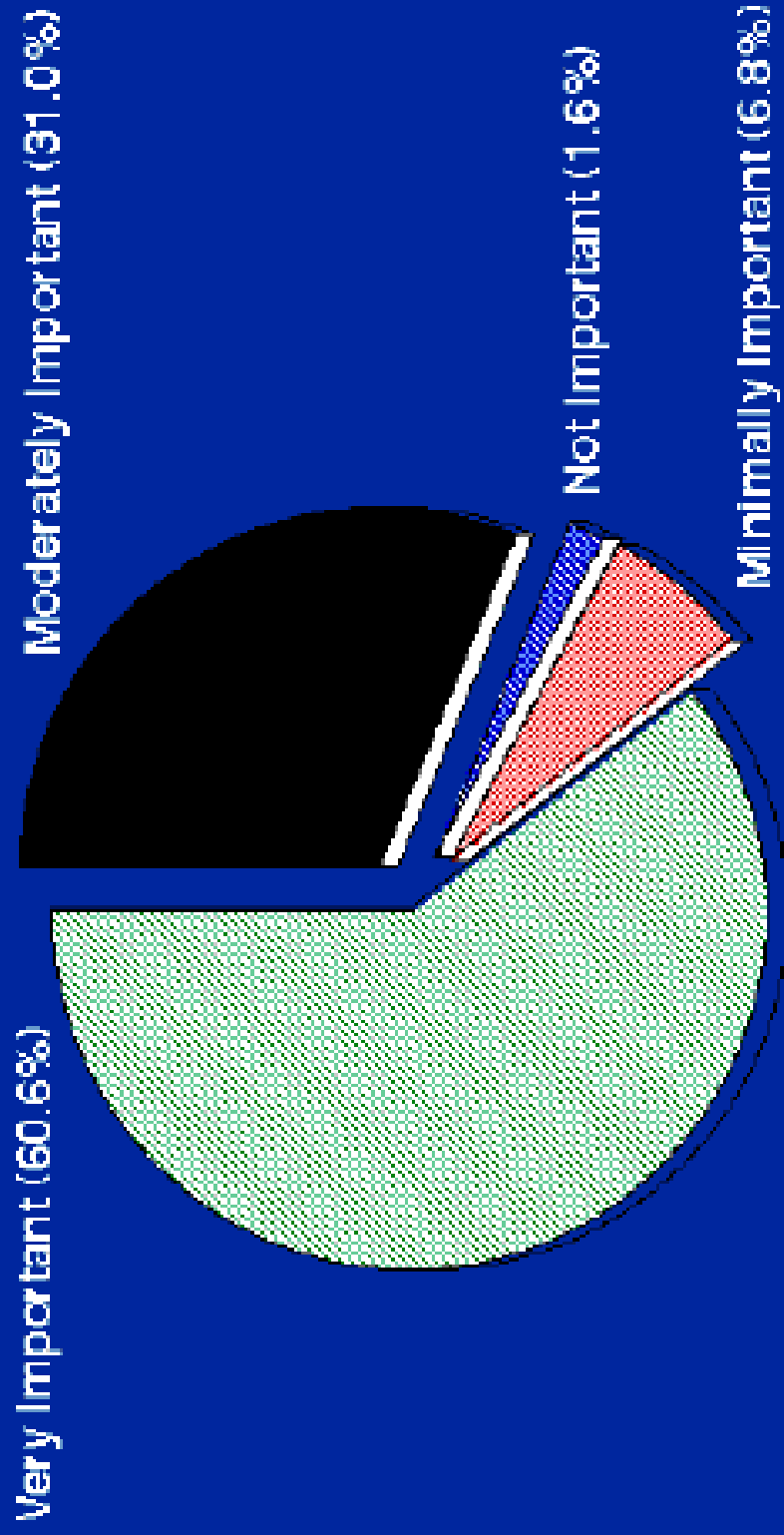


Chapter 28: Sample Preparation

Importance of Sample Preparation

