Instructional Resources for the Teaching of Green Analytical Chemistry

GREEN CHEMISTRY | sdsu

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REU SITE in Environmental/Green Chemistry

Environmental and **Green Chemistry** span a chemical continuum from natural to industrial processes. South Dakota State University, Black Hills State University (BHSU), and Northern State University (NSU) have established a three-year REU Site focused on environmental and green materials chemistry that provides 10 students per year with multi-disciplinary research experiences aligned with **Green Chemistry Principles** 3, 5, 6, and 9 and the chemistry of natural environments. Interactions with the project's nine faculty mentors enable student participants to undertake research in catalysis/less hazardous synthesis, energy efficiency/safer solvents, and the environmental chemistry of natural systems. An integrated program of research, professional and career development, and student activities is facilitated by the state-of-the-art, internet-based communication technology known as the "Access Grid".

Applications for the REU Site in Environmental/Green Chemistry Summer 2016 student cohort can be submitted by clicking on the link which will take you to the application page. Review of applications begins **February 1st** and continues until all positions are filled. Please note that in addition to the information requested by the application form you will need to arrange for two letters of recommendation from 2 professors and a copy of your college

MISCONCEPTIONS

Microscale = Green

Yes, a microscale method will be greener than its larger-scale counterpart, but you must still keep in mind sampling theory and appropriate sample size.

MISCONCEPTIONS

No Organic Solvents = Green

Aqueous solvents may be less toxic than most organics, but you still must consider wastewater generation or the energy needed for solvent evaporation. Consider all 12 Principles, not just toxicity or flammability.

MISCONCEPTIONS

We don’t need to teach Green Analytical Chemistry or we can’t fit it into the curriculum.

Informal survey of 40 members of Society of Western Analytical Professors, 100% no response or do not see the need to teach green analytical chemistry.

WHAT IS ANALYTICAL CHEMISTRY?

"Analysis of a sample is not the true aim of analytical chemistry… the real purpose of the analysis is to solve a problem."

H. A. Laitinen, *Anal. Chem*. 1966, *38*, 1441.

GREEN CHEMISTRY

Green chemistry is the use of a *set of principles* that reduces or eliminates the use or generation of hazardous substances in the design, manufacture, and application of chemical products.

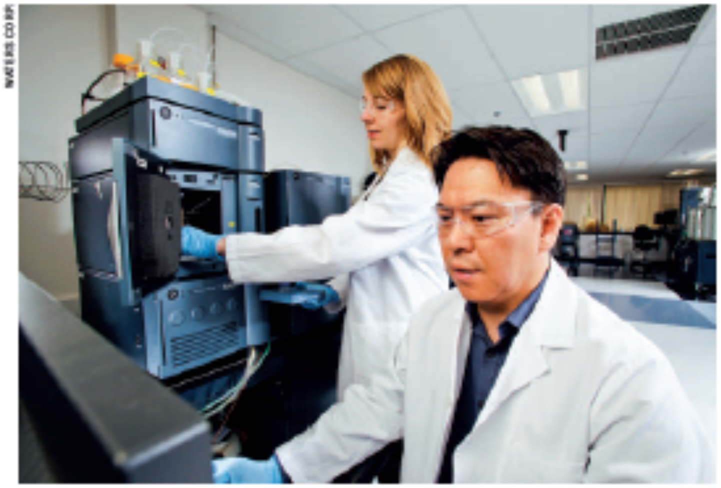
P. T. Anastas and J. C. Warner, **Green Chemistry: Theory and Practice**, Oxford Press, 1998.

GREEN ANALYTICAL CHEMISTRY

"Green analytical chemistry can be defined as research that optimizes analytical processes to provide the required information in a manner that is inherently safe, nontoxic, and environmentally benign, and with the least possible consumption of material and energy and generation of waste."

M. Koel, M. Kaljurand, *Crit. Rev. Anal. Chem.*, **42**, 192-195 (2012).

WATERS CORP.



REDUCE USE Waters's Acquity UPLC system consumes less eluent than traditional HPLC.
[redacted]

GREENING THE ANALYTICAL LAB

Although GREEN CHEMISTRY is a latecomer to the lab, instruments and analysis methods are changing

ANN M. THAYER, C&EN HOUSTON

GREEN CHEMISTRY principles have been seeping into the chemical community's consciousness for at least 20 years, but they haven't fully permeated all corners. One such corner is the analytical lab.

"In some respects, the analytical community has been slower to embrace green chemistry than the organic community," says Douglas Raynie of South Dakota State University. An industrial scientist turned academic, Raynie teaches a green analytical chemistry course at the annual Pittsburgh Conference on Analytical Chemistry & Applied Spectroscopy, or Pittcon.

