is so important in this test because a pH >2 can yield false positives.

TOC and DOC: Maintenance

- Daily Maintenance includes:
  - Checking the water levels in the humidifier and drain pot
  - Check O-rings on the top of the combustion chamber
  - Make sure all line are rinsed and clean sample syringe with DI water and a Q-tip
  - Check sample syringe for air bubbles
  - Fill rinse container with DI water
  - Check oxygen tank and regulator

TOC and DOC: Time and Costs

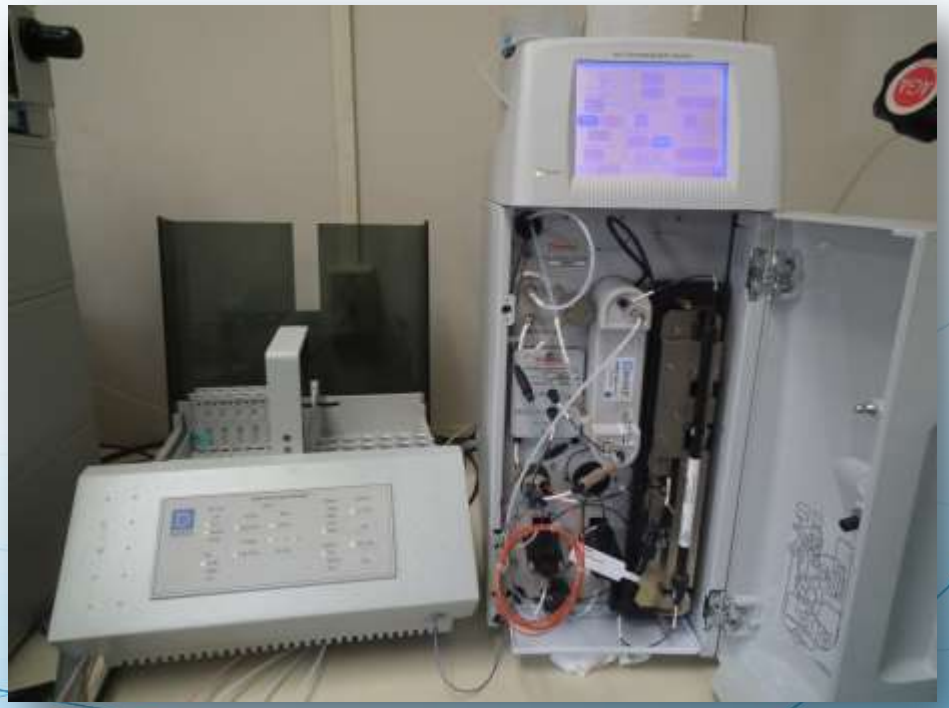
- The average run of 30 samples and all necessary QC takes ~16 hours to run on the instrument not including prep time
- The average run is ~35% QC
- Each sample is injected 3-5 times in order to obtain results

Ion Chromatography (IC)

- A process of separating ions and polar molecules
- Used for methods
  - 300.0
  - 300.1
  - 300.1 UCMR3
  - 314
  - 218.7, 218.6

IC: How it works

- The sample is carried through the sample loop by the mobile phase and is injected onto the column
- The ions are separated in the column and are eluted at different times based on the mobile and stationary phases
- The separated ions then pass through some form of detector and the software turns that signal into a concentration value.



IC: Sample and Instrument Preparation

- All samples are filtered prior to analysis to prevent clogging of lines and columns
- Fresh eluent is made daily for analysis

IC: Interferences

- As with every method there are common interferences that must be addressed by the analyst. Some of the interferences for the IC are:
  - Matrix
  - Tailing caused by other ions
  - Coinciding retention times
  - Oxidation/Reduction
  - Glassware contamination
  - Particles clogging and/or damaging columns and flow systems

IC: Maintenance and Time

- Check for leaks daily
- Watch and record system pressure
- Replace or service parts
- Check flow rates regularly during analysis
- Flush lines and columns to prevent build up
- Depending on the method, it takes 20-45 minutes to run one sample
- After analysis, lines and column must be flushed for ~30 minutes to prevent build up
- Approximately 40% of analysis time is QC work
- Column, Guard Columns, and Suppressors are replaced biannually

1C: MDLs and PQLs

- 300.0
  - The PQL is 2.0 mg/L and the MDL is ~0.4
- 300.1
  - Depending on the ion the PQL is between 5 and 10 µg/L, with an MDL between 0.3 and 2.2
- 314
  - Has a PQL of 1.0 µg/L and a MDL of ~0.2
- 218.7, 218.6
  - Has a PQL of 0.05 µg/L and a MDL of ~0.02

