Safer and More Efficient Organic and Inorganic Analysis

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Why is this Important?

- Less exposure to hazardous chemicals, including solvents, reduces illness and exposure to liability
- More efficient analysis reduces costs and increases laboratory capacity

How can this be Achieved?

- Smaller sample sizes where homogeneity can be preserved
- Use of less toxic solvents where possible
- Increased automation to reduce exposure and extend operating hours
- New technology incorporating the latest features to improve analytical performance, reliability and efficiency, such as SPE, ICP-MS with cell technology, etc.

Examples

This presentation will give a few examples of increased safety, reduced cost and improved performance

- Reducing the use of methylene chloride
- Changing solvent for Oil and Grease extraction
- Increasing the use of closed system digestion for metals sample preparation

Solvent Reduction Background

- Through Title V and State Implementation Plans up to 10 tons of chlorinated solvent and up to 25 tons total of solvent may be emitted with a valid permit
- For extremely small emitters, no permit is required if they are not at risk of exceeding the limit
- In 2014, four labs in Massachusetts were fined for exceeding this limit without a permit
- Concern that the issue would spread across the states
- Concern that solvent recovery would become mandatory, even for small laboratories

Lab use of Methylene Chloride

- Methylene chloride ($MeCl_2$) phaseout proposed under TSCA in 2023 (88 FR 28284, May 3, 2023)
- Final Rule published 89 FR 39254, July 8, 2024
- Proposed Rule published 100 FR 22214, May 27, 2025 to extend compliance requirements for 18 months for select categories of use, such as environmental monitoring methods
- ACIL Environmental Sciences Section (ESS) submitted comments about the unique requirements of established methods in EPA-HQ-DPPT-2020-465-0258, June 6, 2023
- ACIL ESS plans to work collaboratively with the Environmental Monitoring Coalition and EPA Regulatory Programs to identify larger methylene chloride consuming methods suitable for change and to target them to develop methods meeting that goal (In progress, contact Judy Morgan, Kim Ramsey or David Friedman)

Traditional Environmental Analysis

- Water-sample 1Liter
- Extract at acid pH with 60 mL of $MeCl_2$ three times
- Extract at basic pH with 60 mL of $MeCl_2$ three times
- Evaporate solvent to 1 mL
- Inject 1 µL into GC/MS, with split

How to reduce Solvent Emissions?

- Reduce sample size collected, requiring less solvent for extraction
- Reduce extraction solvent needs, for example solid phase extraction
- Recover solvent used

Reduce Sample Size

- 1-L sample size set decades ago based on:
- Sample homogeneity
- Analytical instrument sensitivity

- Sample homogeneity shown to be less of a concern than originally thought
- Analytical instrument sensitivity has dramatically increased
- Benefit of lower sample shipping costs and hazards
- Possible to do additional sampling at a lower cost

Reduce Sample Size

EPA methods are acknowledging smaller samples as they are updated:

- Method 521(2004), Nitrosamines in Drinking Water, specifies 500 mL of water sample size
- Method 535 (2005), Chloroacetanilide and other Acetamide Herbicide Degradates in Drinking Water, specifies 250-mL water sample size
- Method 522 (2008), 1,4-Dioxane, specifies 100 or 500-mL water sample size, depending upon the SPE adsorbent chosen
- Method 3511(2002), Microextraction for Selected Compounds, approximately 35-mL sample size
- Method 625.1 (2016), flexible sample volume based on the detection limits needed for compliance. Sample size can be reduced from 1000 mL to a volume above 100 mL

Instrument Sensitivity Improvements

- Manufacturers have improved analytical instrument sensitivity over the past few decades
- Split can be changed to improve sensitivity
- SIM can be used, especially now that scanning can be acquired simultaneously
- Triple quad?
- Large-volume injection becoming more common, inject up to 50 µL sample

Reduce Solvent Usage

- Smaller samples require less solvent for extraction
- Solid-phase extraction (SPE) requires less solvent for analyte elution

Summary:

- Water is passed through the SPE disk and analytes are retained
- Analytes are eluted with a small volume of solvent
- Depending on sample complexity 80-180 mL of solvent are needed for elution compared to 360 for a typical acid/base neutral liquid-liquid extraction

Solvent Recovery

- The less solvent that needs to be evaporated to obtain the sensitivity needed in the analytical step, the less that might be emitted
- Recovery of evaporated solvent is the last step to consider in the full process
- Consider the potential for recovery when considering evaporators
- Evaporators that combine water vapor with solvent vapor will make recovery challenging

