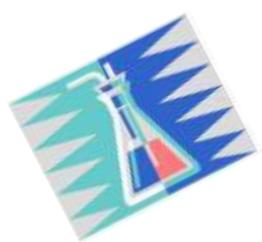


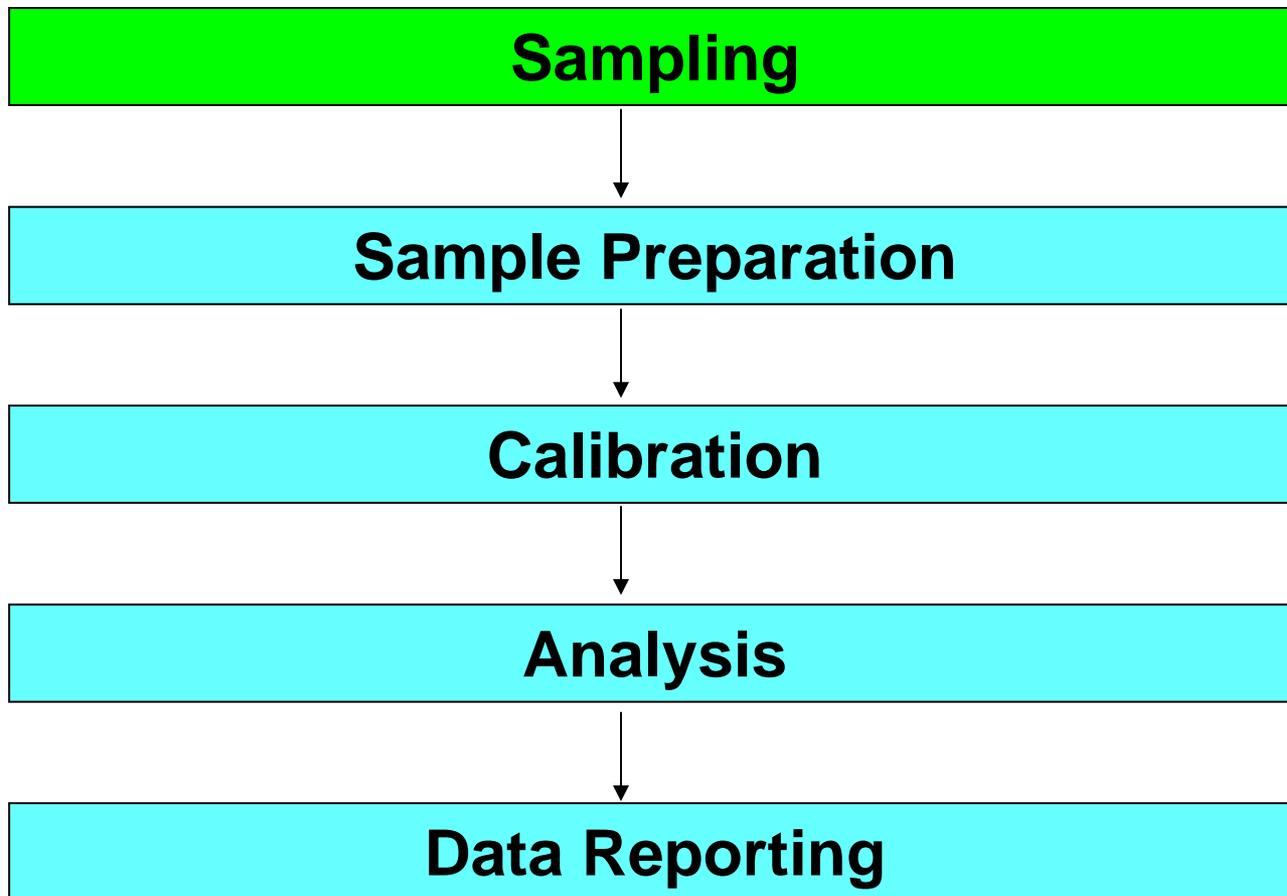
Field Work

Preparing and Field Analytical Measurements (On-site)





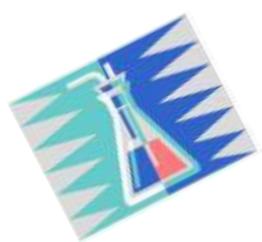
Basic Steps of Environmental Analysis





Field Work - Outline

- **Preparing to go to the field**
- **Field Analytical Measurements (FAM)**
 - **Field necessary tests**
 - pH – Temperature – Dissolved Oxygen – Turbidity
 - **Field screening using hand-held technology**
 - Vapor screening – FID-PID-IMS-FTIR-Raman
 - Electrochemical – Colorimetric-XRF
 - **Field Analytical with Portable GC**
 - PID-TCD-MS
- **QA/QC in the field**

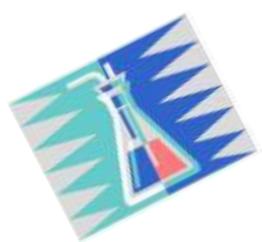


Preparing to go to the Field

Field staff should know what the objectives are.

- Read sampling plan – including QA/QC
- Be aware of sampling methods and field hazards (dermal, confined space..)
- Have appropriate personal protective equipment (PPE) - clothing
- Have appropriate sample equipment including sample containers, labels and coolers.
- Have necessary documentation ready (chain of custody-lab books-sample log)
- Training-training-training





Sample Preparation and Storage Important for Accuracy and Precision



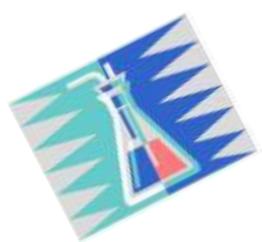
Well labeled and
preserved samples



Sampling Activities are Performed with On-Site Analysis

- **On-site analysis has many advantages**
 - It is essential for physical and chemical properties that will change with storage:
 - temperature
 - pH - dissolved oxygen - turbidity
 - Hotspot identification
 - Screening for hazards
 - Rapid
 - When combined with a good sampling plan may lead to very high quality results





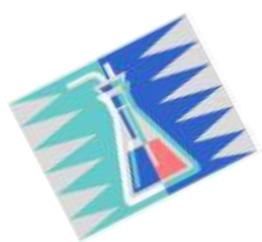
Portable Instrumentation Provides Necessary Information

Some measurements should be made in the field. Notations including site information should be kept in field book.

- Temperature
- pH
- Dissolved Oxygen
- Turbidity
- Conductivity
- Alkalinity
- Hardness



Example : Hach Co.



Hand-held Meters can be Very Effective in the Field



Combined:
pH-DO-Conductivity

Source: Hach



Pocket colorimeter
can do metals and
other water
chemistry.



Problems conductivity meters
can be easily filled and
rinsed.

Source: Myron



Appropriate PPE and Sampling Equipment is Essential

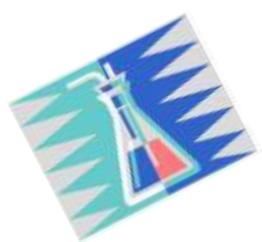


pH – Necessary to test on-site along with temperature



Conductivity – measurements are also effective in the field

Source: Pakistan Council of Research in Water Resources



Intended use of Data Guides Analysis

Data Level (suggested only)

- **Level 1 – Field based analytical screening procedures using organic vapor analyzers and other essentially non-calibrated instruments. Reportable data includes method, detection limit, result, date, time and person conducting analysis.**



Hand-held Flame Ionization Detector or Photoionization Detector



PID is more sensitive than FID
Can be selective by changing lamp
Humidity can affect reading of both instruments

PID

Principle : UV lamp ionizes-electrometer detects

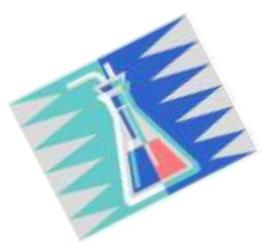
Source: RAE Systems

FID

Principle : Flame ionizes-electrometer detects



Source: Photovac



Hand-held FTIR and Ion Mobility Analyzers are Useful Tools



Fourier Transform Infra Red Analyzer – especially good for organic compounds

Principle : IR absorbance (vibrational spectroscopy)

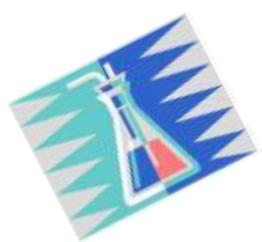
Source: Ahura



Hand-held Ion Mobility Spectrometer- especially good for explosives

Principle : ionized gas separated by mobility in electric field

Source: Smiths



Export Import Testing Using Raman Spectroscopy



Principle : Light scattering vibrational spectroscopy

Raman Spectroscopy is especially good for qualitative detection of organic compounds

Source: Ahura



Screening for Metal Contamination using Portable X-ray Fluorescence Spectroscopy

Elemental analysis
Soil and solids testing
• EPA method 6200
Lead paint applications

Principle : X-ray
ionization followed by
fluorescence emission



Source: Bruker



Source:Innov-x

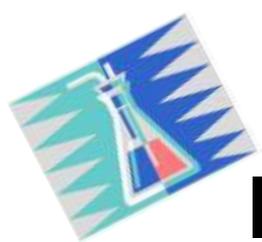


Specialized Analysis Tools

- **Soil vapor sampling can include:**
 - Summa canister
 - Tedlar bags
 - Tenax adsorption tubes
- **Colorimetric vapor tests:**
 - Tubes
 - Chip measuring system
- **Hanby test - hydrocarbons**



Source: Dräger



Intended use of Data Guides Analysis

Data Level (suggested only)

- **Level 2 – Field based analysis using instruments that are calibrated and blanks are performed to ascertain contamination. May include data from field GCs and other advanced screening methods. Reportable data include method, detection limit, results, date, time and person conducting analysis, and may include information on blanks.**



Portable Spectrophotometers used for a Wide Variety of Water Analytes



Principle : Visible or ultraviolet light absorption

Portable spectrophotometer for on-site water analysis. Includes iron, silica , PO_4^{-3} , NO_3^{-1} and much more.

Source: Hach





Small Spectrophotometers and Colorimeters are Very Versatile

Pre-Programmed Tests

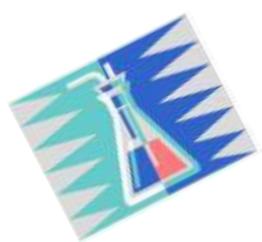
Test Name	Spectro Range ppm	Test Name	Spectro Range ppm
Alkalinity UDV*	15-200	Iron - Phenanthroline	0.04-4.50
Aluminum	0.01-0.30	Lead	0.1-5.0
Ammonia Nitrogen (Fresh Water)	0.02-1.00	Manganese LR	0.02-0.70
Ammonia Nitrogen (Salt Water)	0.10-1.00	Manganese HR	0.3-15.0
Ammonia Nitrogen HR	0.05-4.00	Mercury	0.02-1.50
Benzotriazole	1-30	Methylethylketoxime	0.02-3.00
Biguanide	5-70	Molybdenum HR	0.2-15.0
Boron	0.05-0.80	Nickel	0.06-8.00
Bromine LR	0.04-9.00	Nitrate Nitrogen LR	0.05-3.00
Bromine UDV*	0.3-22.0	Nitrate TestTabs	2.5-60.0
Cadmium	0.02-1.00	Nitrite Nitrogen LR	0.02-0.80
Calcium & Magnesium (Total) Hardness UDV*	10-500	Nitrite TestTabs	0.025-1.250
Carbohydrazide	0.005-0.900	TNitrogen, Total	2-25 mg/L
Chloride TestTab	0.5-30.0	Oxygen Scavengers	Various
Chlorine	0.02-4.00	Ozone LR	0.02-0.40
Chlorine - Free UDV*	0.01-10.00	Ozone HR	0.05-1.50
Chlorine - Liquid DPD	0.025-4.000	pH CPR (Chlorphenol Red)	pH 5.0-7.0
Chlorine - Total UDV*	0.1-10.0	pH FR (Phenol Red)	pH 6.6-8.4
Chlorine Dioxide	0.04-7.00	pH TB (Thymol Blue)	pH 8.0-9.5
Chromium (Hexavalent)	0.01-1.00	Phenol	0.05-6.00
Chromium (Total, Hex & Trivalent)	0.01-1.00	Phosphate LR	0.04-3.00
Chromium TestTab	0.03-1.00	Phosphate HR	1-70
COBALT	0.02-2.00	TPhosphorus, Total - LR	0.07-3.50 mg/L
TCOD LR with Mercury	5-150	TPhosphorus, Total - HR	5-100 mg/L
TCOD LR without Mercury	5-150	Potassium	0.5-10.0
TCOD SR with Mercury	50-1500	Silica LR	0.03-2.50
TCOD SR without Mercury	50-1500	Silica HR	1-50
TCOD HR with Mercury	500-15,000	Sulfate HR	5-100
TCOD HR without Mercury	500-15,000	Sulfide LR	0.02-1.00
Color	15-1000	Surfactants	0.5-8.0
		Tannin	0.2-10.0