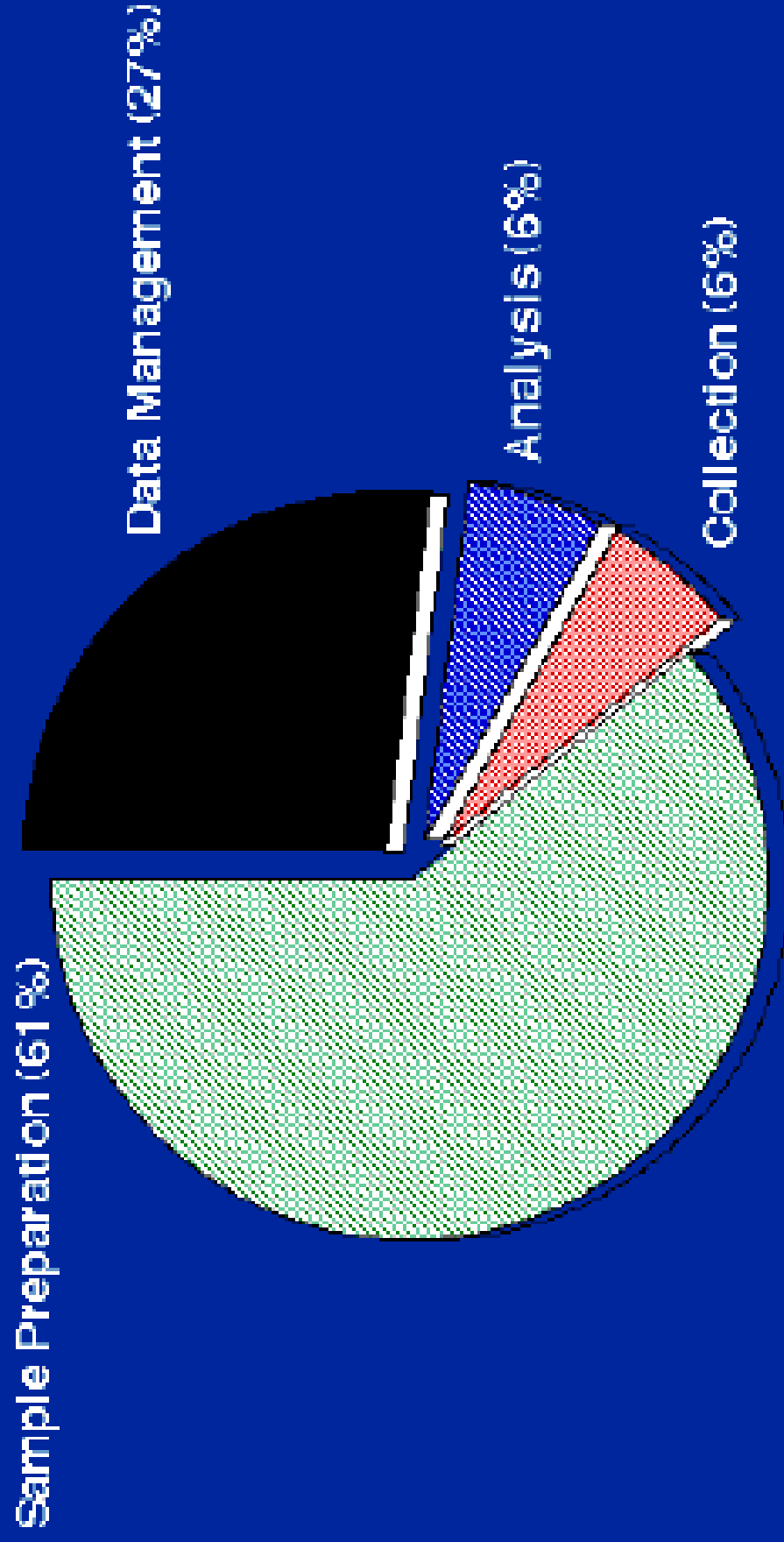


Ronald E. Mejors, "An Overview of Sample Preparation" LC-GC, Vol18, No. 1, 1991.



