Sampling, Storage and Pre-Treatment Techniques

1. Sampling Protocol
   → Sample needs to be representative of the body of water (or other matrix) from where it originates.

Sampling Considerations

A. Location
B. Frequency (hourly, daily)
C. Spatial and temporal considerations
D. Matrix
E. Safety Issues
F. Filtered -vs- Non Filtered

Automated –vs- Grab Samples

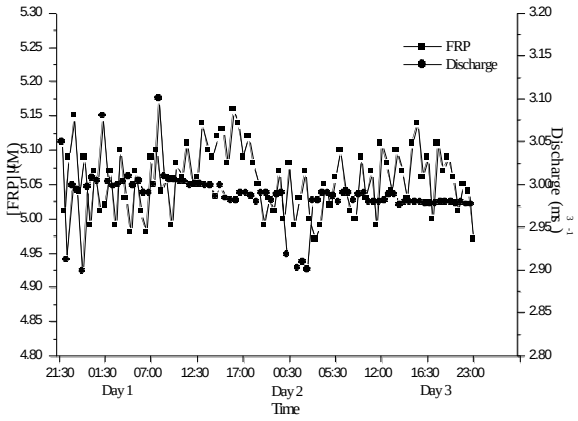
↓

In Situ Instrumentation

Sampling, Storage and Pre-Treatment Techniques

Month	Discharge ($m^3 s^{-1}$)	Alkalinity (mEq L^{-1})	Calcium (mEq L^{-1})	pH	Conductivity (µS)	$EpCO_2$	Temp. (°C)	Sunlight (h day^{-1})	FRP (µM)	TP (µM)
January	7.14	3.94	4.79	8.03	524	6.40	5.05	1.78	4.38	7.38
February	6.48	3.95	4.82	8.00	518	6.88	5.50	2.65	4.04	6.88
March	4.69	4.12	4.94	8.04	530	6.55	7.74	4.02	3.44	5.97
April	4.82	3.98	4.81	8.07	518	5.94	9.24	5.59	2.87	5.54
May	5.07	4.09	4.86	8.08	515	5.93	12.28	6.97	3.38	6.22
June	5.24	4.09	4.77	8.08	520	5.92	15.25	6.64	4.67	8.23
July	5.42	4.12	4.86	8.06	515	6.59	18.05	7.36	5.34	7.88
August	6.47	4.14	4.93	8.02	521	6.98	18.15	7.06	5.47	8.87
September	7.09	4.00	4.75	7.96	518	7.85	14.24	4.60	5.70	9.40
October	6.78	3.90	4.73	7.84	516	9.51	11.06	3.99	5.70	8.44
November	6.64	3.75	4.61	7.85	510	9.4	7.66	2.31	4.89	7.88
December	6.78	3.85	4.59	7.9	506	8.4	4.78	1.78	4.36	8.29

Sampling, Storage and Pre-Treatment Techniques



Sampling, Storage and Pre-Treatment Techniques

1. Sampling Protocol
   - A. Cleaning Procedure (Paper Handout – Read!)
     What issues are we concerned with?
     1) Biological activity
     2) Sample container composition
     3) Breakdown of organic compounds

   - B. Sample Collection
     1) Simple and avoid contamination or interferences
     2) Grab samples -vs- automatic samples
     3) Sample bottles rinsed with sample (3x)
     4) Collected halfway between surface + sediment
        Why?

Sampling, Storage and Pre-Treatment Techniques

C. Filtration

→ differentiation between dissolved + particulate portions

- Dissolved = that portion which passes through a 0.45 μm filter.
- High solids can cause interference (e.g. optical spectroscopy)
- Also removes bacteria and plankton
  - → may release nutrients when cell ruptures
  - → 0.20 μm filter