High Pressure Liquid Chromatography (HPLC)

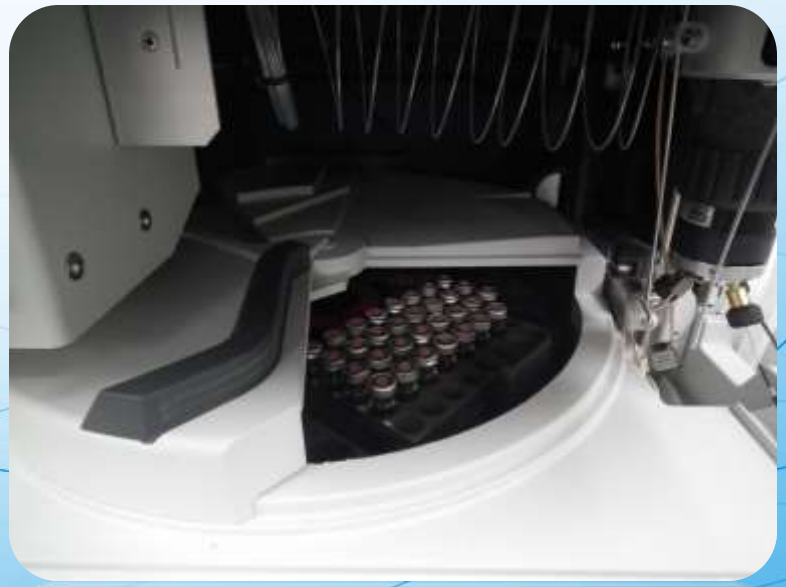
- The HPLC is used for methods:
- 531.2
  - PQLs are 0.5 µg/L, MDLs vary between the 12 compounds
- 547
  - PQL is 6.0 µg/L, MDL is ~1.0
- 549.2
  - PQL is 0.4 µg/L, MDL is ~0.2 µg/L

HPLC: How it Works

- The sample is injected onto the column where it is then mixed with the mobile phase
- Depending on the characteristics of the column and mobile phase the sample is separated
- As the separated sample elutes off the column it is mixed with post column reagents that make it detectable by a fluorescence detector
- The detector then transmits the signal to the software where the area under the peak is converted to a concentration value

HPLC: Sample Preparation and Time

- Samples are filtered and loaded on the auto sampler, dilutions being made when necessary
- Sample preparation is relatively short, but analysis time is significant
  - 547 take 30 minutes per sample
  - 531.2 takes 1 hour per injection
    - Initial QC and equilibration takes 12 hours before samples are even injected



HPLC: Maintenance

- With the instrument being new it is fairly reliable
  - Downside of a new instrument means most of the routine maintenance requires a trained professional to perform it
- Typical maintenance is changing restrictors in the pumps or the needle of the auto sampler
- Columns must be replaced yearly with heavy use

HPLC: Advantages and Disadvantages

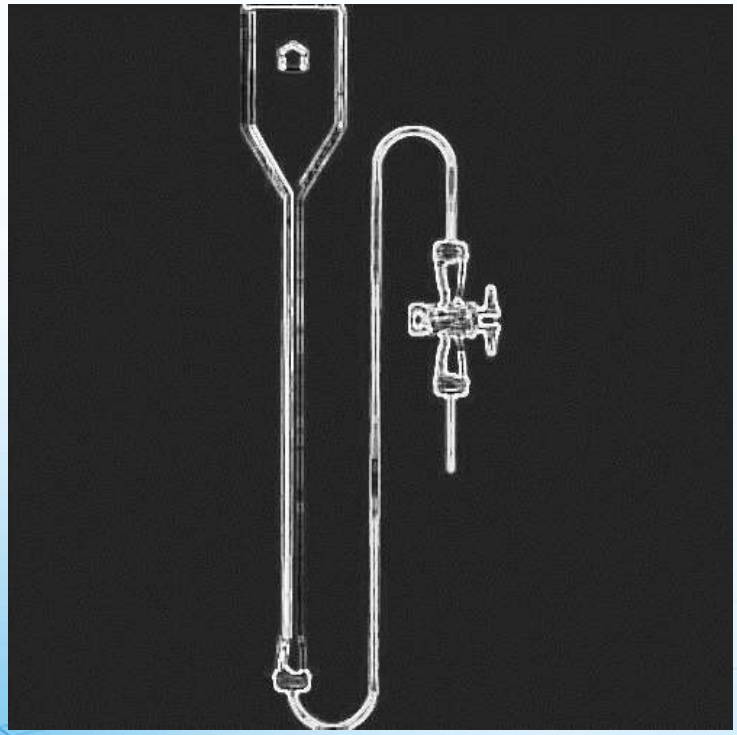
- The specificity of the derivatization keeps interferences at a non existent level
- Highly automated, very consistent and precise
- Low flow rates allow the instrument to run longer
- Incredibly long equilibration and run times
- Reagents do not last long and must be remade for every run
- Complexity of the instrument leaves lots of room for things to go wrong