Dr. H. M. Kingston

Distribution of Time Analytical Chemists Spend on Sample Analysis

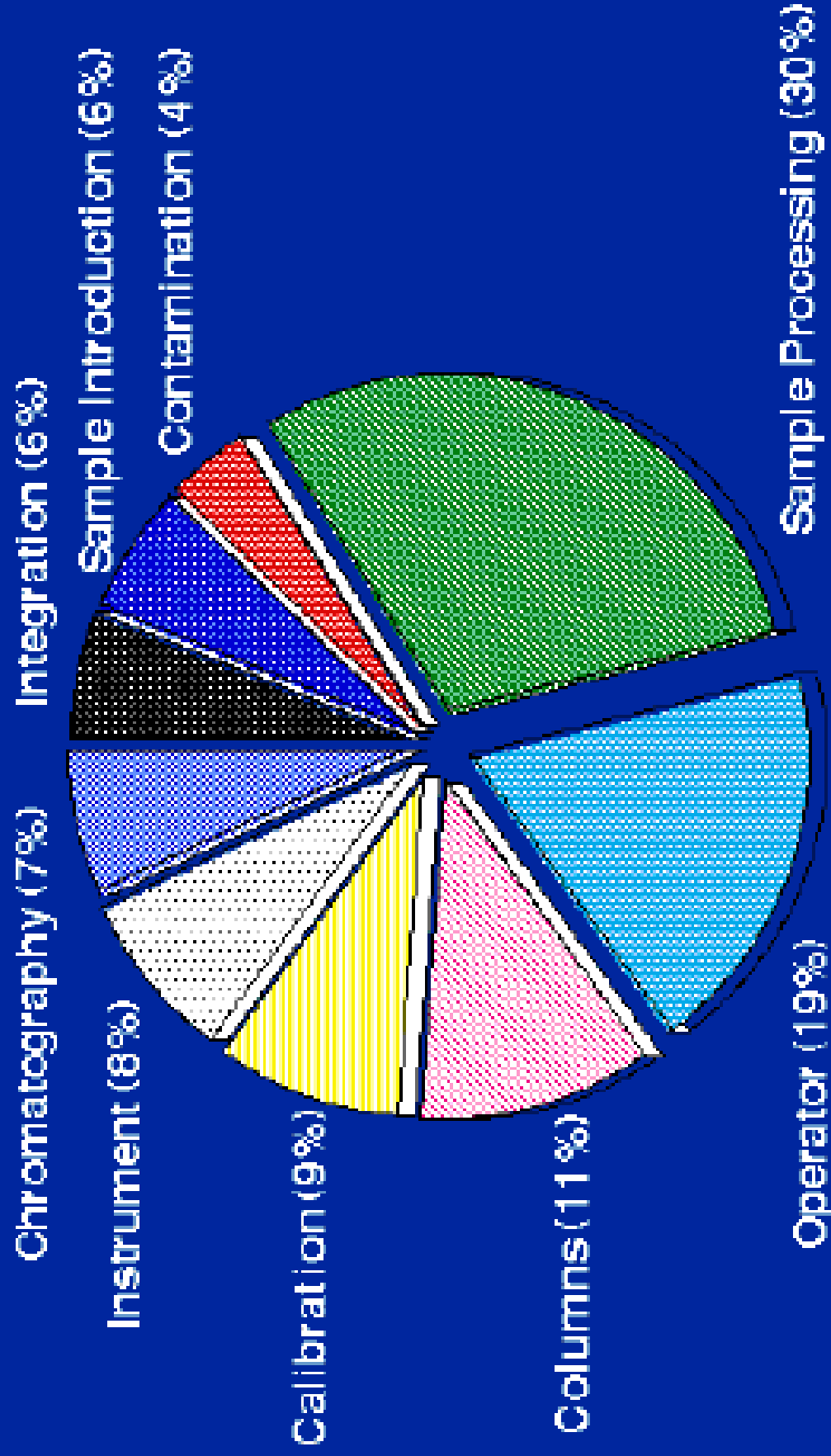


Ronald E. Majors, "An Overview of Sample Preparation" LC-GC, Vol19, No. 1, 1991.

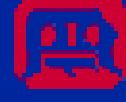


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Distribution of Errors Generated During Sample Analysis



Ronald E. Majors, "An Overview of Sample Preparation" LC-GC, Vol 9, No. 1, 1991.



