Bureau of Laboratories

Air Chemistry & Gravimetrics Section

What does **GRAVIMETRIC** mean anyway ??????????

- According to the Webster's dictionary, the noun **GRAVIMETRY** is the measurement of weight or density.

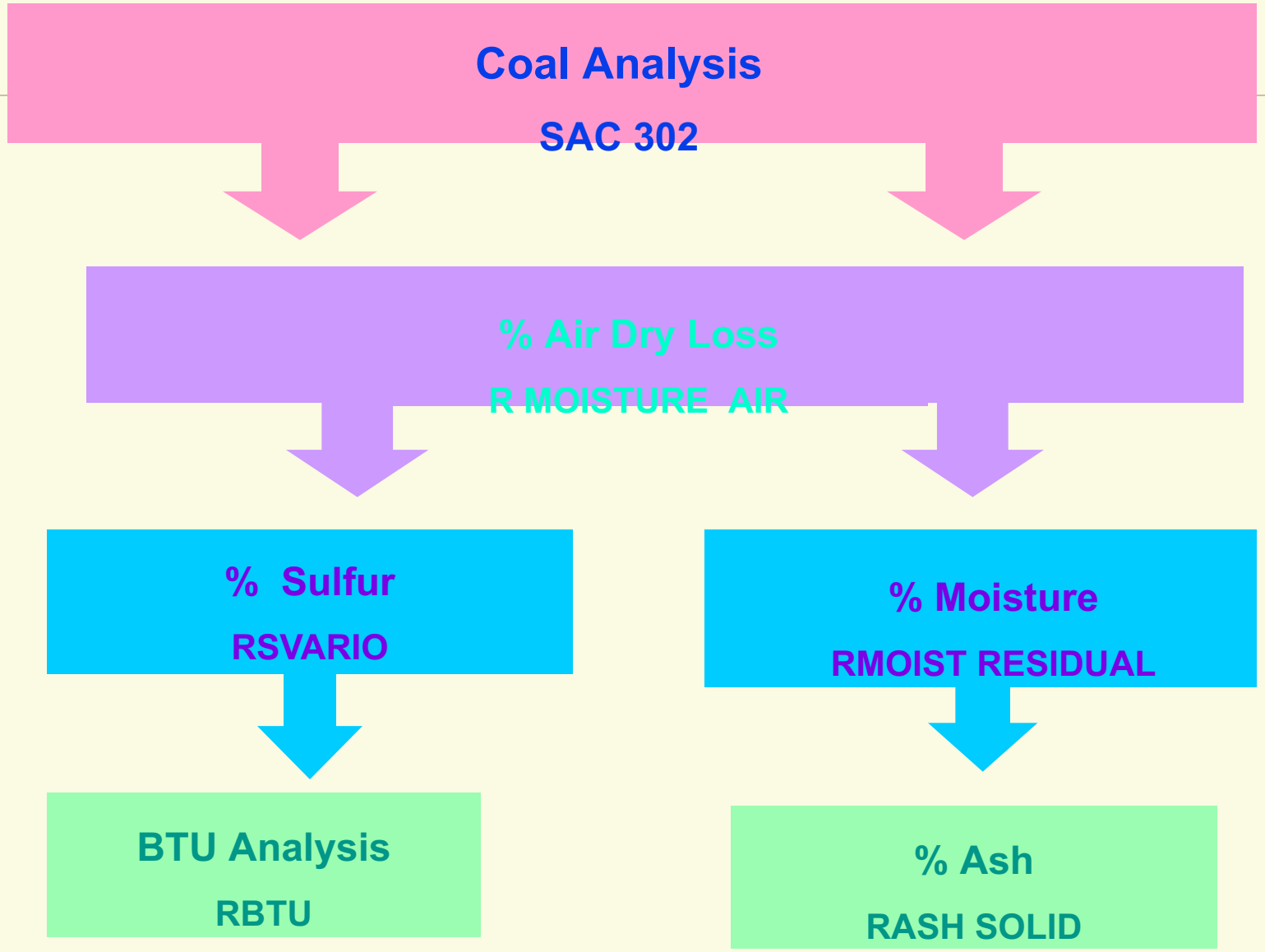
- According to Wikipedia, **GRAVIMETRIC ANALYSIS** describes a set of methods in analytical chemistry for the quantitative determination of an analyte based on the mass of a solid. An example is the measurement of suspended solids in a water sample - a known volume of water is filtered, and the collected solids are **weighed**.