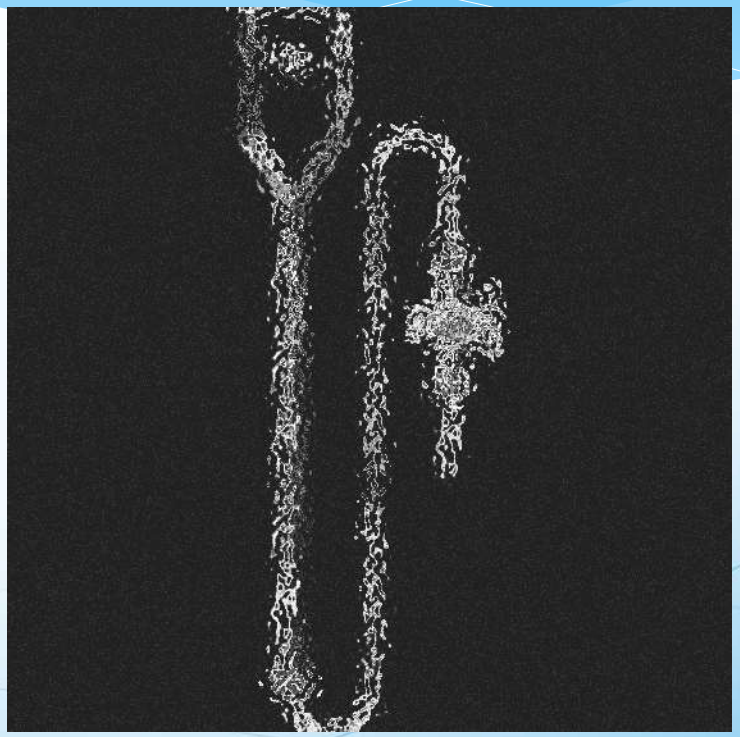
Lachat

Samples are mixed with reagents and analyzed using colorimetric technique

- TKN
- Nitrate
- Nitrite
- Ammonia
- Cyanide

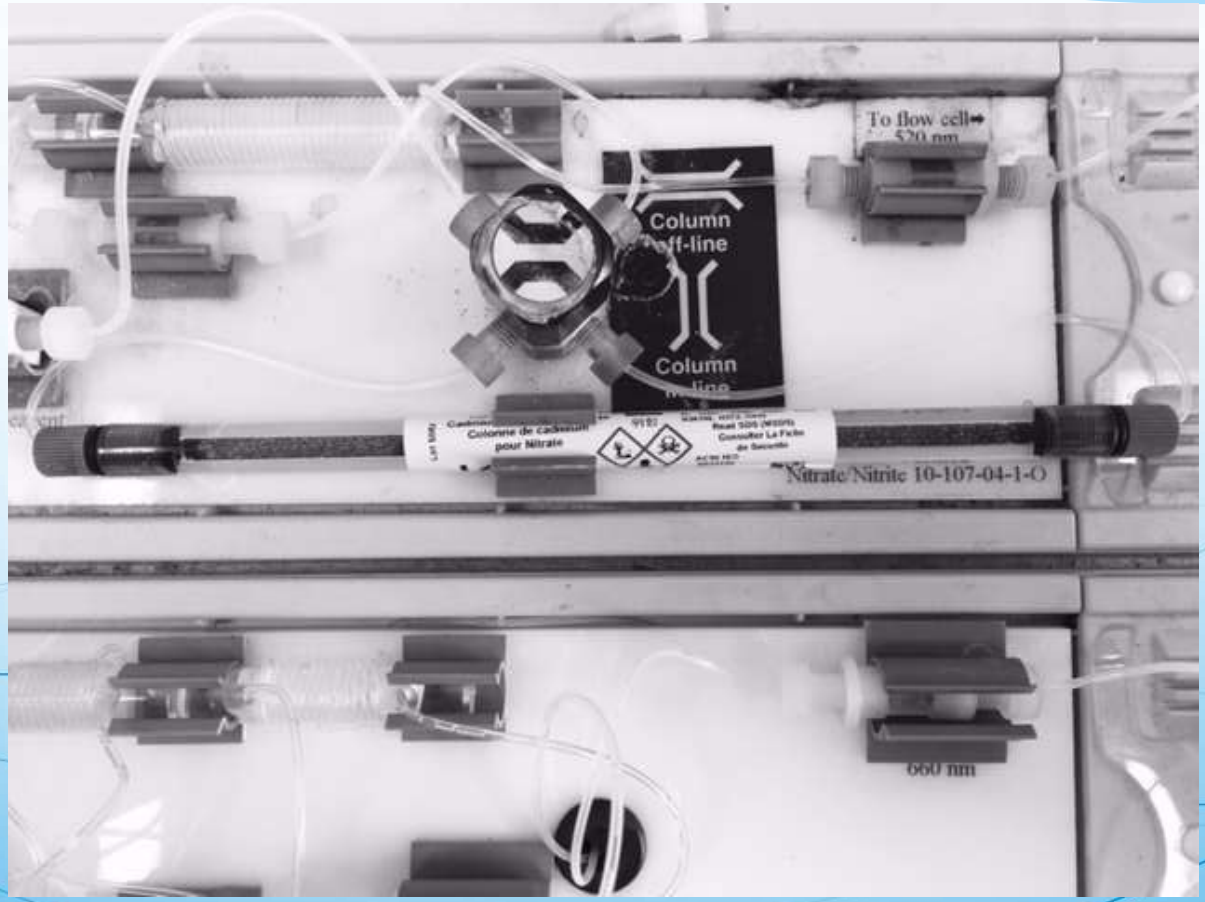
Nitrate Reduction Column





Lachat Reduction Column

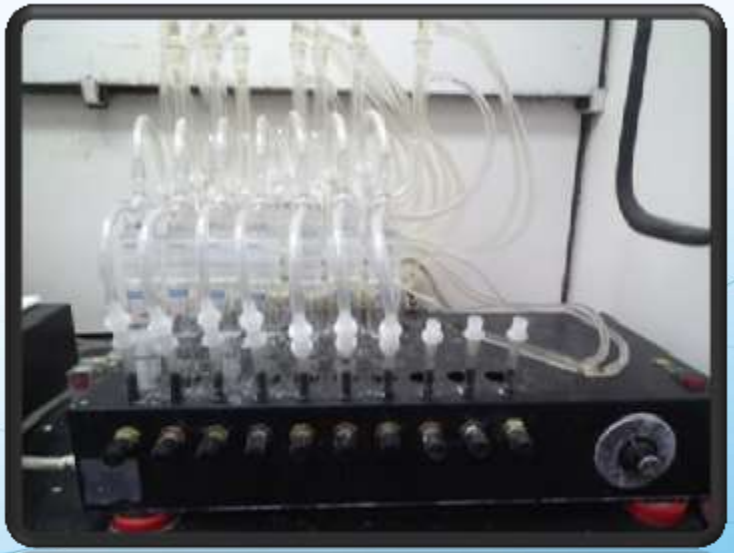
Lachat Reduction Column



Lachat: Sample Preparation

Ammonia, Nitrate, and Nitrite are direct injection methods
TKN and Cyanides both require distillations

TKN Distillations



Cyanide Distillation

Lachat: Running the Samples

- TKN preparation takes ~ 6 hours but run on the instrument at 1 minute per sample
- Cyanide preparation takes ~90 minutes and also runs at 1 minute per sample
- Nitrate and Nitrite run at 1 minute per sample
- Ammonia runs at 2 samples per minute
- Each run contains approximately 40% QC

Lachat: Interferences

- Cyanide:
  - Sulfides will affect the colorimetric process
- TKN:
  - High Nitrate levels can yield low TKN values
- Nitrate and Nitrite:
  - High Chlorine levels
  - High concentrations of Iron, Copper or other metals
  - High Turbidity of samples