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Preparing samples

- The sample is to be converted into a form more suitable for chemical analysis
 - Solids \implies solutions or vapors
- Preserve “representativeness” of the sample
- Minimize losses of analyte
- Minimize contamination
- Remove matrix components as needed
- Get concentration into an appropriate range

Analyte Recovery

$$\text{Percent recovery} = 100 * [\text{found}] / [\text{known}]$$

(The concentration of a standard reference material is measured, and the found results are compared to the known concentration)

The “spike recovery”

Percent Spike Recovery =
 $100 * (\text{SSR} - \text{NATIVE}) / \text{SA}$

SSR = spiked sample result
NATIVE = native sample result
SA = spike added

<http://environmentalet.hypermart.net/env1221/leadinpaint.htm>

Other ways to assess recovery

- **Yield tracers** - add a radioactive form of the analyte and measure recovery by counting
- **Surrogates** - add a non-native substance which emulates the chemical behavior of one or more analytes

Analyte loss

- Incomplete dissolution or extraction
- Volatilization
- Precipitation after dissolution
- Mechanical losses (splashes, spills)
- Decomposition during dissolution, storage
- Adsorption onto container walls
- Incomplete separation or collection during a preconcentration process

Dissolution and extraction processes for organic constituents

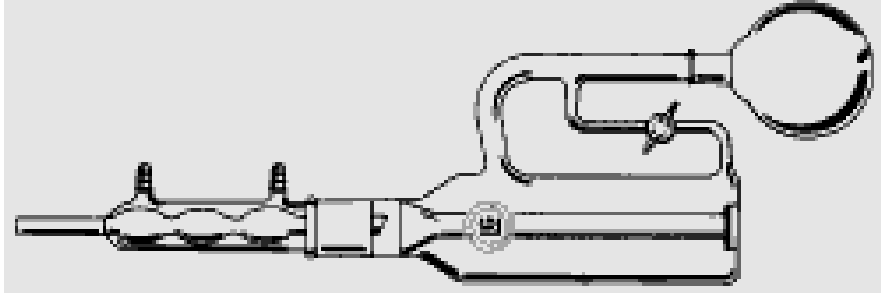
- Soxhlet extraction - “like making coffee with methylene chloride”
- Liquid-liquid extraction
- Supercritical fluid extraction
- Sonication with a solvent

The Soxhlet extractor



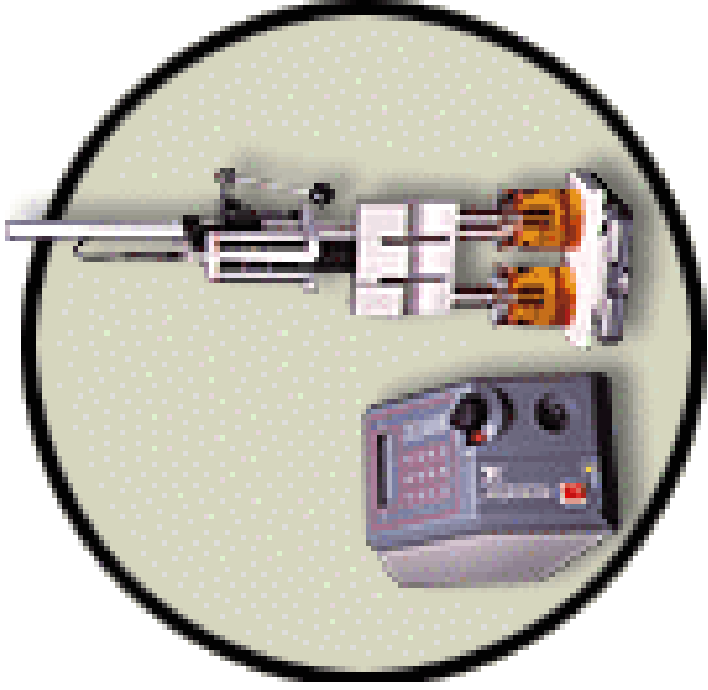
- Sample is placed in a thimble and the solvent is placed in the bottom flask.
- Solvent is boiled, condensed, and the condensed solvent is percolated through the sample.
- The dissolved components collect in the flask at the bottom of the apparatus.