Sampling, Storage and Pre-Treatment Techniques

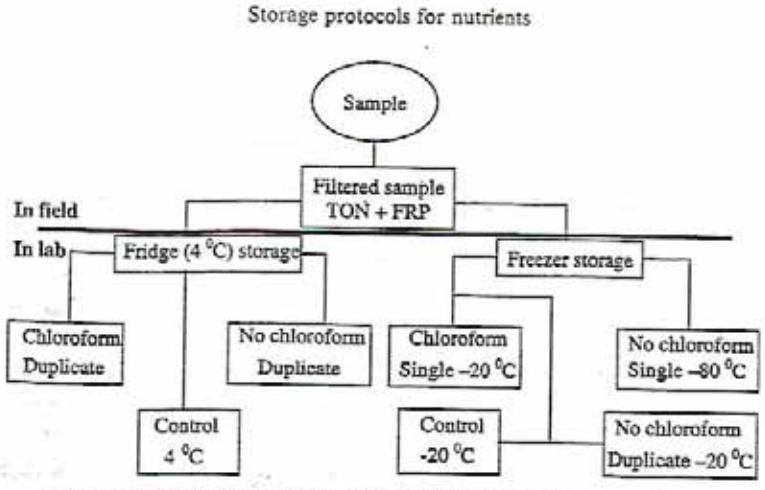


Fig. 1. Schematic distribution of sub-samples during storage experiment.

Sampling, Storage and Pre-Treatment Techniques

D. Sample Storage and Preservation

1) Chemical Methods

a) Acidification (e.g. trace metals) – why acidify?

b) Chloroform (0.1%) – prevents biological growth

c) Mercuric chloride – prevents biological growth

2) Physical Methods

a) Refrigeration (4˚C)

b) Freezing (-20˚C)

c) Deep freezing (-80˚C)

→ Problems associated with freezing?

Sampling, Storage and Pre-Treatment Techniques

D. Sample Storage and Preservation

- The effectiveness of the preservation method depends on:

1) Matrix
2) Filtration technique
3) Container type and size
4) Temperature
5) Type of chemical addition
6) Biological activity

Note: Very matrix specific

Sampling, Storage and Pre-Treatment Techniques

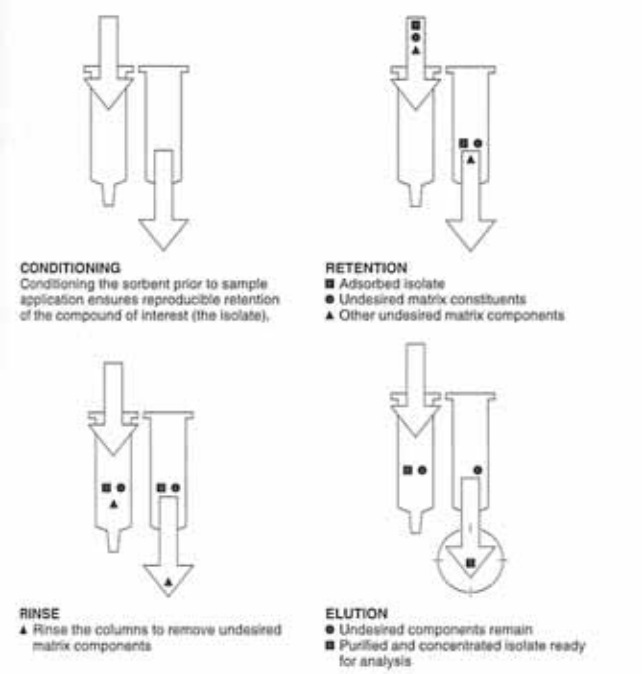
E. Extraction Methods (Solid + Liquid)

→ used to remove or isolate analytes or compounds of interest for analysis.

1) Liquid-Liquid (separatory funnel + toxic organic solvents)

2) Solid Phase Extraction

→ uses a a solid + liquid phase to isolate analytes from solution



Sampling, Storage and Pre-Treatment Techniques

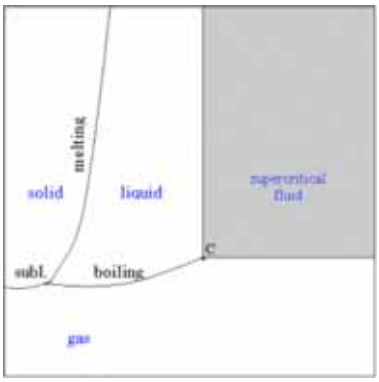
3) Liquid phase microextraction (LPME)

→smaller sample volumes – sample extracted from an aqueous sample (1-5 ml volume) through a porous hollow fiber into a micro liquid-phase acceptor solution

4) Supercritical Fluid Extraction

→ "Fluid" is neither a gas or a liquid but intermediate.