Overview

- The Air Chemistry & Gravimetrics Section performs various analyses of fuels including coals, waste liquids and virgin oils, paints and coatings, filters, dustfalls and microscopic analyses in samples for the DEP Bureau of Air Quality and analysis of water and soil samples for various analyses including TOX, HEM & SGT-HEM, total solids, total suspended solids, and total dissolved solids for DEP, DCNR and other state and federal agencies.

FUEL ANALYSIS

Coal Flowchart



COAL ANALYSIS

- Coal samples that have not been ground when received in the Lab are weighed, spread out in a shallow pan and are air dried for twenty-four hours. The samples are reweighed and the **% Air Dry Loss** is calculated.
- The samples are then ground and pulverized to a minus 60 mesh size.
- Laboratory analysis includes **BTU, % Sulfur, % Moisture and % Ash.**

Coal Analysis Continued

- **BTU Analysis** is performed using a **Parr 6400** Bomb Calorimeter.
- BTU is the heat content of the coal sample. The BTU is determined by burning a weighed sample of coal under controlled conditions, in an atmosphere of oxygen, in a calibrated microprocessor controlled isoperibol calorimeter. Isoperibol refers to a constant temperature environment.
  - Heat correction factors include:
  - the **ignition thread consumed** during combustion,
  - the **amount of Na_2CO_3 used to titrate** the sample
  - the **Sulfur result** and
  - the **% Air Dry Loss** is entered as the Moisture factor to calculate results on an **as received basis** (analytical data calculated to the moisture condition of the sample as it arrived at the laboratory and before any processing or conditioning).

Coal Analysis Continued

- Reference method for the **BTU** analysis is ASTM D 1989.
- **%Sulfur -** analysis is performed on the **elementar VarioMax Sulfur Analyzer** and measured using a Thermal Conductivity Detector (TCD).
- The VarioMax automated instrument, operated in *Carbon, Nitrogen and Sulfur Mode* (CNS Mode), determines the sulfur content of coal samples. Samples are oxidized via catalytic tube combustion at 1140 ^{o}C. The nitrogen, carbon and sulfur in the combustion gas are separated by specific absorption columns in a purge and trap system. The nitrogen, carbon and sulfur are then successively released and pass through a Thermal Conductivity Detector (TCD) for measurement. The sample's TCD signal is compared to the TCD signals of Certified Coal Standards to determine the %S.

Coal Analysis Continued

- Reference method for **Sulfur Analysis in Coal and Coke** is ASTM D 4239-97. **Sulfur** result is reported as % S.
- **The % Ash** and **% Moisture** analysis is performed using a **TGA701 Thermogravimetric Analyzer.** Empty crucibles are loaded into the furnace carousel, the tare weight is determined, coal sample is loaded and the initial sample weight is determined. The weight loss is monitored and the furnace temperature is controlled according to the selected analysis method for determination of the moisture or ash content.
- **% Ash -** % **Air Dry Loss** is required to calculate results on an **as received** basis.
- **% Moisture** -% **Air Dry Loss** is required to calculate results on an **as received basis.**