Lachat: MDLS and PQLS

- The PQL is the lowest level the laboratory can report to with confidence.
- MDLS are performed annually or whenever major changes with the equipment occur.
  - Ammonia: 0.015 with a PQL of 0.05 mg/L
  - Nitrate: 0.008 with a PQL of 0.05 mg/L
  - Nitrite: 0.011 with a PQL of 0.05 mg/L
  - Cyanide: 0.002 with a PQL of 0.005 mg/L
  - TKN: 0.151 with a PQL of 0.05 mg/L

Lachat: Maintenance

- For all methods the tubing will need to be changed as needed
- For Nitrates the Cadmium Column will need to be replaced about every 3 months

Gas Chromatography and Mass Spectroscopy (GC/MS)

GC/MS: Sample Preparation

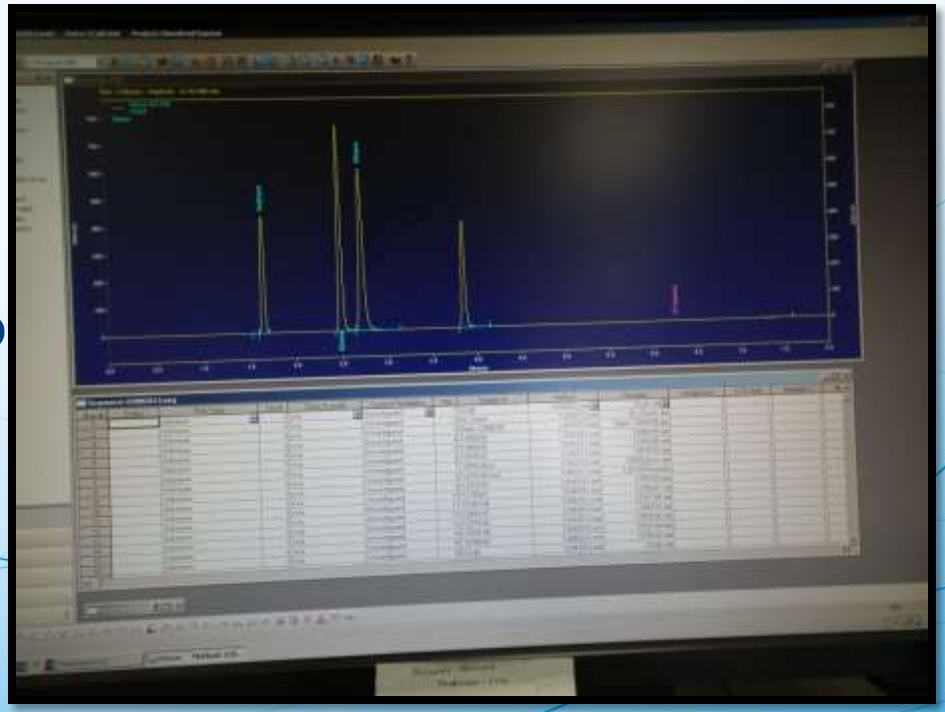
- Sample preparation is very much method dependent when using GC/MS. Some samples can just be directly injected while others will need extracted using either:
  - Liquid-liquid extraction
  - Liquid-solid extraction
  - Purge and Trap Extraction
  - Microextraction
  - Headspace

GC/MS: How it Works

- The sample/extract is injected into an injection port where it then moves to the column
- GC columns are long silica tubes lined with a retentive material
  - They vary in length, diameter, and film thickness
  - Column is chosen based on the analytes your trying to see

GC/MS: How it Works

- After samples are separated in the column they are hit with an electron beam, which fragments the compounds in a consistently unique way in the mass spectrometer
- The signal is then reported to the software which changes it to concentration data



Mercury- Cold Vapor

Analysis of Mercury is performed using methods 245.1, SW846, 7470A in

- Drinking waters
- Surface, ground, industrial, and domestic wastewater
- And extracts

Mercury- Cold Vapor: How it Works

Uses Cold Vapor Atomic Absorption

To Reduce Mercury to it elemental state

Passes through a cell into a light path of an AA Spectrophometer

The Peak height is measured to yield the concentration on Mercury

Mercury- Cold Vapor: Sample Preparation

- Samples are preserved in plastic bottles containing 50% HNO_3
- All samples must be digested prior to analysis
- Different acids and reagents are added
  - Sulfuric and Nitric Acids
  - Potassium Permaganate Solution
  - Potassium Persulfate
  - Sodium Chloride Hydroxylamine Sulfate
  - Stannous Chloride