→ only one phase exists



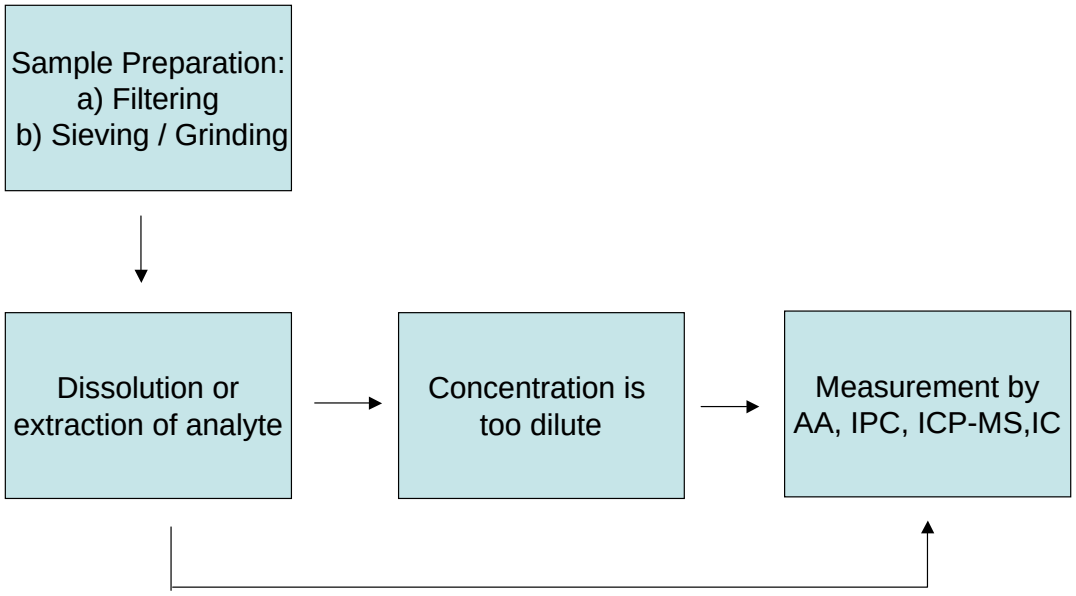
http://sunny.vemt.bme.hu

Advantages
1. Non toxic solvents
2. Higher degree of separation
3. Cheaper in long run

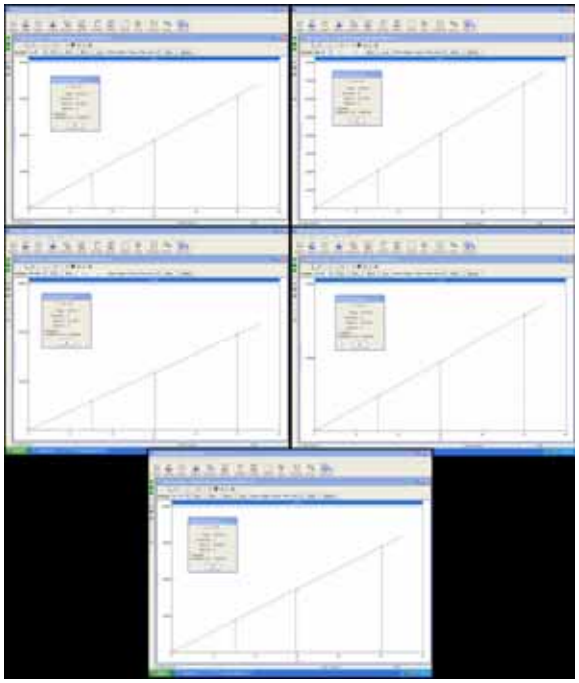
Disadvantages
1. High initial cost
2. Elevated pressure required