Coal Analysis Continued

Virgin Fuel Analysis

Virgin Fuel Flowchart

VIRGIN FUEL OILS

SAC 303

% SULFUR
HORIBA X-RAY
99006A

BTU ANALYSIS
BOMB CALORIMETER
99003A

API GRAVITY
PAAR DENSITY METER
API60

% OIL ASH
99005

Virgin Oil Analysis

- **Samples are submitted in 500 ml Nalgene plastic containers.**

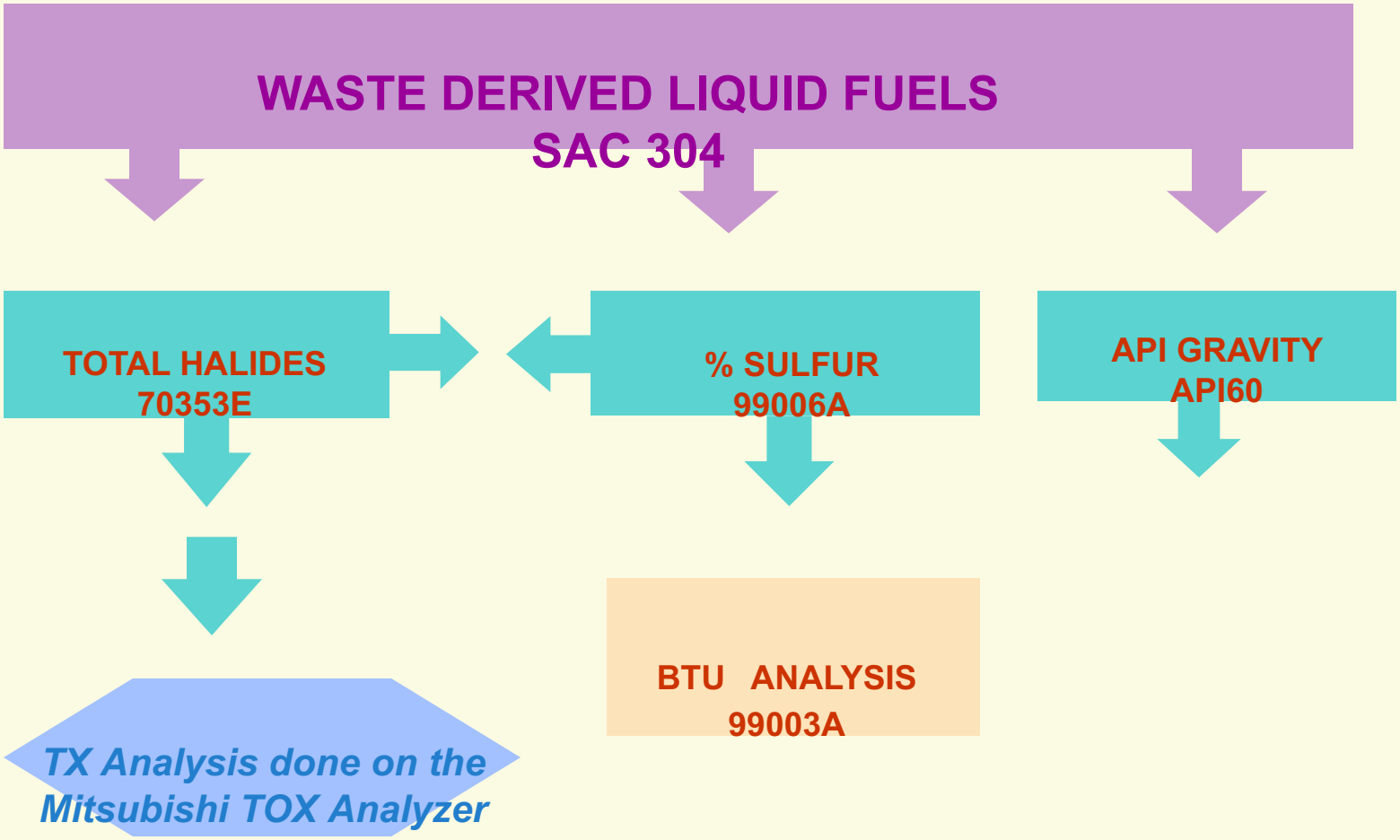
- **Laboratory Analysis includes:**
- **BTU - Analysis is performed on Parr 6400 Bomb Calorimeter.**

  - **Heat correction factors** include:
    - the **ignition thread consumed** during combustion,
    - the **amount of Na_2CO_3 used to titrate** the sample and
    - the **Sulfur result**

Notes on Virgin Oil Analysis

- **% Sulfur -** Analysis is performed on the **Horiba X-ray Sulfur Analyzer.** Reference method is ASTM D 4294. The sulfur analyzer uses energy-dispersive X-ray fluorescence spectroscopy to determine the sulfur content of petroleum products including fuel oil and diesel fuel.
- **API Gravity -** Analysis is performed on the **Paar Digital Density Meter.** This method determines the specific gravity of petroleum (waste and virgin oils) through the use of a digital density meter. The American Petroleum Institute specific gravity is calculated internally by the density meter. The reference method is ASTM D 5002.
- **Oil Ash** is analyzed according to ASTM D 482.

WDLF Flowchart



WDLF Analysis

- Samples must be submitted in **275 cc seamless aluminum containers**.