Methods Quick Reference Guide

Test	Method	Number	DR 6000 Range	DR 6000	DR 1000	DR 1000 w/ DR 1000	DR 1000	DR 1000	Product Catalog Item #	Product Number
Lead	Lead/alk Fast Column Extraction	8317	5 - 150 µg/L	*	*	*	*	*		23750.00
Lead	Dithione	8333	3 - 300 µg/L	*	*	*	*	*		22-40100
Lead (TNTplus)*	PAR	10216	0.1 - 2.0 mg/L	*	*	*	*	*		TNT860
Manganese, LR	PAR	8149	0.005 - 0.700 mg/L	*	*	*	*	*		2681700
Manganese, HR	Periodate Oxidation	8334	0.1 - 20.0 mg/L	*	*	*	*	*		24300.00
Mercury	Cold Vapor Mercury Concentration	10365	0.1 - 2.5 µg/L	*	*	*	*	*		2688300
Methylethylketoxime (MBKO)	Iron Reduction	8140	15 - 1000 µg/L	*	*	*	*	*		24-466.00
Molybdenum, Molybdate, LR	Ternary Complex	8169	0.02 - 3.00 mg/L	*	*	*	*	*		24-404.00
Molybdenum, Molybdate, HR	Microspectroscopic Acid	8336	0.2 - 40.0 mg/L	*	*	*	*	*		2604100
Molybdenum, Molybdate (Ascorbic), HR	Microspectroscopic Acid	8336	0.2 - 40.0 mg/L	*	*	*	*	*		—
Nickel	PAR	8150	0.005 - 1.000 mg/L	*	*	*	*	*		26916.00
Nickel	Heptoxime	8337	0.02 - 1.80 mg/L	*	*	*	*	*		22-495.00
Nickel (TNTplus)†	Dimethylglyoxime	10220	0.1 - 6.0 mg/L	*	*	*	*	*		TNT866
Nitrate, Nitrogen, LR	Cadmium Reduction	8192	0.01 - 0.50 mg/L	*	*	*	*	*		24208.00
Nitrate, Nitrogen (TNTplus), LR	Dimethylphenol	10206	0.25 - 13.5 mg/L	*	*	*	*	*		TNT836
Nitrate, Nitrogen, HR	Cadmium Reduction	8171	0.1 - 10.0 mg/L	*	*	*	*	*		2106160
Nitrate, Nitrogen (Ascorbic), HR	Cadmium Reduction	8171	0.1 - 10.0 mg/L	*	*	*	*	*		26110.25
Nitrate, Nitrogen	UV Screening	10349	0.1 - 10.0 mg/L	*	*	*	*	*		—
Nitrate, Nitrogen (Test 'N Tube), HR	Chromotropic Acid	10320	0.2 - 20.0 mg/L	*	*	*	*	*		2608345
Nitrate, Nitrogen, HR	Cadmium Reduction	8339	0.3 - 30.0 mg/L	*	*	*	*	*		2106160
Nitrate, Nitrogen (Ascorbic), HR	Cadmium Reduction	8339	0.3 - 30.0 mg/L	*	*	*	*	*		26110.25
Nitrate, Nitrogen (TNTplus), HR	Dimethylphenol	10206	5 - 35 mg/L	*	*	*	*	*		TNT836
Nitrite, Nitrogen, LR	Diazotization	8507	0.002 - 0.200 mg/L	*	*	*	*	*		2107160
Nitrite, Nitrogen (Ascorbic), LR	Diazotization	8507	0.002 - 0.200 mg/L	*	*	*	*	*		26120.25
Nitrite, Nitrogen (Test 'N Tube), LR	Diazotization	10370	0.003 - 0.500 mg/L	*	*	*	*	*		2608345
Nitrite, Nitrogen (TNTplus), LR	Diazotization	10207	0.015 - 0.600 mg/L	*	*	*	*	*		TNT836
Nitrite, Nitrogen (TNTplus), HR	Diazotization	10237	0.4-6.0 mg/L	*	*	*	*	*		TNT840
Nitrite, Nitrogen, HR	Ferrous Sulfate	8153	2 - 250 mg/L	*	*	*	*	*		21076.60
Nitrogen, Ammonia (See Ammonia, Nitrogen)										
Nitrogen, Total (Test 'N Tube), LR	Vanadate Digestion	10371	0.5 - 25.0 mg/L	*	*	*	*	*		2672245
Nitrogen, Total (TNTplus), LR	Vanadate Digestion	10238	1 - 16 mg/L	*	*	*	*	*		TNT836
Nitrogen, Total (TNTplus), HR	Vanadate Digestion	10335	5 - 40 mg/L	*	*	*	*	*		TNT827

<http://www.lamotte.com/>

<http://www.hach.com/>



Field Gas Chromatography Can be Very Effective

Principle : Gas Chromatographic Separation - PID

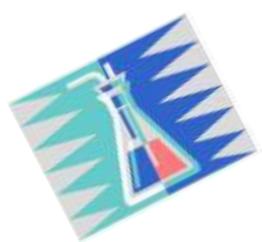


Source: Photovac

Principle : Gas Chromatographic Separation - TCD



Source: Agilent

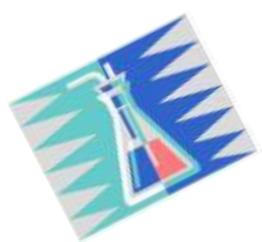


Portable GC/MS Provides Separation and Mass Spectra to give Highest Analytical Power



Principle : Gas
Chromatographic
Separation – Mass
Spectra Detection

Source: Inficon



QA/QC in the Field

- **If doing field analysis – keep good records use appropriate analytical procedures**
- **Representative sampling**
- **Reduce contamination of sample**
 - decontaminate sampler
- **Keep good records**
- **Label all samples thoroughly**
- **Preserve samples as appropriate**
- **Ship or transport to the lab**

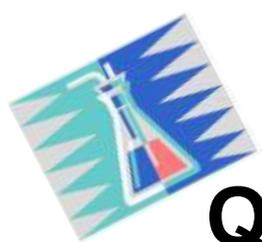


Quality Assurance Means Getting the Best Data at a Reasonable Cost



- **P** - Precision
- **A** - Accuracy
- **R** - Repeatability
- **C** - Completeness
- **C** - Comparability





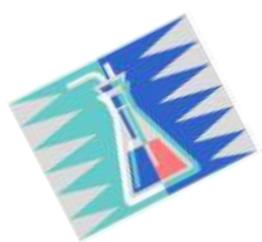
Quality Control Methods: QC Samples

- **Greater than 50% of all errors found in environmental analysis can be directly attributed to incorrect sampling**
 - Contamination
 - Improper preservation
 - Lacking representativeness
- **Quality control (QC) samples are a way to evaluate the PARCC parameters.**



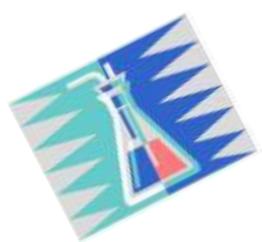


Class Exercise



Special Example - Contaminated Water

- **First screen using public knowledge – “What has happened here?”**
- **Suspended solids**
- **Test for harmful microorganism – coliform bacteria (MPN or colilert test)**
- **BOD and COD**
- **Metals screening – more advanced (Flame AA)**
- **Pesticide screening – most advanced (GC/MS)**



Common Measurements for Water Quality

Alkalinity – Acid neutralizing capacity

Acidity – Base neutralizing capacity

Hardness – Ca^{+2} , Mg^{+2} salts

pH – Acidity

Dissolved organic matter – humic-fulvic acids

Total organic carbon

Salinity – Na^+ Cl^-

Cations – Na^+ , K^+ , Ca^{+2} , Mg^{+2} ,

Anions – Cl^- , HCO_3^- , SO_4^{-2}

Heavy metals – Fe , Cu , Pb , As , Cd

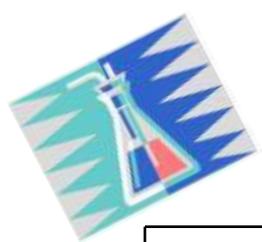


Source: Pakistan Council of Research in Water Resources



Typical Wastewater Contaminants

- **Bacteriological,**
 - **Vibrio Cholerae, Campylobacter, Salmonella , Shigella,**
- **Viruses**
 - **Hepatitis A, Norovirus**
- **Protozoan**
 - **Giardia, Cryptosporidium, Entamoeba**
- **Biological oxygen demand**
 - **Organic matter causes algae to thrive and deplete dissolved oxygen**
- **Nutrient removal to prevent eutrophication**
 - **Nitrogen and phosphorus from waste, and agriculture**



What Does Wastewater Look Like?

Measurement	Value	Units
Total Suspended Solids (TSS)	210	mg/L
BOD	190	mg/L
TOC	430	mg/L
COD	140	mg/L
Organic Nitrogen	15	mg/L
Free Ammonia	25	mg/L
Nitrite/Nitrate	0/0	mg/L
Phosphorous	7	mg/L
Total coliform	10^7 - 10^9	colonies/100mL
Fecal coliform	10^4 - 10^6	colonies/100mL
Cryptosporidium oocysts	0.1-10	no./100mL
Giardia lamblia	0.1-100	no./100mL

Source: Wastewater Engineering, Metcalf and Eddy- medium strength WW





Routine Bacterial Testing Consists of Measuring Indicator Organisms

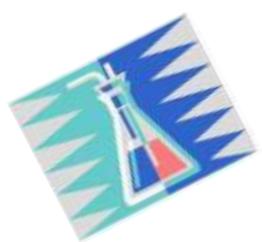
- Testing for pathogens directly is expensive and hazardous
- Indicators from the family *Enterobacteriaceae* are used (*E. coli*, *Citrobacter*, *Enterobacter*, *Klebsiella*)
- Grow bacteria on a specified media and count the number of colonies after incubation
- Other assays are used and are approved by the US EPA (Colilert shown-SOP on CD)





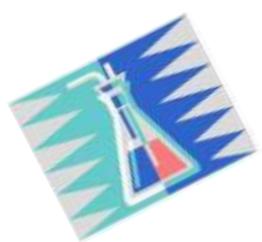
Sampling Equipment





Appropriate Sampling Equipment is Essential to get Acceptable Samples

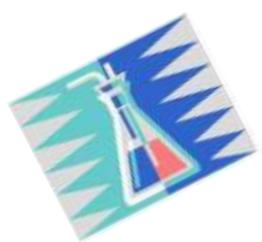
- **Air Sampling**
 - Continuous / compositing
 - Spot sampling
- **Water Sampling**
 - Continuous / compositing (often at treatment works)
 - Spot sampling
- **Soil Sampling**
 - Spot sampling (“hot spots”)
 - Grid sampling
 - Shallow or deep sampling



Sampling Tools - Representative and Easily Cleaned

Guiding principle - Sample tool should get a representative sample of the environment and be easily decontaminated with no sample carryover.