Continuous liquid-liquid extraction



- Often used to extract trace quantities of organic compounds from water.
- The immiscible extraction solvent (e.g. chloroform) is boiled, condensed, and is allowed to dribble through the sample.
- Analyte collects in the extraction solvent

Sonication - use ultrasonic agitation to improve dissolution



- *Summary of EPA Method SW846-3550 I.*
- ## **PREPARATION FOR ANALYSIS OF PESTICIDES/PCBS IN SOIL**

- Weigh 30g sediment sample into 400mL beaker and mix with anhydrous sodium sulfate.*
- Add 100mL of 1:1 methylene chloride/acetone to the sample.

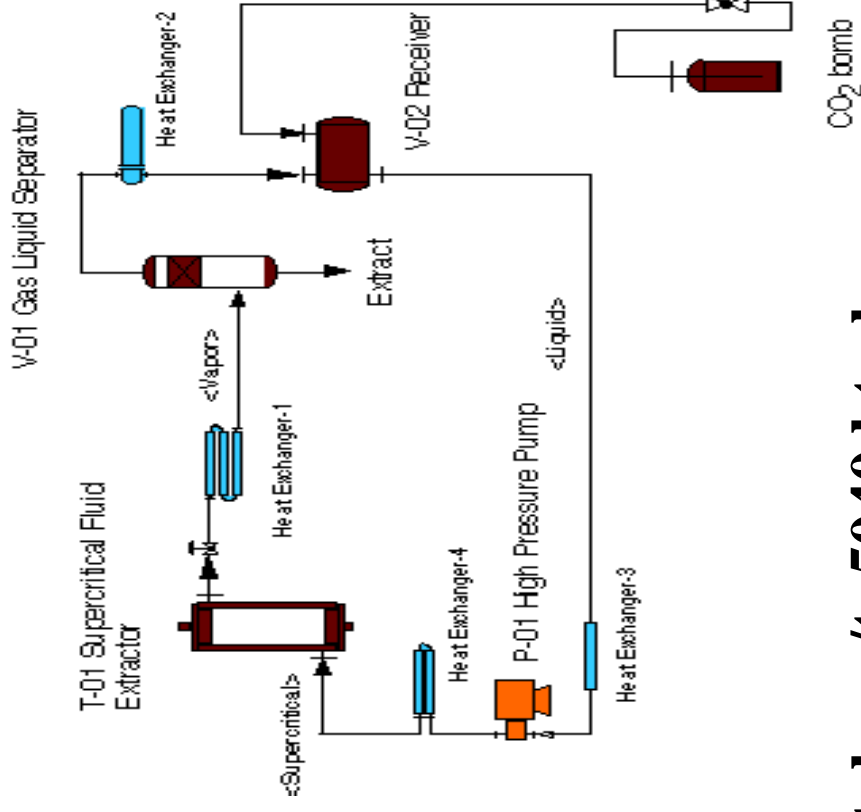
Supercritical fluid extraction

- In supercritical fluid extraction, common gases (i.e. CO₂) are elevated above their critical points and used to extract organic contaminants from environmental samples. Supercritical fluids have properties of both liquids and gases which facilitates rapid and highly selective extractions (40min), compared to the Soxhlet approach (48hrs). SFE using CO₂ is environmentally-friendly, requiring minimal (2-10mL) use of hazardous solvents.



Supercritical fluid extraction - industrial uses

- -Agroindustry, food industry, toilet preparations, Spice oils and oleoresins
- -Essential oils: flavours and fragrances
- -Bitter from hops
- -Herbal medicines, Natural pesticides
- -Food colours and preservatives, Vitamin E (tocopherols), Nicotine/tar free tobacco, Decaffeinated coffee and tea, Cholesterol free food products



<http://www.apctt.org/database/to5040.html>

How would one measure airborne mothball vapors?