Laboratory Analysis includes:

- **BTU** - Analysis is performed on **Parr 6400 Bomb** Calorimeter.
  - **Heat correction factors** include:
    - the **ignition thread consumed** during combustion,
    - the **amount of Na2 CO3 used to titrate** the sample, and
    - the **Sulfur result** from the **Horiba X-ray Sulfur Analyzer**

- **API Gravity -** Analysis is performed on the **Paar Digital Density Meter.**

WDLF Analysis Continued

- **Total Halides (TX)** is a measurement used to estimate the total quantity of halogenated material in new or used petroleum products. It is sensitive to compounds containing chloride, bromide and iodide, but does not detect fluorinated compounds.
- The TX of waste fuels is analyzed by high temperature pyrolysis micro-coulometric determination on the **Mitsubishi TOX Analyzer**.
- A 2 – 5 mg aliquot of a well-mixed sample of new or used petroleum product is placed into a quartz boat. The sample is then combusted to convert the total halides to a titratable species. It is then titrated electrolytically and measured using a microcoulometric detector. The TX is reported based on the chloride ion.
- Reference method for TX is **EPA Method 9076.**
- The TX result is reported is as mg/g.

WDLF Analysis Continued

TX of waste fuels is analyzed by high temperature pyrolysis micro-coulometric determination.

PAINT & SURFACE COATING ANALYSIS

PAINT ANALYSIS FLOWCHART

H_2O - BASED PAINT or COATING

SAC 301

Volumetric
Karl Fischer Titration
99105A

Density
Digital Density Meter
99010E

Volatile Organic Content
99012E

PAINT ANALYSIS FLOWCHART

SOLVENT - BASED PAINT or COATING

SAC 300

Coulomatic
Karl Fischer Titration
99005A

Density
Digital Density Meter
99010E

Volatile Organic Content
99012E

NOTES ON PAINT ANALYSIS

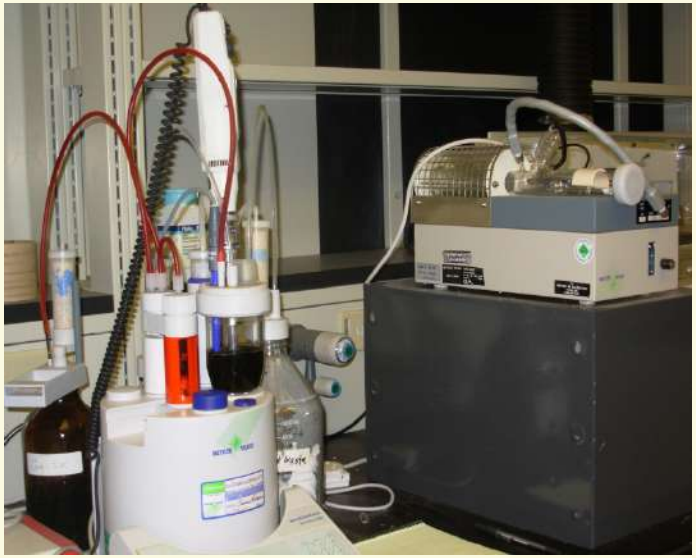
- **Water- based coatings** contain **greater than 5 % water.**
- **Solvent- based coatings** contain **less than 5 % water**.
- A **Manufacturer's Safety Data Sheet** or a **Production Specification Sheet** should be included with every paint sent to the laboratory.
- A **Paint sticker** must be attached to every paint sample submitted for analysis.
- The **submission sheet** should identify the coating sample as being either **water-based** or **solvent-based**.
- **Catalyzed coatings** set quickly. Samples of those coatings **must be submitted in fractions** with the **mix ratio provided.**
- The **sample cans** should be **filled to the neck** of the container and **shipped the same day** to prevent the loss of volatiles.
- Samples must be submitted in **275 cc aluminum containers**.

NOTES ON PAINT ANALYSIS Continued

- The reference method for **Water in Paints and Coatings by Karl Fischer Method** is ASTM D 4017. The paint is dissolved in an appropriate solvent and titrated directly with a standardized reagent to an electrometric end point to determine the **% water** in the sample. The water analysis is performed using the Mettler Toledo DL-38 Karl Fischer Titrator.

- The reference method for **Volatile Content of Coatings** is ASTM D 2369. The sample is weighed into an aluminum dish containing 3 mL of an appropriate solvent, dispersed and heated in an oven at 110 ^{o}C for 60 minutes. The **% Volatile Content** is calculated from the loss in weight.

- The reference method for **Density** of Liquids by Digital Density Meter is ASTM D 1475. A small volume of the sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with the calibration data to determine the density of the sample. The **density** analysis is performed using the Paar DMA 48 Density Meter.



% NONVOLATILE CONTENT OF PAINTS

ASTM Method D 2697 - Volume Nonvolatile Matter in Clear and Pigmented Coatings (% nonvolatiles by weight).