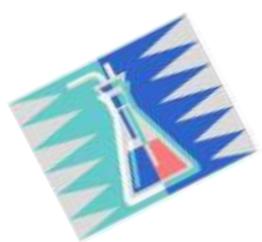
- **Air-** (adsorption/ desorption – Summa canister – tedlar- gas bulbs- impingers)
- **Water-** (sampling vials, groundwater and surface water)
- **Soil-** (augers, penetrometers, shovels, riffers)
- **Passive-** sampling techniques (adsorbents)
- **Special Matrices-** multilayer, tissue, plant



US EPA Criteria Air Pollutants

- Carbon Monoxide (CO)
- Lead (Pb)
- Nitrogen Dioxide (NO₂)
- Ozone (O₃)
- Sulfur Dioxide (SO₂)
- Particulate Matter (PM)





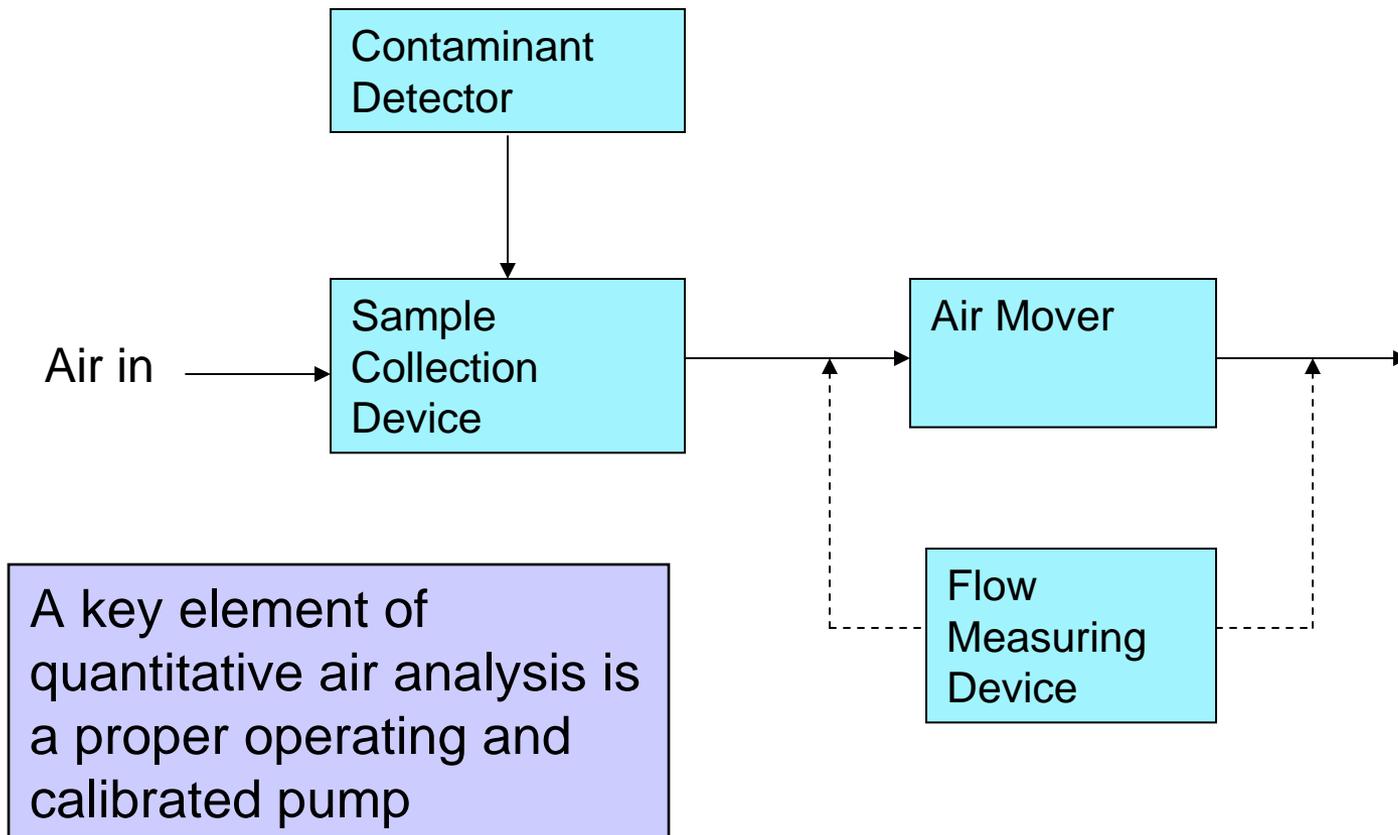
Air Quality is Measured using a Variety of Techniques

- CO – nondispersive IR
- Pb (Lead) – Atomic absorption spectrometry
- NO₂
 - Continuous emission monitor
 - Impingers
- Ozone monitors
 - Impingers
 - UV spectroscopy
 - IR
 - chemiluminescence
- SO₂
 - EPA Method 6 impinger-titration
 - chemiluminescence
- Continuous particle analyzers



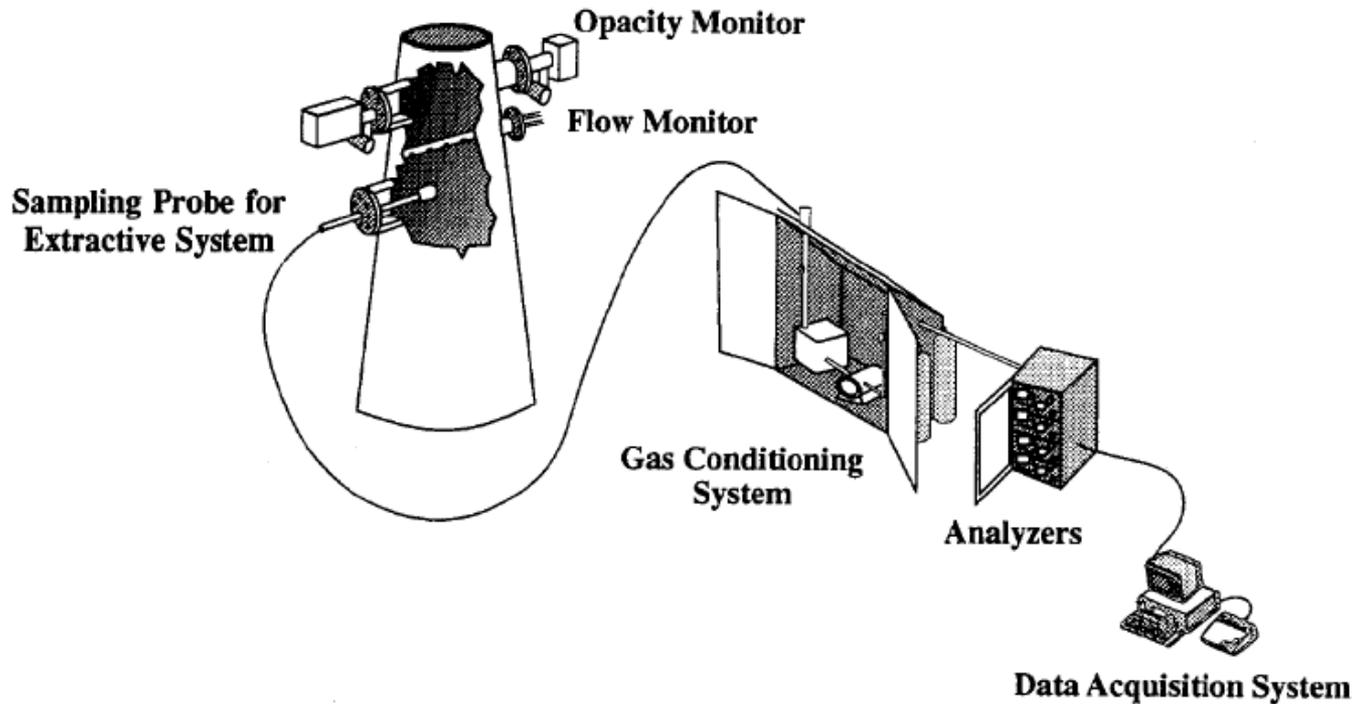


Basic Unit Operations of Air Sampling





Continuous Emissions Monitoring



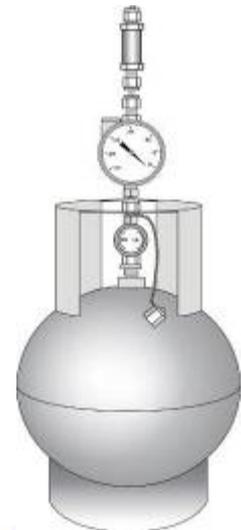
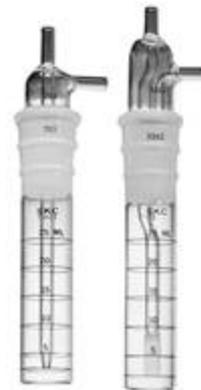
Source: An operators guide to eliminating bias in CEM systems EPA/430/R-94-016, Nov 1994

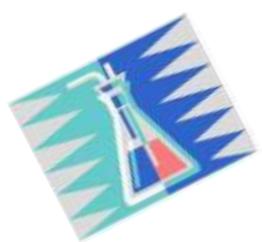


Air Sampling Equipment

Adsorption/ desorption – Summa canister – tedlar- gas bulbs- impingers)

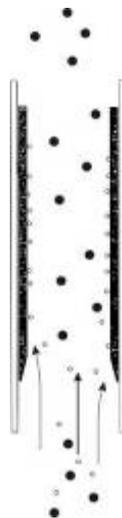
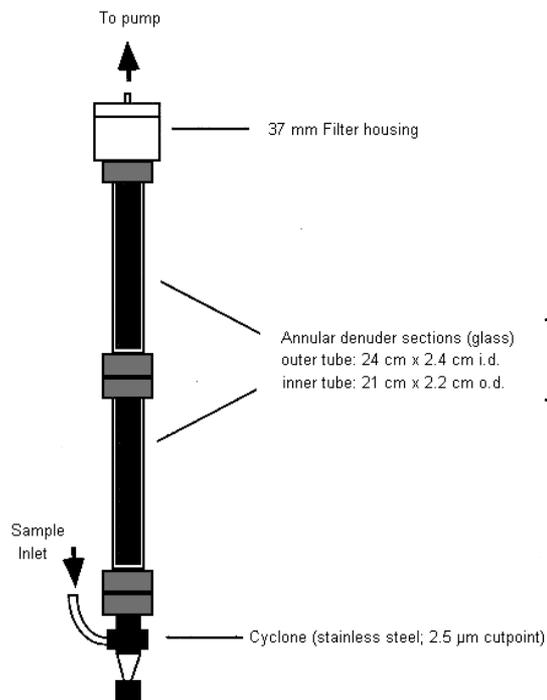
- stainless steel (e.g., passivated canisters)
- Glass – impingers, bubblers
- Glass bulbs
- Pliable plastics (e.g., Mylar®, Tedlar®, Teflon®, aluminized PVC)
- Adsorbent tubes