Benefits of Solvent Recollection

Solvent Recollection:

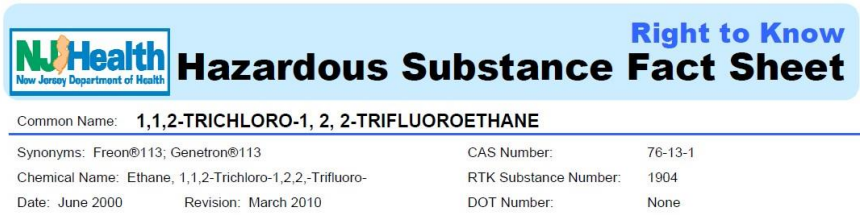
- Prevent harmful solvent vapors from being released to the atmosphere
- Collect solvents for proper disposal or potential redistillation and reuse
- Protect workers from exposure to harmful solvent vapors as evaporation takes place

What to Do with the Collected Solvent?

- Disposal through proper channels
- Redistill to the quality required by the lab for reuse
- Sell to another facility for different use requiring less quality (such as metal finishing, etc..) with appropriate license

Choose Less Toxic Chemicals

- Oil and Grease analysis (a method-defined parameter) was performed by extraction with Freon 113 and the solvent evaporated and the residue weighed or an Infrared procedure performed in the late 70's, using EPA Methods 413.1 or 413.2 for wastewater or 9070 or 9071A under RCRA
- The 1990 Montreal Protocol phased out the use of Freon 113 because it was promoting development of the hole in the stratospheric ozone layer. The Clean Air Act Amendments of 1990 specified that it be phased out in the US by 1996
- This resulted in EPA evaluation of various alternative solvents such as hexane, cyclohexane, methylene chloride, and others


NJ Health New Jersey Department of Health

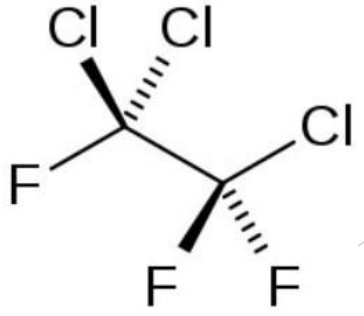
Right to Know **Hazardous Substance Fact Sheet**

Common Name: **1,1,2-TRICHLORO-1, 2, 2-TRIFLUOROETHANE**

Synonyms: Freon®113; Genetron®113 — CAS Number: 76-13-1

Chemical Name: Ethane, 1,1,2-Trichloro-1,2,2,-Trifluoro- — RTK Substance Number: 1904

Date: June 2000 Revision: March 2010 — DOT Number: None



Path to a New Solvent

- Method 1664, using hexane, took several years of painstaking effort to evaluate and determine that this was the best choice of the alternative solvents considered
- Method 1664 was proposed in 1996 and promulgated in 1999
- At one meeting William Telliard commented “We have proven freshman chemistry”

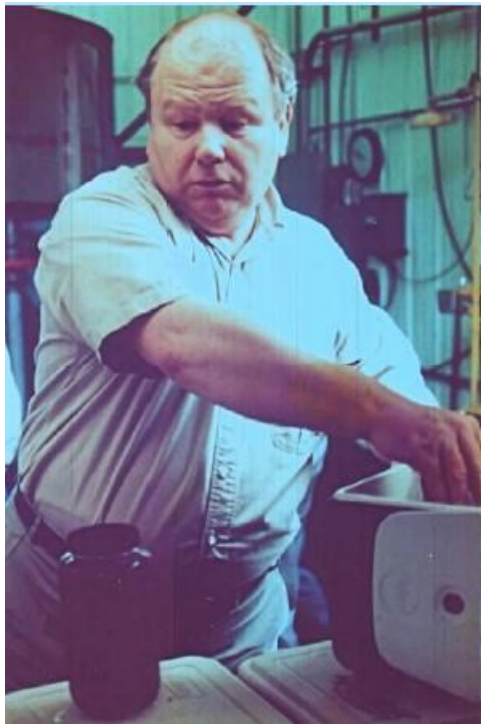
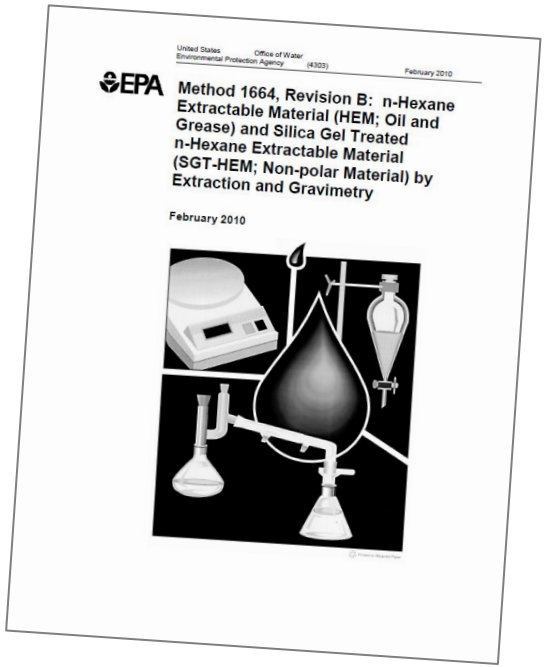