- Air is drawn through a selective sorbent, the analytes are preconcentrated, then eluted (solvent, thermal desorption, supercritical fluid) in some manner for analysis



<http://www.skinc.com>

Preparations for elemental constituents

- Leaching with acids: HCl, HNO₃
- Complete dissolution of silicates with HF-containing mixtures
- Destroy organic matter with oxidizing agents such as HClO₄, H₂O₂
- Complete dissolution of silicates by molten salt fusion

Acid dissolution in open beakers

- The sample is mixed with appropriate reagents, and is heated in an open container.
- Simple, but slow, tedious, and prone to contamination



http://envexp.com/metals_digestion.html

Microwave-assisted digestion

- Sample and reagents are mixed and heated in a closed, pressurized container.
- Higher temperatures due to “pressure cooker” effect
- Faster digestion
- Dangerous, expensive



<http://www.aurora-instr.com/mw500.htm>

Separation and preconcentration of the analyte from the sample matrix

- **Distillation**
- **Preparative chromatography**
- **Solvent extraction**
- **Ion exchange resins**
- **Precipitation and coprecipitation**
- **Dialysis**
- **Purge and trap**

Solid-phase extraction

- A solution containing the analyte + matrix is passed through a column or disk containing extractant.
- Analyte is concentrated and eluted under different solution conditions



<http://www.3m.com/empore/library/primer/>

Purge-and-trap

- Takes advantage of Henry's Law - relatively volatile analytes are easily removed from aqueous solution by “sparging” (bubbling) with an inert gas.
- Analyte in gas stream is then trapped on a sorbent



<http://www.cdsanalytical.com/purge.htm>

Sources of contamination in the sample preparation process

- **Reagents** - levels of impurities vary greatly; should be screened before critical uses
- **Containers** - may intrinsically contain analyte, or may contain residues from previous uses - cleaning protocols important
- **Atmosphere** - deposition of atmospheric particles should be controlled/avoided

Reagent purification

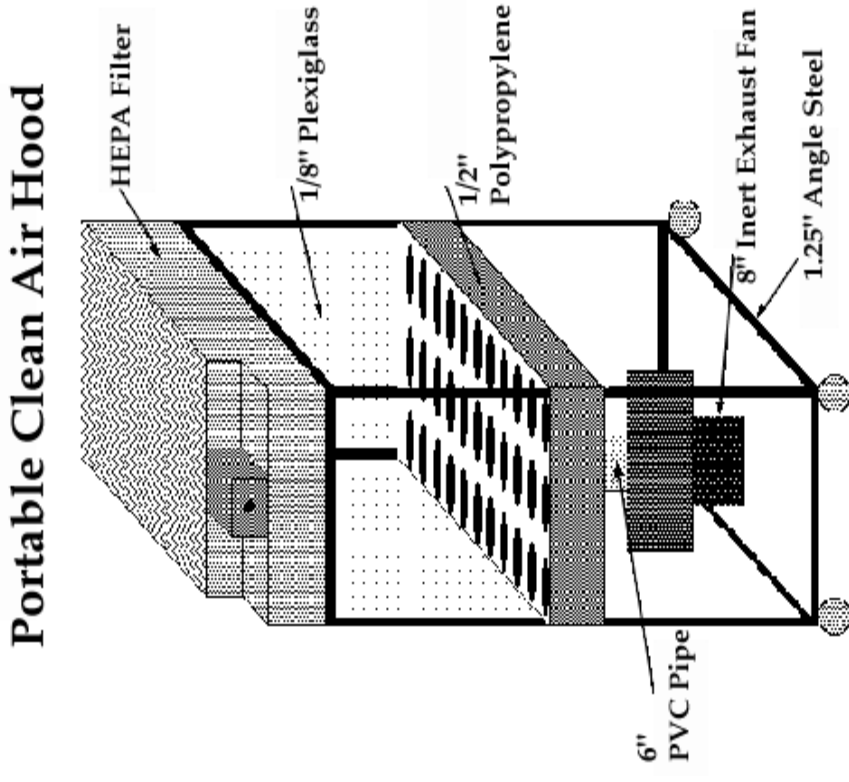


- Distillation in Teflon or fluoropolymer vessels is often used to produce high-grade acids for elemental analysis.

<http://www.milestonesci.com/duoPUR.htm>

“Clean” sample preparation

- To minimize introduction of contaminants during the sample prep process, the prep is conducted under HEPA-filtered air



<http://www.sampleprep.duq.edu/dir/clean.html>