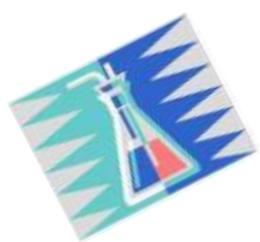
Semivolatile Organic Compounds in Air

- High volume air sampler with denuder and polyurethane foam (PUF) adsorbent

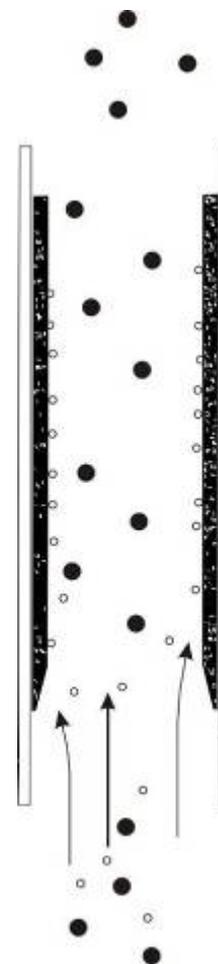
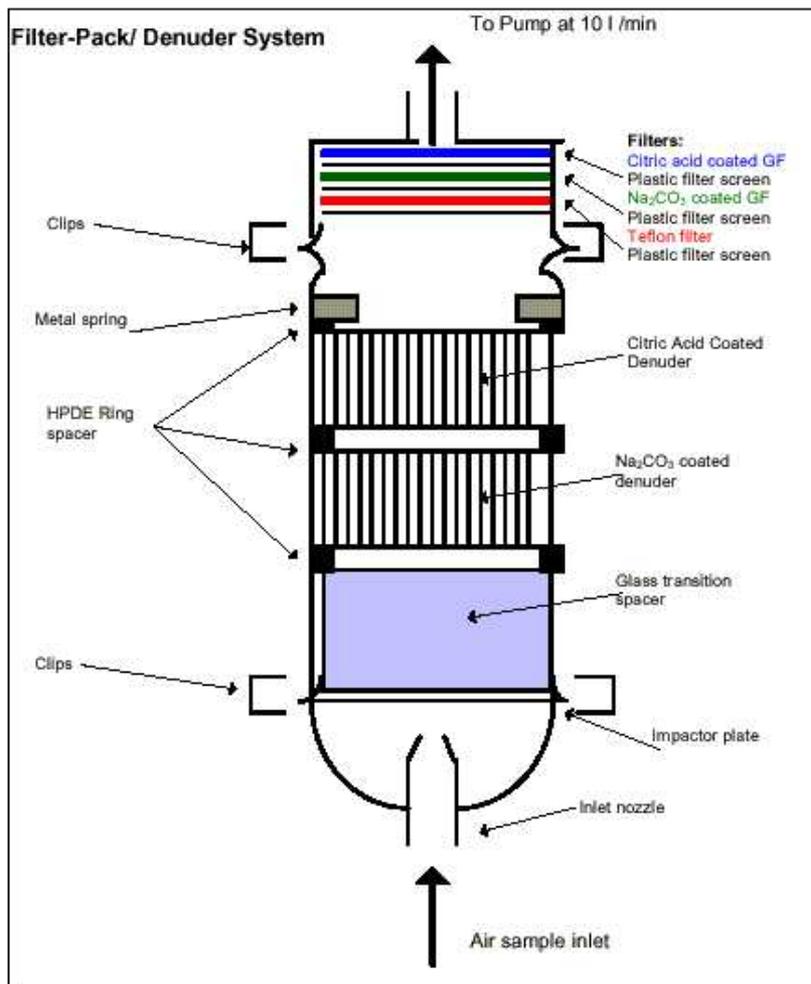


Denuder cross section

Denuders and adsorbents are often extracted for subsequent GC/MS analysis

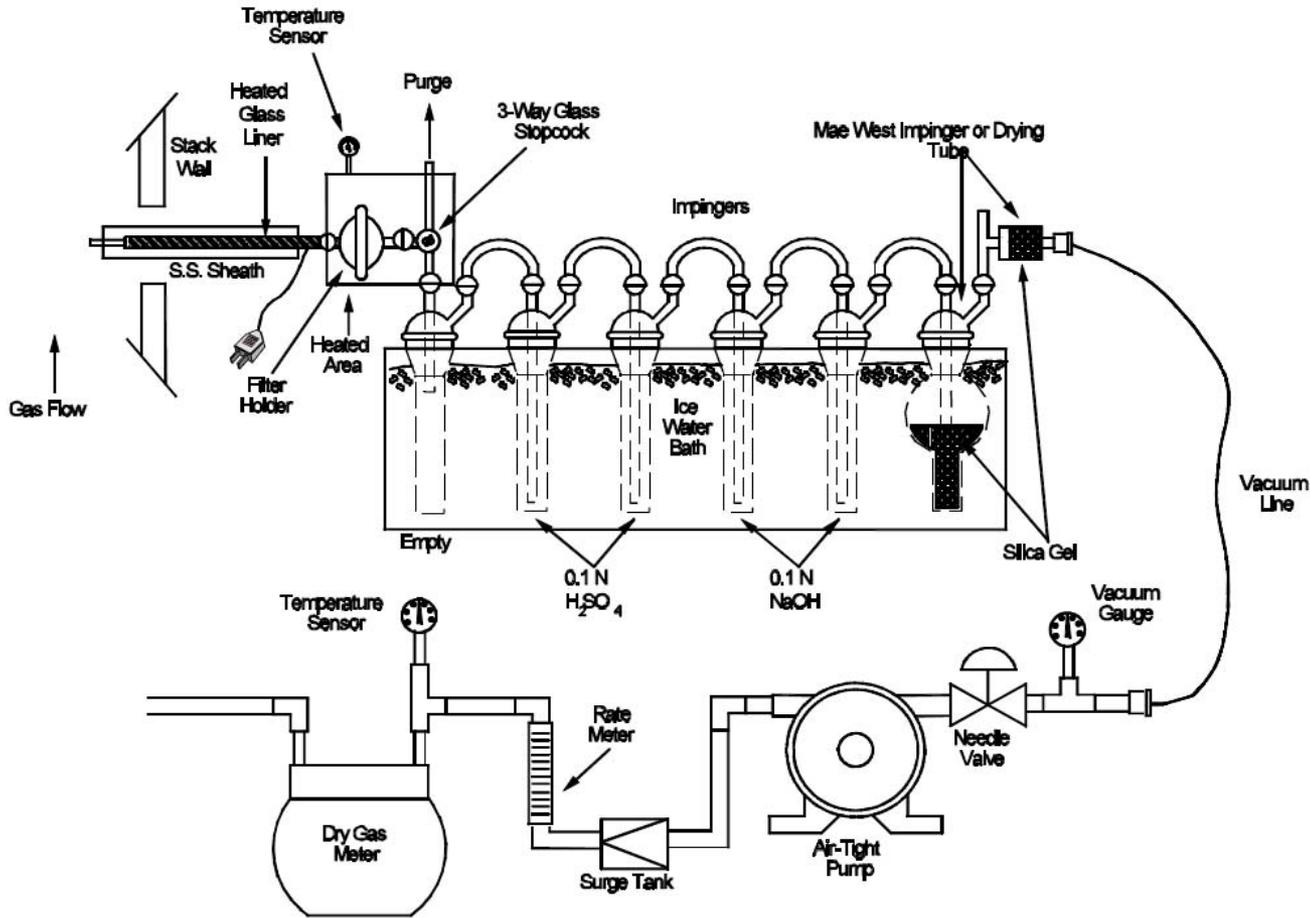


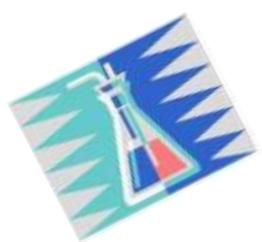
Denuder Application for Inorganic Compounds in Air





EPA Method 26 – HCl-Halides-Halogens





Most Field Activities Involve Soil and Water Matrices





Water Sampling Equipment

Groundwater Samplers

- Bailers
- Bladder pumps
- Peristaltic pumps
- Piston pumps
- Gear pumps
- Air-lift pump



Bailers

Surface water Samplers

- Dip sampler
- Peristaltic pumps
- Van Dorn
- Kemmerer
- Collection bottles



Van Dorn



Kemmerer

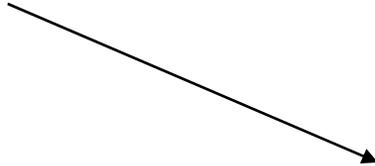


Automated or Composite Sampling is used for Basic Water and Wastewater

**Peristaltic sampler
(automatic vials)**

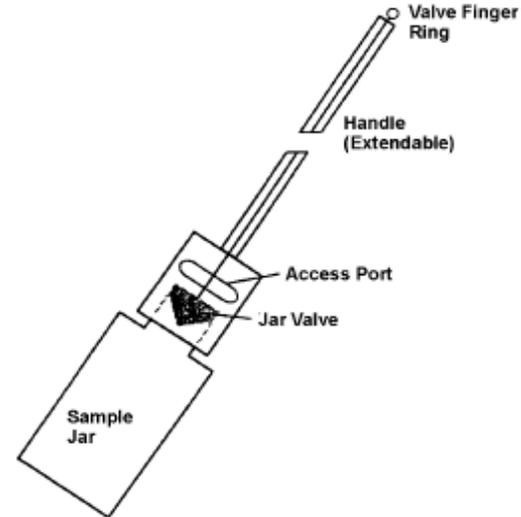
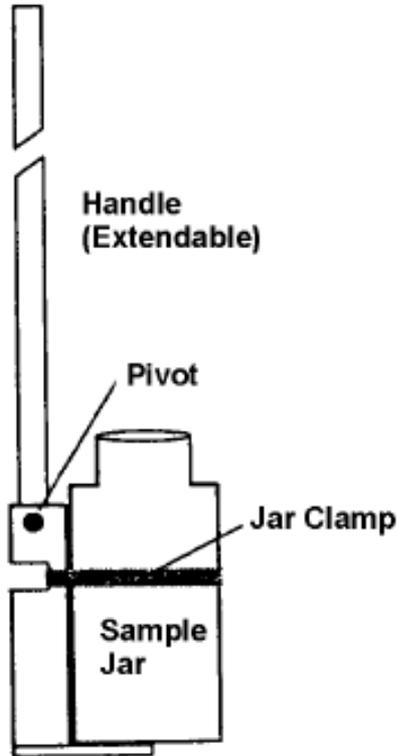


**Collect composite or
discrete samples**





Specialized Water Sampling Vials are Often Used



Source: RCRA Waste Sampling Draft Technical Guidance EPA530-D-02-002 August 2002



Water Sampling Containers are Filled in the Field

Polypropylene vials for microbiological tests for water and wastewater



Pre-cleaned high density polyethylene (HDPE) wide mouth 1 L bottles for metals and water parameters (Ca, Mg, Cl, SO₄...)



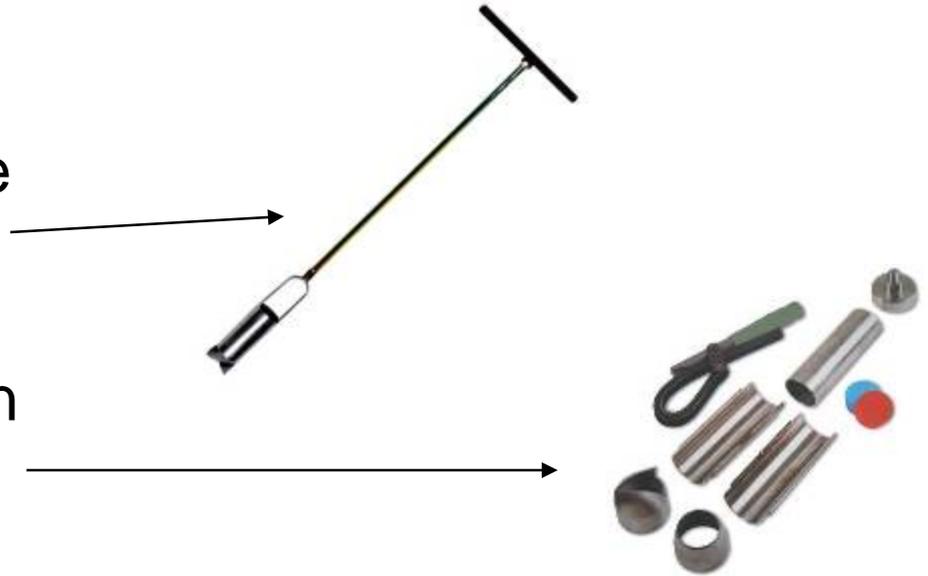
40mL Borosilicate vials with Teflon/silicone septa for Volatile Organic Analysis (VOA). No headspace or bubbles are allowed.