The weight and volume of stainless steel disk is determined by weighing in air and in a liquid of known density.

After the disks are coated with paint and dried, the weight and volume of the coated disk is determined by weighing in air and in a liquid of known density.

The volume of the paint film is equal to the quotient of the weight loss of the coated disk (due to the Archimedes buoyancy effect) divided by the density of the liquid displaced.

% NONVOLATILE CONTENT OF PAINTS Continued

From the measured weights and volumes of the disk before and after applying the coating, the weight and volume of the dried coating film are calculated.

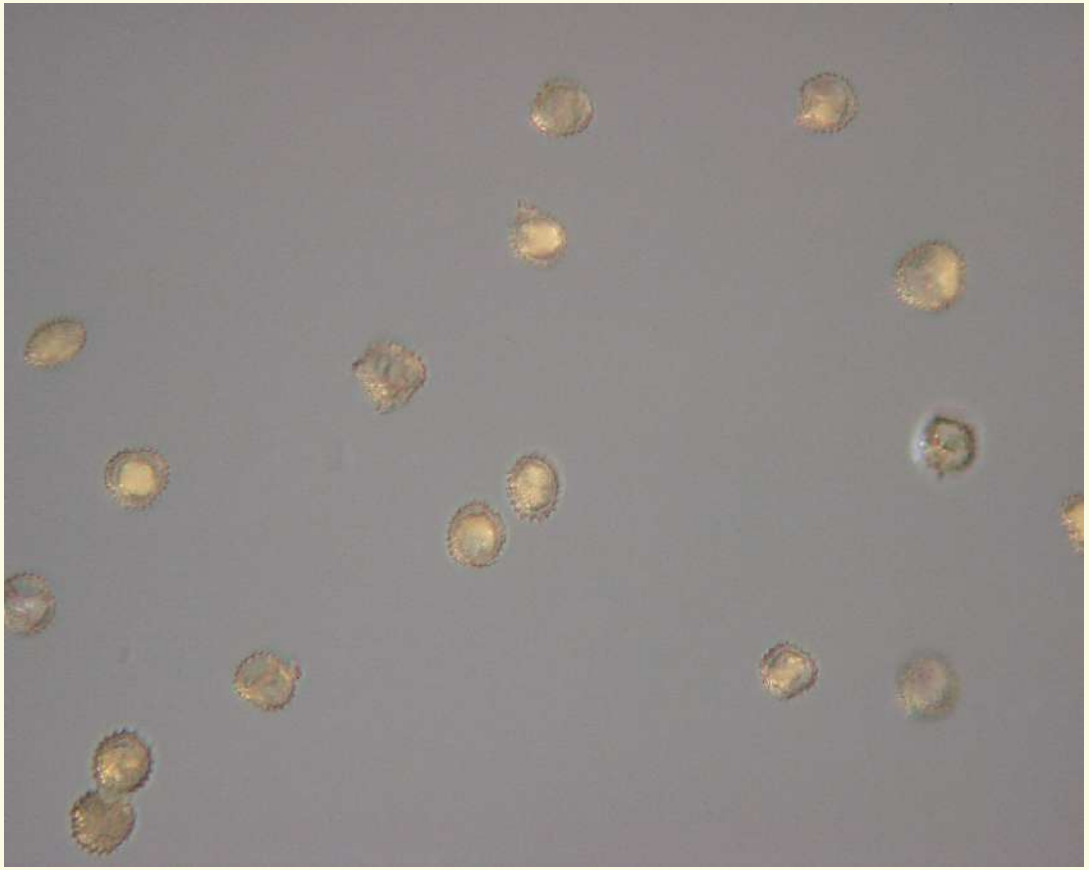
Based on the density of the liquid coating and the weight percent nonvolatile matter, the volume of the liquid coating deposited on the coated disk is calculated.

The volume of the dried coating divided by the volume of liquid liquid coating, multiplied by 100, equals the volume % nonvolatile matter in the total liquid coating.