Photo from **They Said it Couldn’t be Done: A Brief History of Environmental Water Monitoring**, presented at NEMC 2020, Harry B. McCarty, Ph.D.

Oil and Grease Today

- Method 1664, Revision B, employs hexane for extraction
- Solid phase extraction can be used to reduce the volume of hexane required
- Smaller sample sizes and other modifications permitted to the method are specified, provided all quality control is met

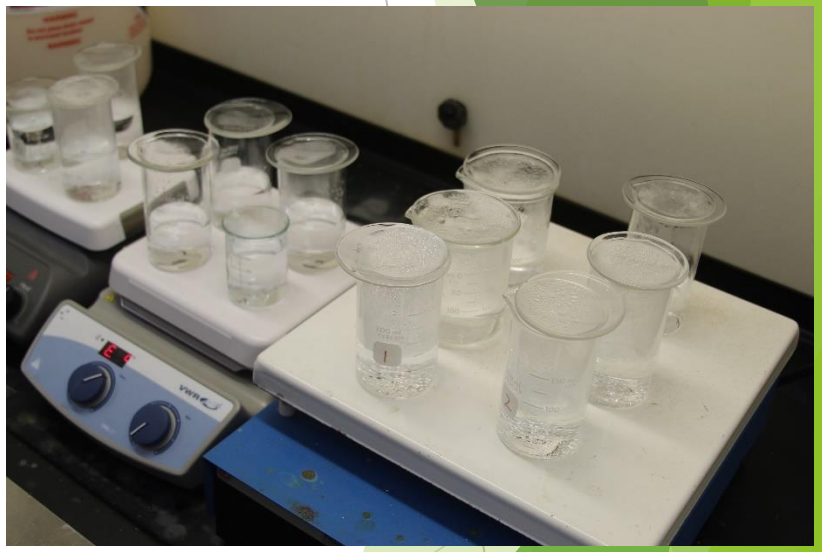


Closed Digestion Systems

- ICP-MS for metals analysis has become increasingly adopted in environmental and other types of laboratories
- ICP-MS detection limits are lower than previous inorganic techniques, such as Flame and Furnace AA and ICP-OES
- Achieving lower detection limits requires a cleaner digestion sample preparation
- ICP-MS can incorporate a large suite of elements in one method, including volatile elements, such as mercury

Closed Digestion Systems

- Open digestion systems released acid and sample vapors into the hood where they were performed
- Volatile elements may be lost
- Contaminants in the air and hood system may make their way into the digesting samples
- When glass beakers were used, the material would also contaminate the samples
- Closed digestion techniques provide a cleaner digestion, retain volatile elements and reduce acid vapors in the lab



Summary

- Advances in analysis safety and efficiency continue
- Some, such as the push to decrease the use of methylene chloride are driven by concerns expressed in regulations
- Oil and Grease analysis was made safer for the environment through change of Freon 113 used in extraction, to hexane, although the change was not easy and took several years to evaluate alternative solvents
- To reduce expose to acid vapors and take full advantage of newer technology, closed digestions provide advantages for metals analysis

Bibliography

- Preliminary Report of EPA Efforts to Replace Freon for the Determination of Oil and Grease, EPA 821-R-93-011, Revision 1, September 1993.
- Report of EPA Efforts to Replace Freon for the Determination of Oil and Grease and Total Petroleum Hydrocarbons: Phase II, USEPA, April 1993.
- **Federal Register** Vol. 64, No. 93 Friday, May 14, 1999, pages 26315-26327.
- They Said it Couldn't be Done: A Brief History of Environmental Water Monitoring, presented at NEMC 2020, Harry B. McCarty, Ph.D.