Soil Sampling Equipment

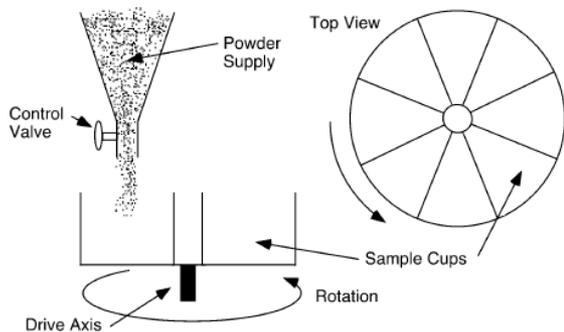
- Consolidated soils can be sampled with an augers
- Unconsolidated cores can be sampled with closed bit augers
- Shallow samples can be taken with shovels





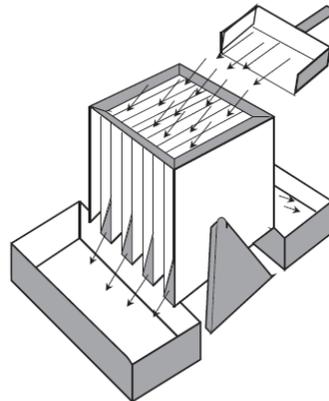
Solid Sampling is Prone to Segregation and Discrimination

Spinning Riffler



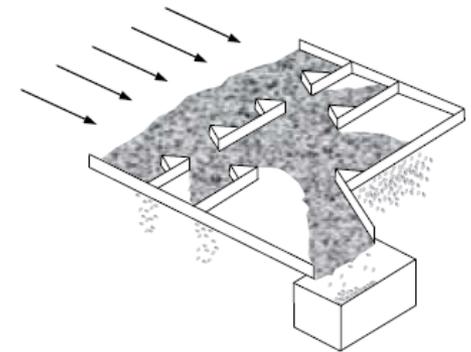
Lowest segregation

Sample Splitter-chute separation

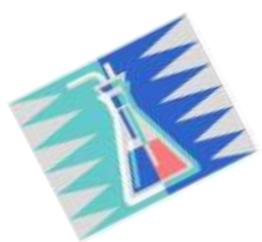


Must have even number of chutes

Table Sampler

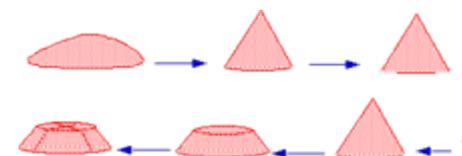


Inclined plane with sample split



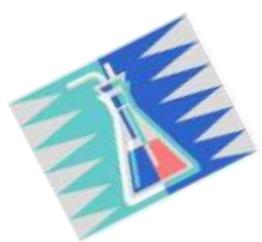
Sampling Errors Associated with Different Techniques

Method	Estimated max error %
Cone & Quartering	22.7
Scoop Sampling	17.1
Table Sampling	7.0
Chute Riffler	3.4
Spinning Riffler	0.42



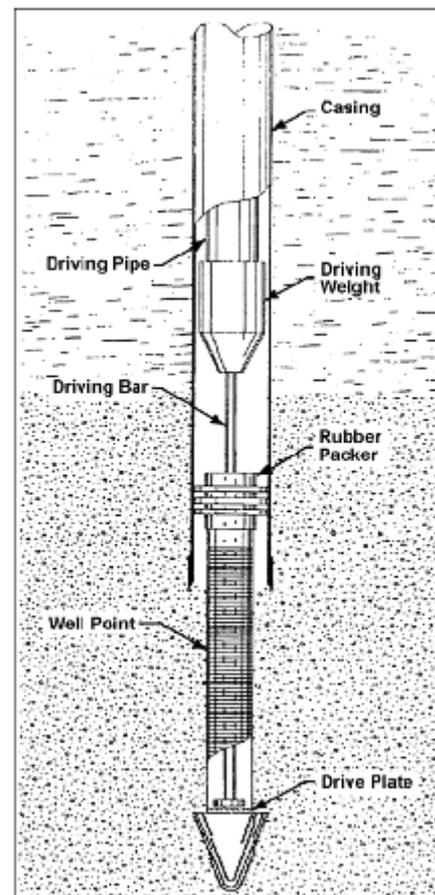
Cone and Quartering Technique

Source: T. Allen Particle Size Measurement Chapman and Hall 4th Edition 1993 Page 39. Figures based on a 60:40 sand mixture.



Direct Push Techniques - Cone Penetrometers, Geoprobe

- Less expensive than drilling
- Less disruptive to area
- Can be combined with measurement
 - Soil conductivity
 - Laser induced fluorescence
 - Soil gas sampling
- Shallower “refusal” than drilling



Source: ASTM (2001e)



Geoprobe Pushes Sample Tube Underground

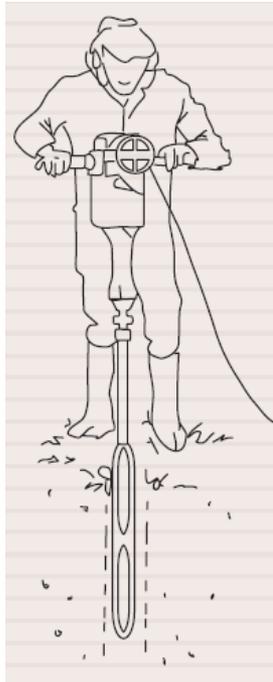


- Can get a soil sample
- Can sample for soil vapor
- Can get a groundwater sample
- Good for shallow applications



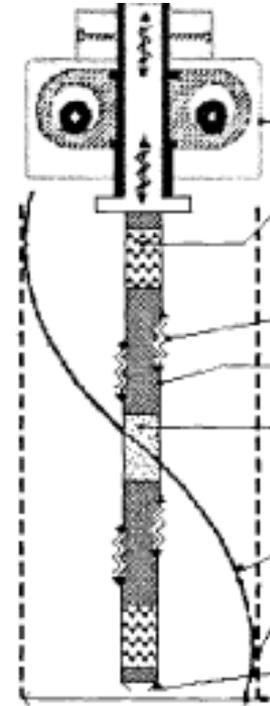


Soil Sampling Shallow and Deep

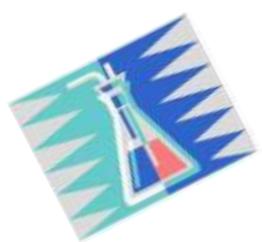


Shallow sample with percussion hammer

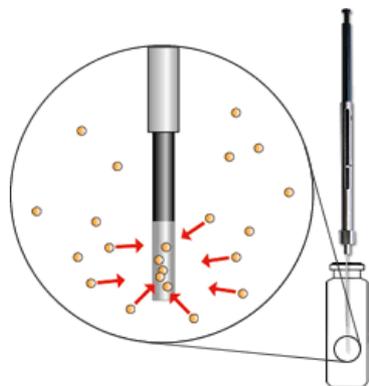
Deep samples - Air rotary drilling, hollow stem augers are used routinely.



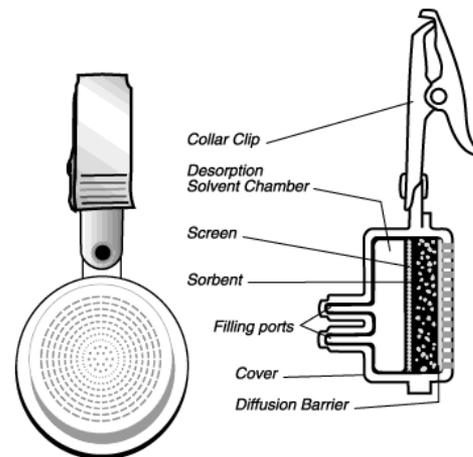
Deep samples - Sonic drilling is an advanced technique



Passive (Diffusive) Sampling uses Badges or Solid Phase Microextractors (no pumping)



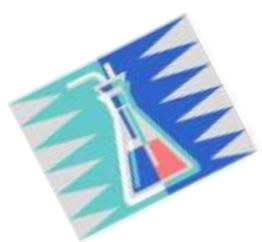
SPME- Supelco



SKC Incorporated

Can be inserted into water sample from a baler
Solvent extracted or thermally desorbed

Can be worn on clothing



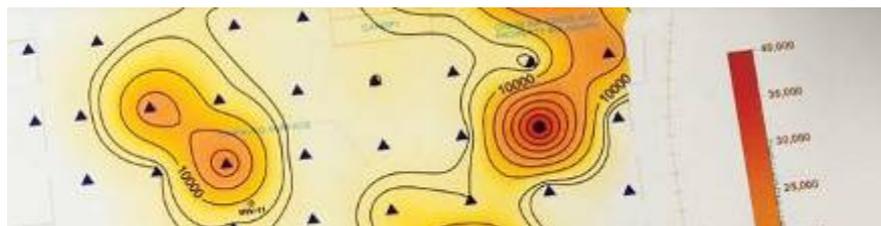
Passive Samplers are also Used to Characterize Soil Environments



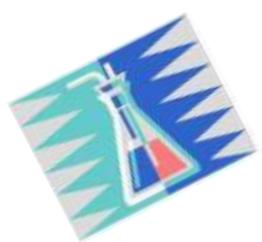
Beacon Environmental



Gore Sorber



Typically carbon adsorbents are submersed and solvent / thermal extracted for GC/MS for soil gas survey



Special Sample Matrices Require Special Sampling

- Headspace for chemical liquids
- Sampling drums
- Multilayered liquids
- Sediments and slurries
- Agricultural products
- Animal and plant tissues
- Surface seawater (for oil sheens)





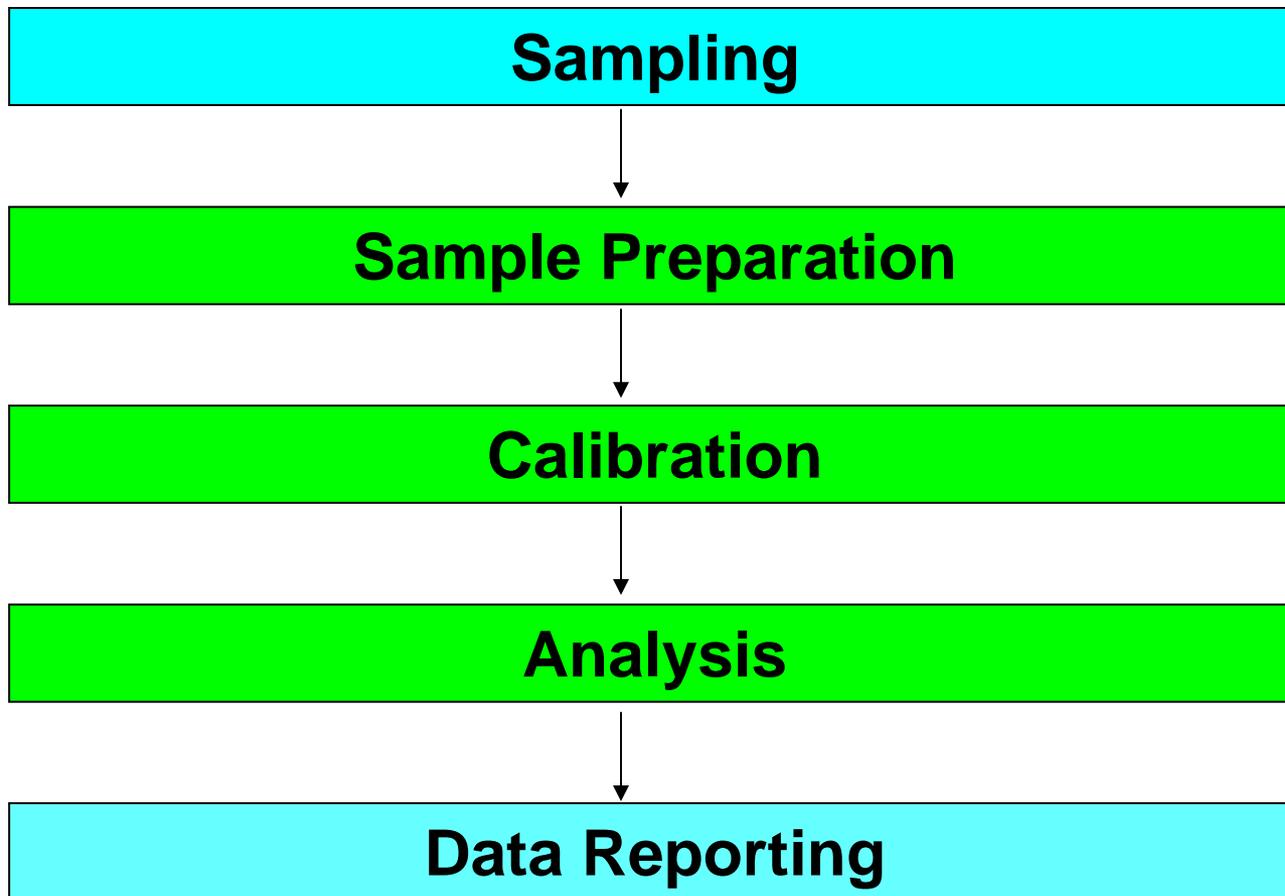
Method Selection and How It Affects Cost and DQO Results



*Pick Methods Carefully or
You'll Pay the Price Later*



Basic Steps of Environmental Analysis (Method selection)





Method Selection

Selection of methods for analysis is critical.