Microscopic ID Collection

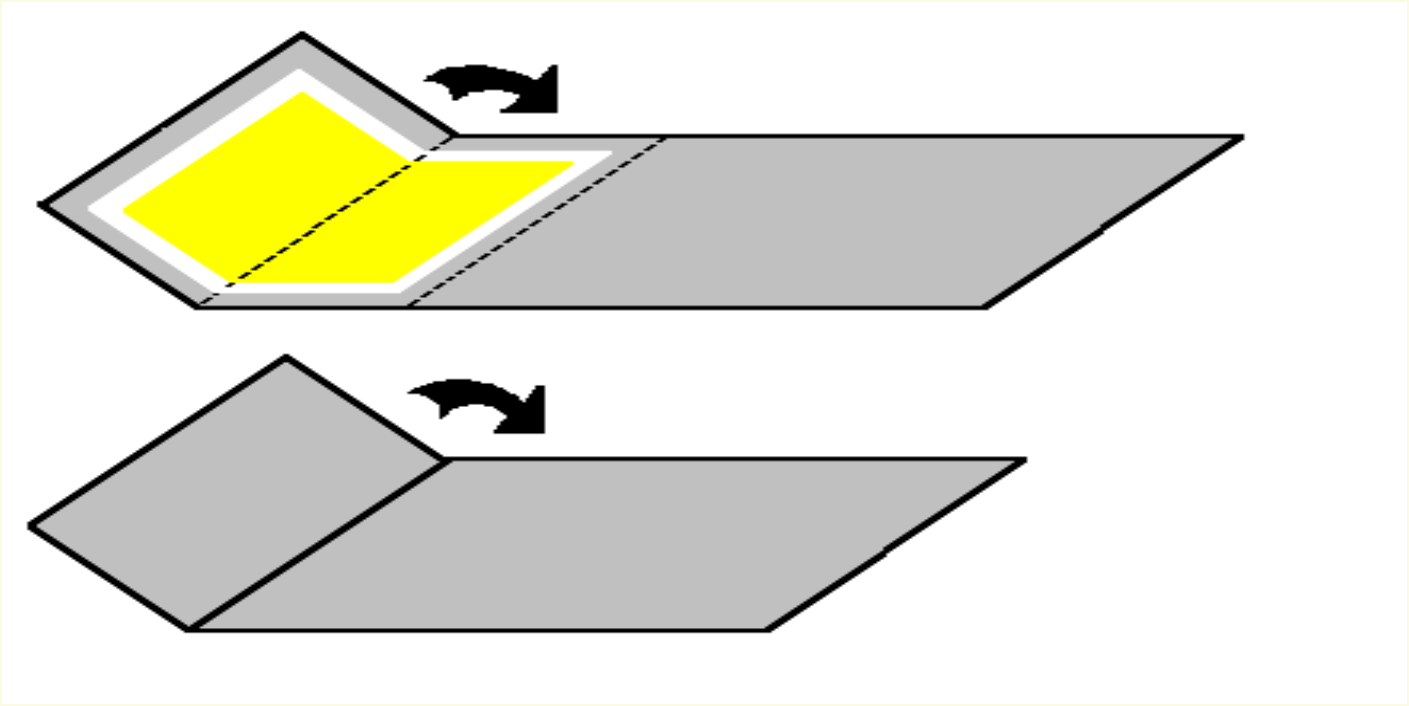
- Use small bottles or plastic bags for collection
- **Do not** use paper towels or cotton swabs to collect samples
- List possible sources of the material on the submission sheets
- Collect reference samples for difficult cases

Microscopic ID Continued



Hi-Vol Sampling Tips

- Fold the 8 x 10 inch filter "***long-ways***" so that the particulate is contained on the **inside** of the fold.
- Place any filter fragments inside the folded filter
- **Do not** put ***Dickson charts*** inside the folded filter



Hi-Vol Sampling Tips

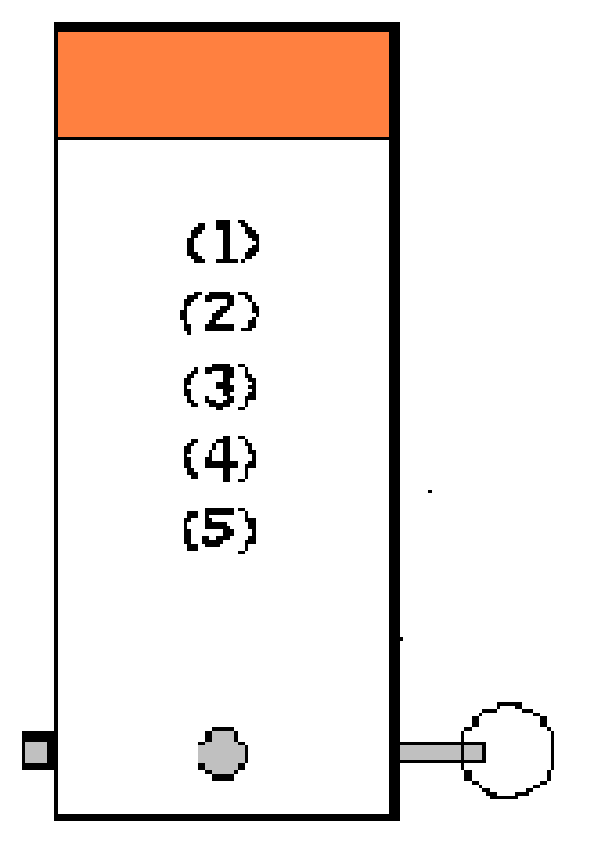
- **Do not** moisten the flap on the mailer (Use the tabs to keep it shut)
- Be gentle with the filters - they tear easily
- Place the *site bar code* in the box on the left side of the filter mailer
- Extra filters may be kept for up to a year from the date on the bar code
- Email lwilkinson@pa.gov if you have questions