Sampling, Storage and Pre-Treatment Techniques

5) Sample Preparation for Trace Metal Analysis



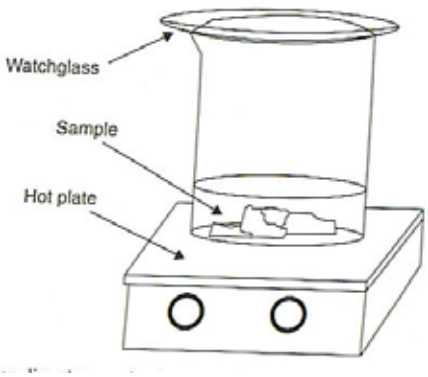
Sampling, Storage and Pre-Treatment Techniques



Sampling, Storage and Pre-Treatment Techniques

Wet Digestion Methods

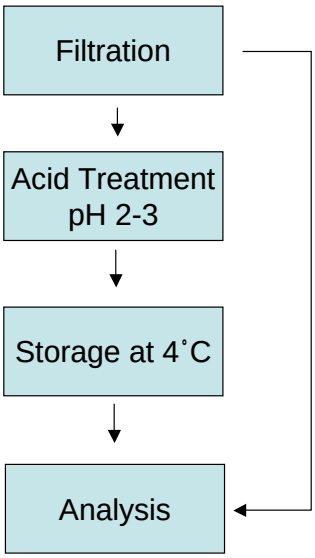
1) Water → Soluble Salts
2) Dilute Acids → Easily oxidized metals and alloys, salts
3) Concentrated Acids → Less oxidized metals, steels, metal oxides
4) Concentrated Acids w/ oxidizing agent → metals, alloys, soils, particulates



S. Mitra (Ed.) Sample Preparation Techniques in Analytical Chemistry (2003), Wiley-Interscience

Sampling, Storage and Pre-Treatment Techniques

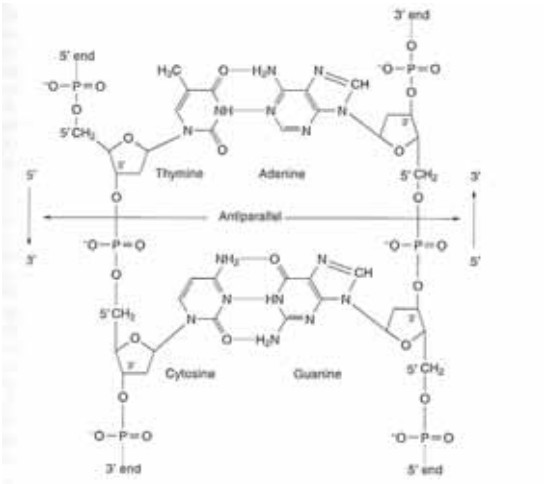
Ex: Water Samples



Sampling, Storage and Pre-Treatment Techniques

Ex: Sample Preparation in DNA Analysis

a) Chemical Properties



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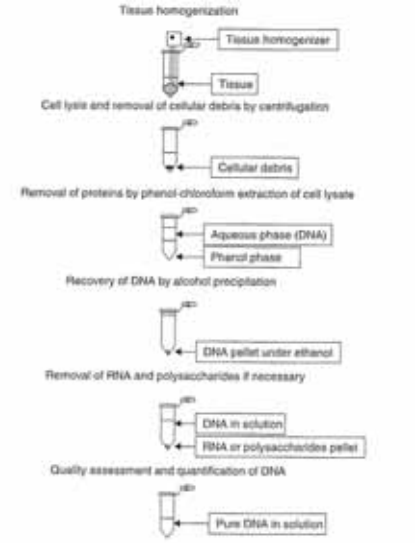
Sampling, Storage and Pre-Treatment Techniques

DNA Analysis:

a) Polymerase Chain Reaction (PCR)

method for amplifying DNA from a small amount of DNA catalyzed by DNA polymerase w/ a pair of primers (oligonucleotides).



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Sampling, Storage and Pre-Treatment Techniques