Many projects simply select old methods used in the past instead of those that would be best for a project's specific needs, time and budgets.



How Are the “Best” Methods Selected and Who Selects Them?

- **Method selection is sometimes a complex task**
 - **Considerations must be balanced with the needs of a project:**
 - **Analytical sensitivity (detection levels)**
 - **Selectivity (specific for a chemical)**
 - **Interferences**
 - **Accuracy & precision**
 - **Cost**
- **Comparisons among several alternate methods when using the full and complete methods text is slow and difficult.**
 - **Methods have different formats, details, and often have long detailed descriptions.**
 - **Method summaries are now available – much easier to use for these kinds of comparisons.**





Fixed Laboratory Methods vs. Field Analytical Methods (FAMs)



Definitive and Screening Methods

- Fixed laboratory methods are often described as “definitive” methods.
 - Assumption that they produce definitive data is **wrong**.
- Field methods are often described as “screening” methods.
 - Assumption that they can not produce definitive data is **wrong**.
- Quality of data produced by a method is dependent on the analyte, the matrix, and the method itself (sample preparation, instrument, etc.).



Screening Methods

- **Screening methods produce lower quality data.**
 - Often less selective and give data on groups of analytes
 - May be subject to interferences (matrix or other factors).
 - Affects confidence in analyte identification.
 - Incorrect identification → false positives/negatives.
 - May be less accurate or precise than fixed lab methods.
 - Affects confidence in analyte quantification.
 - When used properly, can reduce analytical costs.
- **Field analytical methods were screening methods.**
 - Many are now sensitive, selective, and quantitative or semi-quantitative.



Benefits of Field Analytical Methods

- **Rapid, on-site results vs. fixed lab data received several days or weeks later.**
 - Important for making decisions in the field.
- **Less expensive**
 - Cheaper instruments, less operator training, less support
- **Often designed to have low false negatives**
 - Do not miss pollutants if they are present at “action” levels
 - When presence is indicated results are verified by fixed lab
- **Mixture of field & fixed lab methods may be optimum**





Project Requirements are the Same Whether Fixed or Field Methods Used

- **Whether fixed-lab or field-based, the following criteria apply:**
 - **Use qualified staff that are properly trained and supervised.**
 - **Document standard operating procedures (SOPs) and adhere to them, *BUT* be able to change them with documentation as needed.**
 - **Provide correct QC samples for all necessary sampling and analysis method performance criteria including sufficient numbers to meet desired confidence levels.**



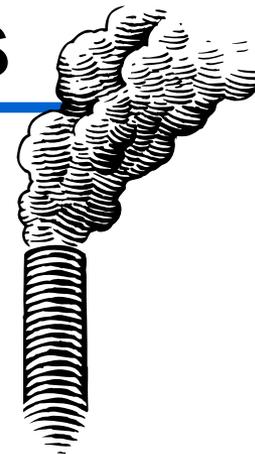
Overview of Various Methods





There are Methods for Different Media and Matrices

- Some are specific for drinking water matrices (US EPA 500 series methods)
- Some are specific for industrial wastewaters (US EPA 600 series methods)
- Some are specific for ambient air (TO-1 to 14)
- Some are specific for indoor air (NIOSH)
- Some are applicable for a variety of media and matrices such as soils, sludges, solid and liquid wastes, etc. (EPA SW-846 methods)
- Newer field analytical methods are very useful





There are Methods for the Major Types of Pollutants

- ***Metals*** (arsenic, chromium, mercury, lead, etc.)
- ***Other inorganic chemicals*** (cyanides, nitrates, phosphates, etc.)
- ***Volatile organic chemicals*** (TCE, benzene, chloroform, vinyl chloride, etc.) – (often abbreviated as **VOCs** or **VOAs**)
- ***Semivolatile organic chemicals*** (pesticides, PCB, dioxins, phthalates, Polycyclic Aromatic Hydrocarbons (PAHs), etc).
- ***Nonvolatile organic chemicals*** (herbicides, haloacetic acids, pharmaceuticals, dyes, etc.).



Principal Method Selection Process





First Criteria For Method Selection

- **Selection criteria developed with systematic planning process are matched with available methods.**
 - **List all potentially appropriate methods for pollutants and media of interest.**
 - **Compare existing methods capabilities to project requirements for sensitivity and selectivity.**
 - **May be multiple “action” (regulated) levels for an analyte**
 - **e.g. More sensitive methods needed for leading edge of groundwater plume than in a source area where concentration levels are high.**
 - **e.g. Do individual PCB isomers need to be identified if they exist at a field site?**





How Does Method Sensitivity Affect Data?

- If a method is selected that is not very sensitive to the target chemicals, they may not be detected even though they are present.
 - The result is a *false negative* conclusion.
- In addition, the concentration level at which they can be measured quantitatively will be higher than if a more sensitive method was used.
- Most regulatory decisions depend on reports that show presence of pollutants above a regulated concentration. **False negatives would cause pollutants to not be regulated when they should be.**





Detection vs. Quantification

- There are separate and distinct issues regarding detection and quantification of chemicals in samples at very low concentrations.
 - Rules for “detection” of analytes are different from rules for determining the “concentration” of that same analyte.

Because analyses at very low concentration levels come very close to the limit of a method’s detection ability.
 - Quantification levels are usually calculated as multiples of detection levels for a given analyte. Conversely, detection levels for an analyte are experimentally determined.
 - In general quantification levels are **10X** detection



EPA's Method Detection Limit (MDL)

EPA's preferred procedure is to experimentally determine a MDL by analyzing 7 replicate spiked samples in reagent grade water and calculate MDL based on measurements of precision.

Using this procedure is supposed to provide greater than a 99% confidence that the target analyte, when detected at or above this concentration, will be greater than zero (meaning that it really was present – not a false positive).

- Source: U. S. EPA, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under Clean Water Act: Final Rule and Proposed Rule," 40 CFR Part 136, October 26, 1984, Federal Register, Part VIII.



Limit of Quantification (LOQ)

- **American Chemical Society (ACS) defines the Limit of Quantification (LOQ) as the level *above* which quantitative results may be obtained with a specified degree of confidence.**
 - **LOQ was recommended as 10 standard deviations above background concentration levels.**
 - **Provides 99% probability that the true concentration of the analyte is within plus or minus 30% of the true concentration.**
 - **The LOQ is thus generally set at 3.3 times the LOD or MDL (i.e., $3.3 \times 3 \text{ SD} = 10 \text{ SD}$).**

Source: L. H. Keith, in “Principles of Environmental Analyses,” Anal. Chem., 52, pp. 2210-2218, 1983





Method Selectivity

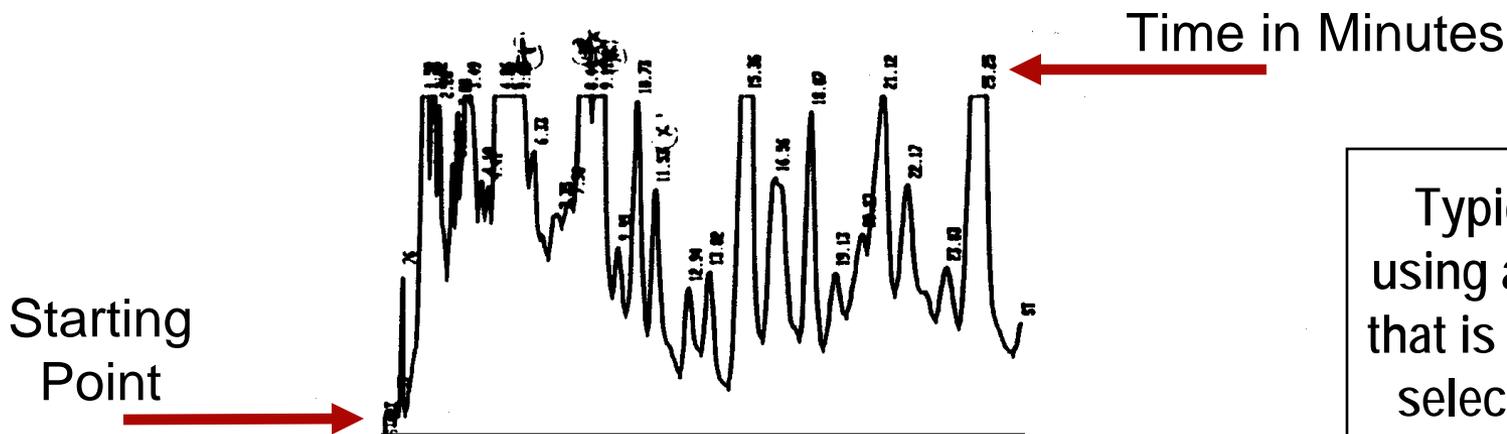


*How Method Selectivity
Affects Data*



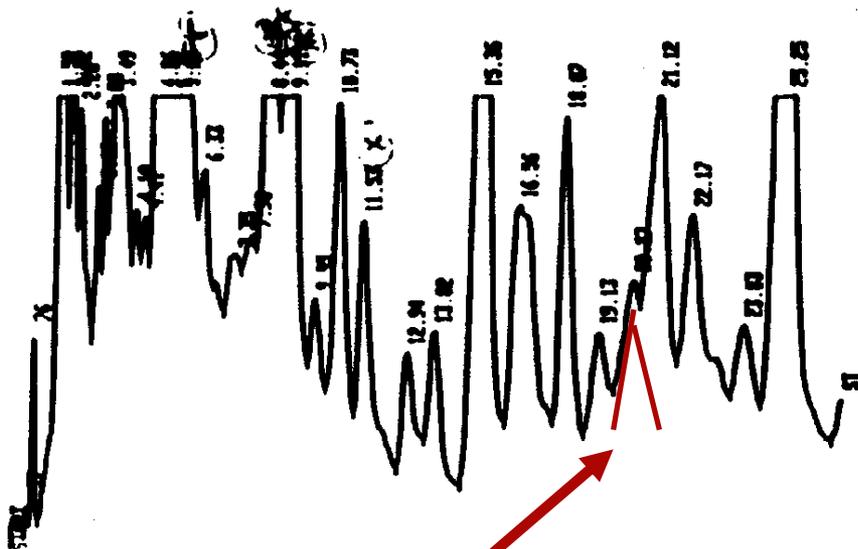
Where is the Chemical Pollutant?