Hi-Vol Filter Sampling

- Air is drawn through the hi-vol sampler and collected on the 8 x 10 inch glass fiber filter.
- The **mass of the particulate** matter collected is determined by the difference in filter weights prior to and post sampling. The concentration of particulate matter is calculated by dividing the weight gain by the volume of air sampled and reported as ug/m^3.
- Filter samples can also be analyzed for sulfate, nitrate, lead and other metals and BaP.

Hi-Vol Filter Sampling

PM2.5 Monitoring



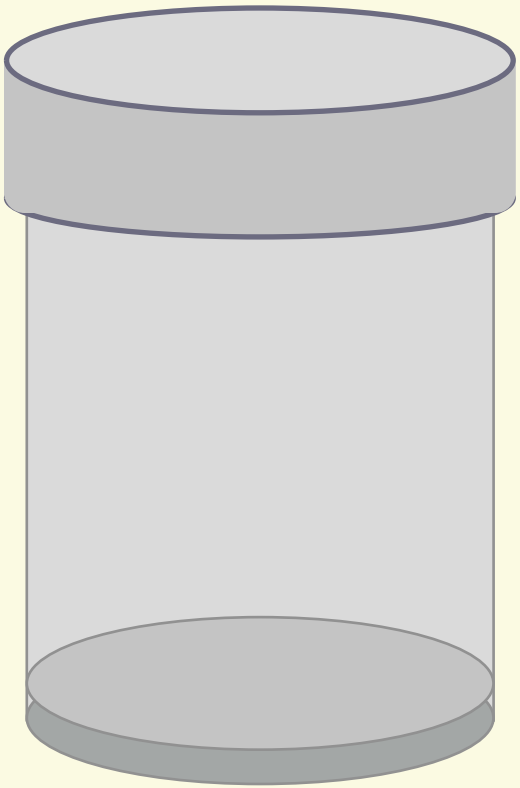
- Do not handle filters
- Apply site bar code to the submission sheet
- Pre-freeze ice packs before shipping
- Reset min/max thermometer before shipping

PM2.5 Monitoring CONTINUED

PM2.5 particulate is defined as any particulate having a diameter less than or equal to 2.5 microns. This procedure determines the mass of PM2.5 matter collected on a Teflon filter. The filter is weighed initially, sent to the field where a specified volume of air is pulled through the filter and then returned to the laboratory for a final weight. The difference in mass is reported and combined with the air volume to determine the concentration of PM2.5 particulate. This is based on method EPA 454/R-98-005.

PM2.5 Monitoring CONTINUED

Dustfall Jars



- Jars are placed in the field for approximately 30 days.
- Add 5 ml Copper Sulfate in summer to prevent algae growth.
- Add 5 ml of Ethylene Glycol to prevent freezing in the winter
- Plastic jars, holders and instructions for sampling dustfalls are available from BAQ Central Office

Dustfall Analysis CONTINUED

- Particulate matter is collected via gravitational settling into an open-mouth container (dustfall jar) for about 30 days.
- The dustfall jar is washed with distilled water, filtered and then evaporated. The insoluble mass is determined by the weight gain of the filter after filtration. The mass of the soluble matter is determined by the weight gain of the beaker after a portion of the filtrate is evaporated.
- Additional analyses performed for dustfall samples include a microscopic examination, various metals and ions if requested.

Dustfall Analysis CONTINUED

- Results reported for the dustfall sample include: dissolved particulate (g), insoluble particulate (g), % insoluble matter, dustfall (tons/sq^2/month) and the microscopic examination of the insoluble particulate.