Mercury- Cold Vapor: Sample Preparation Continued

- Samples are then capped and heated to 95 °C in a block digester for 2 hours
- Samples must then cool to room temperature but be analyzed within 48 hours of digesting
- Prior to analysis additional reagents are added:
  - Sodium Chloride Hydroxalmine Sulfate
  - Stannous Chloride
- An analytical run of 20 samples typically takes 3-4 hours to prepare contains ~60% QC and will take about 2 hours to run through the analyzer

Mercury- Cold Vapor: Interferneces, MDLs, and PQL

- Typical Interferences with this method are:
  - Sulfide
  - Chloride
  - Copper
  - Tellurium

- MDL is run annually and varies somewhat. The typical MDL for this method is 0.05 µg/L
- The PQL is a set number at 0.2 µg/L for this method

Mercury- Cold Vapor: Maintenance

- Daily Maintenance includes:
  - Tubing Changes
  - Mixing Coil thoroughly rinsed to prevent stannous chloride build up
  - Monitoring of the lamp for signs of wear
  - Lamps are replaced about yearly when they become worn

Inductively Coupled Plasma (ICP) and Inductively Coupled Plasma- Mass Spectroscopy (ICP-MS)

ICP

ICP-MS

ICP and ICP-MS: Sample Preparation

- Turbidity Check:
  - >1 sample must be digested, <1 samples can be directly analyzed

- Digestion:
  - 50 mL of sample, 50% HCL and 50% HNO_3 are heated to 95 °C until volume is 20 mL (~4-5 hours)

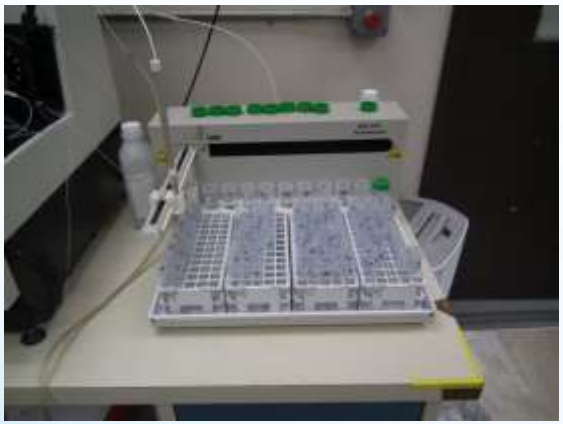
ICP and ICP-MS: How it Works

- The ICP measures element light emitted by optical spectrophotometer using plasma as the source
- Sample is transferred through lines to nebulizer and then into the spray chamber where it is transferred to the plasma, where it can then be detected. The computer software then generates the data

ICP and ICP-MS: How it Works

- The ICP-MS follows the same initial steps as the ICP
- Once sample as been injected into plasma the ions are extracted and moved to the electron multiplier
- The computer software then generates the data

ICP and ICP-MS: How it Works



Sample moves from auto sampler to pump, nebulizer, and spray chamber

From spray chamber to plasma

It is then detected by the detector

ICP and ICP-MS: Pros and Cons

ICP

- Advantages:
  - Multiple elements ran simultaneously
- Disadvantages:
  - Frequent maintenance performed to keep instrument up and running
  - High levels of salts and dissolved solids can cause delivery and analysis problems
- Interferences:
  - Spectral
  - Background
  - Stray light

ICP-MS

- Advantages:
  - Can analyze 20+ metals per sample simultaneously
- Interferences:
  - Matrix issues
  - Excessive wear of internal parts
  - Carryover possibilities in heavier metals

ICP and ICP-MS: Sample Run Time

- The ICP-MS can run a full metal scan in 10 minutes per sample, 1 or 2 metals can run as quick as 3 minutes a sample
- The ICP runs a full scan in 5 minutes, or a few metals in 2 ½ minutes per sample
- The auto sampler of the ICP-MS can hold 240 samples and QC at once

- Both run 50-65% QC for every run

ICP and ICP-MS: Maintenance and Cost

- ICP
  - The torch must be disassembled and cleaned every 3-5 days and replaced when worn
  - Uptake and waste lines changed weekly at a minimum
  - Nebulizer and parts associated, Sipper Probe and auto sampler lines changed quarterly, or sooner, if plugged
  - Chiller coolant changed every six months

Disassembled torch

ICP and ICP-MS: Maintenance and Cost

- ICP-MS
  - Sample uptake and waste lines are changed weekly
  - Peristaltic pump rollers cleaned weekly
  - Skimmer and Sample cones are inspected and cleaned every 3 months and changed as needed
  - Sample probe, nebulizer and detector are changed as needed, when QC results become inconsistent