- This is the way a chemist typically views initial data.
- It is called a chromatogram and each peak represents a chemical.
- Note the many chemicals present and that some chemical peaks overlap one another.
- There is only one chemical of interest - others are "background."





It Appears as a Small “Peak” Partially Obscured by Other Chemicals



Here is the chemical of interest, partially obscured by other chemicals in the sample.

Do you see the problem?

The other chemicals also appearing as peaks may or may not be pollutants.

They may be naturally occurring “background” compounds or they may be contaminants introduced during sample preparation or analysis.



Secondary Method Selection Process





Secondary Criteria For Method Selection

- Once potential methods have been selected for further consideration based on method sensitivity and selectivity, then other criteria are considered:
 - Precision and accuracy
 - Known interferences
 - Applicability to field conditions
 - Cost
- Sometimes cost is considered first.
 - If a cheaper method provides insufficient data that have to be discarded is it still cheaper?





Sometimes Methods are Insufficient

- In spite of all the methods available a selected method may not meet criteria needed for the circumstances at a particular site because of:
 - Matrix interferences
 - Insufficient selectivity (**causing false positives**)
 - Insufficient sensitivity (**causing false negatives**)
 - Insufficient accuracy (also often **caused by matrix**)
 - Insufficient precision
- Prescriptive use of methods did not allow modification of them.





Taking Advantage of Performance Based Measurement Systems (PBMS)



US EPA's Performance Based Measurement System (PBMS)

- **Definition of a Performance Based Measurement System:**

A system that permits the use of any appropriate sampling and analytical accepted technology that demonstrates the ability to meet established performance criteria and complies with specified data quality objectives.

- Draft definition by the National Methods and Data Comparability Board 9/18/98.





Why did US EPA Start Using PBMS?



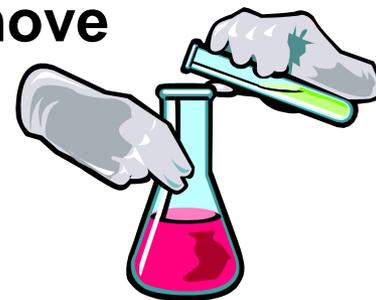
- US EPA recognized the problems of the inability to change or modify methods when they are inadequate (do not meet project requirements).
 - **PBMS** is a system implemented over 10 years ago to help solve this problem.
 - PBMS describes the quality of the data necessary for a specific use or site and then a chemist may use any appropriate method to achieve the required results.
 - Data Quality Objectives (DQOs) and Measurement Quality Objectives (MQOs) describe the quality of the data needed.





Method Changes May Be Minor

- Often minor changes can be made that will allow a method to meet project requirements.
 - Extraction procedures are often easily modified.
 - Chromatographic columns also may be changed
 - Sample clean up step may be added to remove interferences
- None of the above changes affect an instrument's detection and quantification components.
 - These have been referred to in the past as “streamlining” method modifications.





What Does PBMS Mean for Projects?

- Under PBMS, a regulated company (and its laboratory) can use any method(s) necessary to obtain data that meets the specified monitoring requirements.
- Thus, prescriptive methods are not be required - but if they provide acceptable data then labs can (and will) continue to use them.
- However, when current prescriptive methods do not provide acceptable data (or if a modification will result in cheaper data) then labs are free to modify them as long as the modified methods are validated by the laboratory.
- ***BUT the short answer is that it can save time and money while obtaining the quality of analytical data needed for your specific project.***





Summary

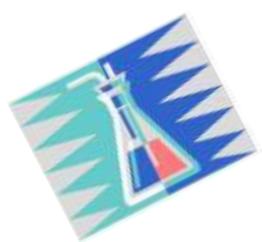
- **Method selection is a critical factor for providing analytical data for many environmental projects.**
- **Important factors include sensitivity, selectivity, accuracy, and precision.**
- **“Definitive” methods do not mean that the data will be better than data from cheaper field methods.**
- **PBMS may allow faster, cheaper, better data.**
- **Systematic planning must involve method selection (so choose carefully based on project needs).**



Laboratory Procedures

- **Sample Receipt**
- **Sample Storage**
- **Sample Preparation**
- **Instrumental Analysis**
 - **Lower Cost**
 - **Higher Cost**
- **NEMI Database**

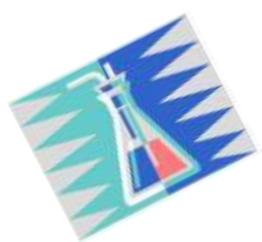




There are Many Stages in a Samples Life



- *Labeling - preservation - storage*
- *Preparation for analysis*
- *Analysis*
- *Archiving and/or disposal*



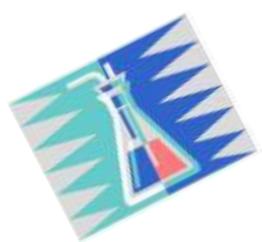
Lab Procedures - Sampling

- **Virtually all samples gathered in the field are either soil or water samples.**
- **Storage is a function of practicality as well as knowledge about the stability of unknown compounds.**
- **Lower temperatures and shorter times usually prevent sample degradation and analyte loss.**



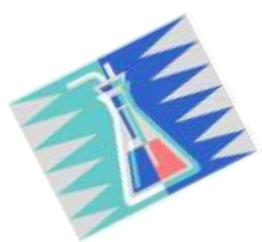
Samples are Usually Transported to the Lab in Coolers





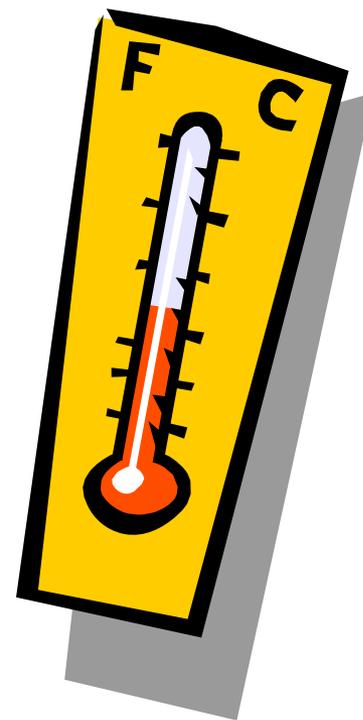
Sample Receipt

- **Sample receipt – Unpack sample container and reconcile with Chain of Custody**
- **Assign sample and QC samples to an analyst**
- **Store in appropriate location – sample refrigerator, out of direct light**
- **Document with Sample log and Sample Prep log**



Sample Storage

- **Segregate VOC samples from metal samples or other samples that could cross contaminate**
- **Keep a temperature log of the refrigerator.**
- **Do not store food items or chemicals in the sample storage refrigerator.**
- **Separate by holding time and assure holding times are met.**





Sources of Sample Loss- Volatiles

- **Sample loss through septum of vial.**
 - Most severe for the most volatile and those that are sparingly soluble. (benzene>toluene)
 - No losses when VOA vial is properly filled and capped. (**must have no headspace**)
 - Diffusion in gas is 10^5 faster in gas
- **Sample loss by microbial degradation**
- **Sample loss by chemical / physical reaction**
 - Oxidation
 - Dehydrohalogenation
 - Photolysis



Sources of Sample Loss - Semivolatiles

- **Sample Degradation**
 - Microbial
 - Oxidative
 - Photolytic
- **Polymerization**
- **Adsorption onto sampling surfaces**
- **Sample segregation**
- **Incomplete extraction**

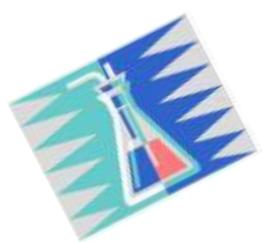




Sources of Sample Contamination

- **Improper sampling - carryover on sampling tool**
- **Exposure to contaminating solvents**
 - **Electrical tape as sealant on VOA vial**
 - **Solvent extraction laboratories in proximity**
- **Degradation of sample- reaction products formed**
 - **Bacterial**
 - **Oxidative**
 - **Photolytic**





Sample Preparation - Reagents

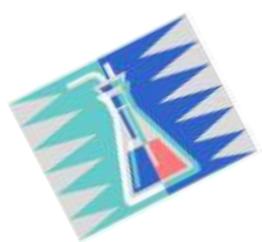
- **Deionized Water** – Typical Reagent Grade
 - 18 M Ω -cm Specific resistance
 - <0.1mg/L TOC
- **HPLC and GC solvents**
 - Spectral grade
 - Pesticide grade
- **Acids** – Spectroscopic Grade
- **Gases** – Ultra high purity (Carrier gases)



Sample Preparation – Water

(many are method specific)

- **Metals Analysis** - Water sample stability can be enhanced by preparation of an extract
 - Extraction is an acid pretreatment often referred to as a digestion
- **Semivolatile Organic Analysis** – Extraction
 - Liquid - liquid extraction
 - Separatory funnel
 - Derivatization



Sample Preparation – Soil

(many are method specific)

Metals Analysis –

Soil samples are digested in acid

Microwave Digestion

Grinding- Ball mill, Ring pulverizer

Borate Fusion

Semivolatile Organic Analysis – Extraction

Liquid - liquid extraction

Separatory funnel

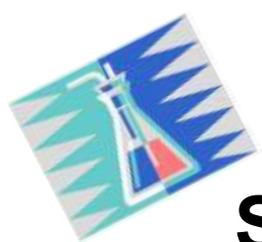
Soxhlet Extraction

Ultrasonic Assisted Solvent Extraction

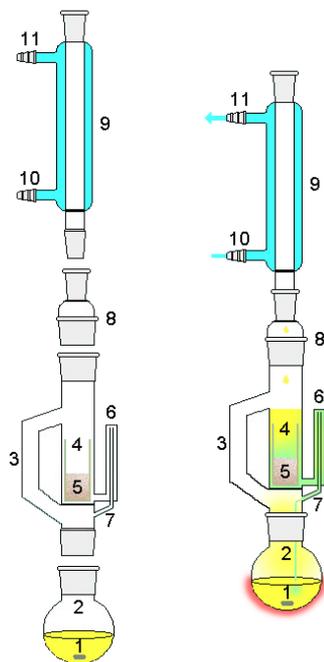
Accelerated Solvent Extraction

Supercritical Fluid Extraction

Derivatization



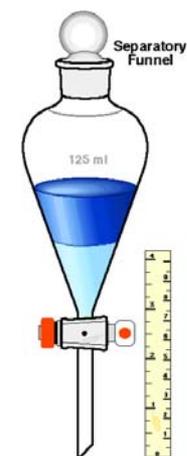
Sample Extraction Can Take Many Forms



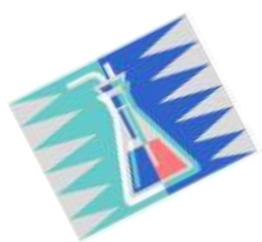
Soxhlet extraction



Accelerated solvent extraction

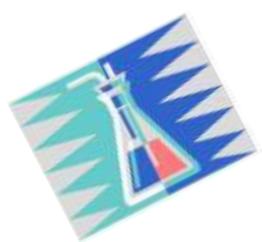


Separatory funnel



Standard Preparation

- **Standards Deionized Water – Typical Reagent Grade**
 - **18 M Ω -cm Specific resistance**
 - **<0.1mg/L TOC**

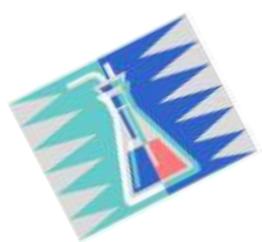


Many Inexpensive Tools are Available for Water Testing

- pH
- Suspended Solids
- Dissolved Oxygen
- Total Organic Carbon
- Turbidity / Conductivity
- Bacterial testing - Coliforms
- Colorimetry / Spectrophotometry – Metals
- Flow Injection Analysis