- Metals analysis is performed on the insoluble portion of the dustfall sample after the microscopic exam is completed.

Analysis of Water Samples

- n-Hexane Extractable Material (HEM) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM)
- TOX - Total Organic Halides
- Osmotic Pressure
- Total Solids, Total Suspended Solids (TSS), Total Dissolved Solids (TDS) and Settleable Solids

n-Hexane Extractable Material (HEM) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM)

- Reference method is EPA Method 1664A
- The sample is extracted with hexane using a solid phase automated extractor. The extract is placed into a pre-weighed aluminum pan and the hexane is evaporated from the extract.
- The pan and the extract is weighed and the HEM is reported as mg/L.
- HEM is the material extracted from the water sample and was formerly called Oil & Grease.
- Has a 28 day holding time.

n-Hexane Extractable Material (HEM) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM) CONTINUED

- If the SGT-HEM analysis is requested, the HEM is re-dissolved in n-hexane.
- Silica gel is added to the HEM to remove the absorbable materials.
- The solution is filtered into a pre-weighed aluminum pan to remove the silica gel.
- The hexane is evaporated and the SGT-HEM is weighed and reported as mg/L.
- SGT-HEM is the material extracted from the water sample and was formerly called TPH – Total Petroleum Hydrocarbon.
- Has a 28 day holding time.

n-Hexane Extractable Material (HEM) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM) CONTINUED

TOX - Total Organic Halides

- Reference method for **TOX** is Standard Methods 5320B.
- A 50 mL aliquot of the sample is passed through a column containing 40 mg of activated carbon. The column is washed to remove any trapped inorganic halides and is then combusted to convert the adsorbed organohalides to a titratable species. It is then titrated electrolytically and measured using a microcoulometric detector. The TOX is reported as ug/L based on the chloride ion.

TOX - Total Organic Halides CONTINUED

- This method detects all organic halides containing chlorine, bromine and iodine that are adsorbed on the activated carbon. Fluorine containing compounds are not determined by this method.
- Has a 28 day holding time.

Osmotic Pressure

- This testing procedure is a BOL developed method and is based on the instrument manufacturer references.
- A 20 uL aliquot of the water sample is pipetted into a sample tube and placed into the osmometer for analysis. The **osmotic pressure** is measured by the instrument and reported as mOsmol/kg H_2O.
- Has a 48 hour holding time.

Osmotic Pressure CONTINUED

- Measuring the osmolality of a water sample is a way of determining the freezing point depression of that sample. Since the amount of total dissolved solids in a sample is directly proportional to the freezing point depression, knowledge of the freezing point depression aids in characterizing the severity of a pollution source.

Total Solids, Total Suspended Solids (TSS) & Total Dissolved Solids (TDS)

- Solids refer to matter suspended or dissolved in water, wastewater or mine drainage samples.
- **Total solids** (TSOL) is the material left in the dish after evaporation at 105 °C.
- TSOL includes the TSS and TDS portions.
- Reference method for TSOL is USGS-I-3750.
- TSOL is reported as mg/L.
- Has a 7 day holding time.

Total Suspended Solids (TSS)

- **Total suspended solids** (TSS) is the portion of material retained by the filter and is dried at 105°C.
- We have three (3) automated weighing systems – robots – used only to weigh the crucibles that are used for the TSS analysis.
- The samples are poured and filtered by one of the Solids area team members.
- Reference method for TSS is USGS-I-3765.
- TSS is reported as mg/L.
- Has a 7 day holding time.

Total Suspended Solids (TSS) CONTINUED

Total Suspended Solids (TSS) CONTINUED

Total Dissolved Solids (TDS)

- **Total dissolved solids** (TDS) is the portion of material that passes through a filter and dried at 180°C depending on the test requested.
- The water sample is filtered through a glass fiber filter and the filtrate is evaporated to dryness in a pre-weighed dish.
- The samples are poured and filtered by one of the Solids area team members.
- Reference methods for TDS are USGS-I-1750 and Standard Methods 2540C.
- TDS is reported as mg/L.
- Has a 7 day holding time.

Settleable Solids

- **Settleable solids** is the material that settles out of suspension of the water sample.
- One liter of sample is required for this analysis and is poured into an Imhoff cone.
- Let the sample settle for 45 minutes, stir and settle 15 minutes longer.
- Settleable solids is reported as mL/L.
- Has a 48 hour holding time.

THE END