Lower Cost

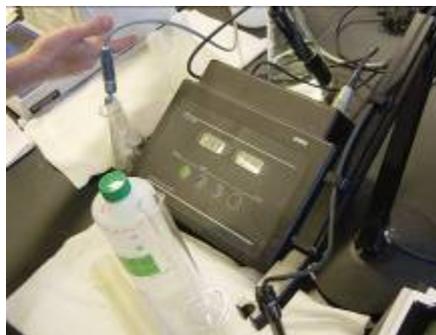




Benchtop Instrumentation can be Purchased for Relatively Low Price



**Portable
digital
titrator**



Conductivity
pH
Alkalinity
Hardness



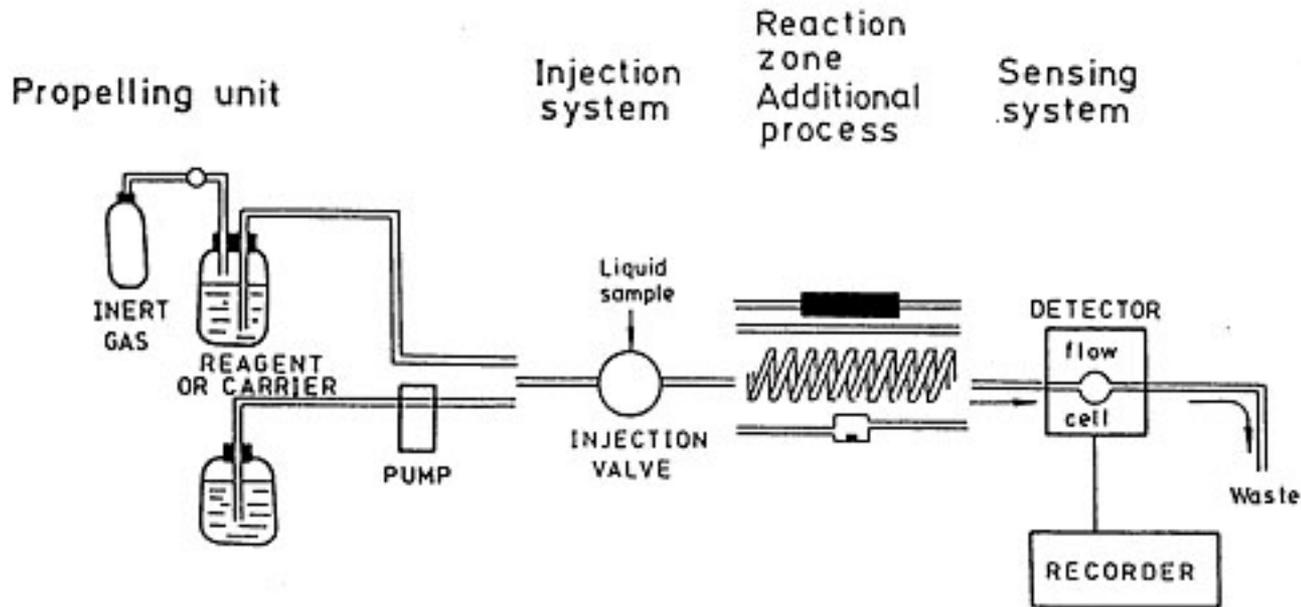
Spectrophotometry
Fe, Cu, Hg, Pb
Silica
Total nitrogen



**Dissolved
Oxygen**



Flow Injection Analysis (FIA) is a Powerful Tool for Large Sample Loads



Basic water chemistry - sulphate, sulphide, chloride, residual chlorine, nitrite, nitrate, phosphate, silicate, cyanide and alkalinity



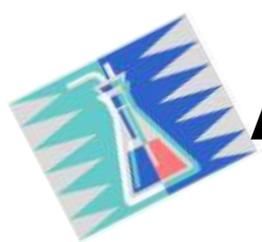
A Large List of FIA Water Chemistries are Accepted by EPA

USEPA Accepted Methods

List of QuikChem® Methods considered "Permitted Options in the Accepted Methods" for the National Pollutant Discharge Elimination (NPDES) program of the U.S. Environmental Protection Agency (USEPA):

Alkalinity		
10-303-31-1-A		
Ammonia		
10-107-06-1-B	10-107-06-1-C	10-107-06-1-I
10-107-06-1-J	10-107-06-1-K	30-107-06-1-A
Bromide		
10-510-00-1-A		
Chloride		
10-117-07-1-A	10-117-07-1-B	10-117-07-1-H
10-117-07-1-I	10-510-00-1-A	
Chromium (Hexavalent)		
10-124-13-1-A		
Conductivity		
10-302-00-1-A	10-302-00-1-B	
Cyanide		
10-204-00-1-A	10-204-00-1-X	
Fluoride		
10-109-12-2-A	10-510-00-1-A	
Hardness, Total		
10-301-31-1-B		
Kjeldahl Nitrogen (TKN)		
10-107-06-2-D	10-107-06-2-E	10-107-06-2-M
Nitrate		
10-510-00-1-A		
Nitrate + Nitrite		
10-107-04-1-A	10-107-04-1-B	10-107-04-1-C
10-107-04-1-J	10-107-04-1-K	10-107-04-1-L
10-107-04-1-O	10-107-04-2-A	10-107-04-2-B
10-107-04-2-D		
Nitrite		

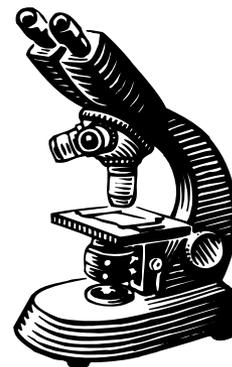


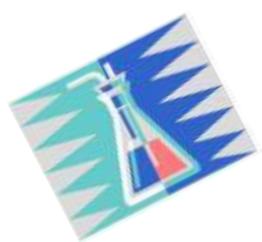


Advanced Benchtop Instrumentation is Powerful and Sensitive

- **Gas Chromatography**
 - **FID-PID-ECD**
 - **Mass Spectrometry (MS)**
- **Inductively Coupled Plasma**
 - **Atomic Emission Spectroscopy**
 - **Mass Spectrometry**
- **Atomic Absorption Spectrometry**
 - **Flame**
 - **Graphite Furnace**
 - **Cold Vapor**
- **Ion Chromatography**
- **Liquid Chromatography**
 - **UV Absorbance**
 - **Mass Spectrometry**

Higher Cost

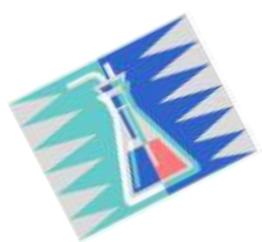




Intended Use of Data Guides Analysis

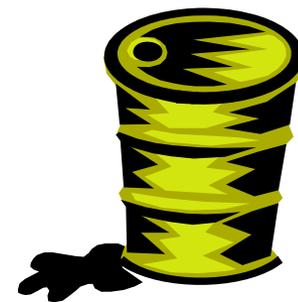
Data Level (suggested only)

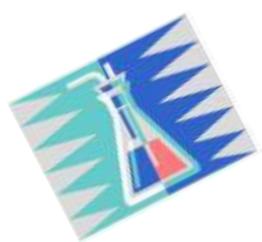
- **Level 3** – Laboratory based batch analyses that use **calibration** and continuing calibration, **blanks**, **QC procedures** to determine accuracy and precision, MDL studies are documented, and the data is of sufficient quality to satisfy most regulatory reporting requirements. Report includes **method**, **detection limit**, **results**, **external chain of custody**. Summaries of QC data, such as date, time and person conducting analysis and batch blanks, surrogate recoveries, accuracy and precision may be supplied with Final Analytical Reports.



Environmental Analytical Chemistry Instruments are Extremely Sensitive to Contamination !

- Solvents should not be used near VOC sample preparation or analysis.
- Deeply contaminated samples should never be put onto highly sensitive equipment
 - **This will lead to instrument contamination that may never go away**
 - Sample screening should be used when in doubt
 - Sample dilution will be necessary
 - Only the most highly trained should be doing the instrumental work





Automated Sampling Enhances Purge and Trap for GC/MS of VOCs



Principle: Gas chromatographic separation by absorption. MS mass separation

• Volatile compounds are purged from the sample and trapped to be thermally desorbed onto GC or GC-MS

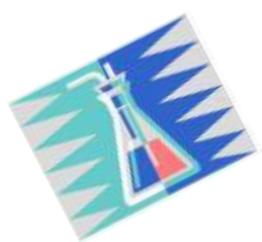


GC for Semivolatile Compounds

Principle: Gas chromatographic separation by absorption. MS mass separation



•Semivolatile compounds are extracted from the sample and injected into the GC or GC-MS



HPLC for Semivolatiles Including Explosives Compounds and Pesticides

Principle: Liquid Chromatographic Separation by Adsorption or Size Exclusion



LC is used for semivolatile compounds- can use UV, IR or MS detection.



Metals Analysis by Atomic Absorption Spectrometer

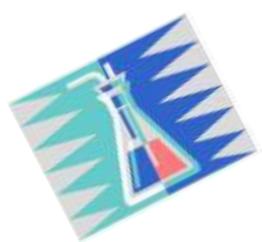
Principle: atomic light absorption



Autosampler



- **Flame AA- shown**
- **Graphite furnace AA**
- **Cold Vapor AA (hydride generation Hg , Se, As)**



Metals Analysis by Plasma Spectroscopy

*Principle:
Elemental mass
separation*

*Principle:
Elemental light
emission*



Autosampler



**Inductively Coupled
Plasma Mass
Spectrometer**

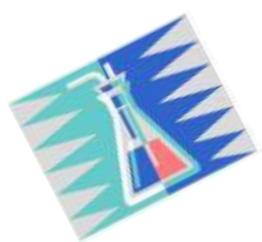
- Simultaneous or single
- Isotope analysis



**Inductively Coupled
Plasma Atomic
Emission**

- Simultaneous or single
- Many emission lines



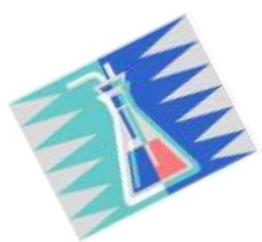


Hydride Generation is Used to Introduce “Volatile Metals” into AA or ICP-MS



Hg Hydride AAS

Source: Pakistan Council of Research in Water Resources



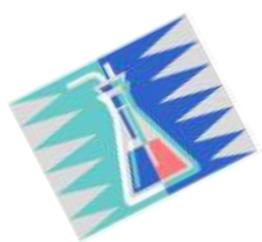
Ion Chromatograph for Anion Analysis

***Principle:
Chromatographic
ion exchange
with conductivity
detection***



**IC is used mostly for
anions
(Cl⁻, Br⁻, F⁻, HCO₃⁻, SO₄⁻²)**





Autosamplers are Very Valuable Way to Improve Precision and Production



Headspace

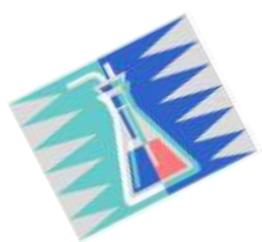


Purge and Trap



Purge and Trap





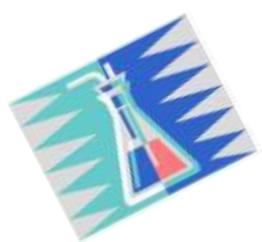
NEMI

National Environmental Methods Index



- Chemical
- Microbiological
- Biological
- Toxicity
- Physical
- Radiochemical
- Regulatory





NEMI

National Environmental Methods Index



- Search by Analyte
- General Search
- Multianalyte Search
- Sample collection - Preparation – Processing
- Green Chemistry

Website:

http://www.nemi.gov/apex/f?p=237:1:2019322167257072::NO::P1_CUR_TAB:N