Scale is a reason. Organic chemists in industry have more opportunity to develop green processes when they scale up reactions, Raynie explains. In contrast, analytical chemistry is seen as a "necessary evil" for one-off purity checks or regulatory compliance tests. "Because they have to do it, people are more willing to tolerate certain inefficiencies," he says.

But analytical lab volumes add up. Thus, instrument makers are making an effort to design equipment that is more energy efficient, uses fewer hazardous chemicals, and generates less waste. They are also designing their machines for environmentally friendly end-of-life disposal.

In many other ways, though, the greening of the instrumentation industry comes not from a desire to do better for the environment but as a by-product of scientific progress. That's good news for researchers, because few of them are willing to sacrifice speed or accuracy for a green seal of approval.

> "If you are doing good analytical chemistry, you are doing green analytical chemistry."

Indeed, despite numerous grassroots efforts among academic researchers, especially around greener sample extraction and analysis methods, customers don't appear to be clamoring for green instrumentation. Only 3% of labs are required by their organizations to purchase green lab products, according to a 2014 survey conducted by K.C. Associates for C&EN Media Group.

About 11% of the 400 labs surveyed are encouraged to consider green alternatives as a first choice in buying lab products, and 21% are so encouraged if the cost and performance are equal. But this attitude applies foremost to office supplies, then to chemicals and solvents, and very much less to equipment and instruments.

"People won't necessarily pay extra for greenness if all of the other attributes are the same," Raynie says. "But if it is green and it is quicker, or green and more sensitive, then there is more of an impetus to buy."

Who is doing the purchasing also comes into play. Progressive companies or younger employees who have grown up with more of an environmental mind-set are more likely to look for something green, Raynie adds.

In fact, the survey found, attitudes have been shifting over the past six years. About 55% of respondents expect that their organizations' requirements to purchase green products will increase over five years.

LARGE COMPANIES looking to cut energy consumption as part of sustainability initiatives may not even look at their analytical instrumentation. "The lab is such a small component of their energy use," says James McCabe, sustainability manager at the instrument maker Waters Corp.

But other savings can be found. For long-lived pieces of equipment, managing solvents, consumables, and hazardous wastes can have a significant impact on operating costs and returns on investments.

McCabe often conducts life-cycle analyses for customers. In one case, a customer asked him to compare the production, transportation, use, emissions, and end-of-life profiles of high-performance liquid chromatography (HPLC) and ultra-performance LC (UPLC), two of the company's big areas of business.

The "use" step includes solvents, energy, glassware, and consumables. Solvents can factor in twice, McCabe explains. Not only is there the up-front cost to buy them, but they can also come with a high cost of disposal, especially if innocuous materials are mixed with hazardous ones.

Life-cycle analyses are part of Waters's move toward "sustainable innovation" to address energy and materials use. Other instrument makers have similar initiatives. PerkinElmer's Eco-Innovative Products and Mettler Toledo's EcoDesign programs try to minimize health and environmental

APPLYING GREEN CHEMISTRY Several of the discipline's defining principles can be adapted for analytical methods.

Prevention
Prevent or reduce the formation of waste, especially in sample preparation, chromatography, and equipment cleaning.

Safer Solvents And Auxiliaries
Use less toxic or less environmentally burdensome chemicals and solvents.

Design For Energy Efficiency
Design energy-efficient analytical systems. Run systems with minimal sample size and number of samples.

Reduce Derivatives
Avoid the use of derivatization reagents or other sample pretreatment. Use direct detection if possible.

Real-time Analysis For Pollution Prevention
Employ in situ analysis along with multianalyte or multiparameter methods.

Inherently Safer Chemistry For Accident Prevention
Use safe chemistry to minimize the potential for accidents, including releases, explosions, and fires.

SOURCES: *Chem. Rev.* 2007, DOI: 10.1021/cr068359e; *Pure Appl. Chem.* 2013, DOI: 10.1351/pac-con-13-02-05; and *Trends Anal. Chem.* 2013, DOI: 10.1016/j.trac.2013.04.010

GREEN ANALYTICAL APPROACHES:

SAMPLING

Not covered by 53% of schools in Griffiths* SWAP survey,
average 0.7 lecture periods.

PLANNING

Statistics covered by all schools in SWAP survey.

Design of Experiments, Chemometrics likely
too advanced for Quant course.

*P. R. Griffiths, *Anal. Bioanal. Chem.* **391**:875-880 (2008).

GREEN ANALYTICAL APPROACHES:

DIRECT ANALYSIS

Ion-Selective Electrodes…Potentiometry covered by 83% of schools in SWAP survey, average 1.5 lecture periods.

Reflectance Spectroscopy, Surface Analysis likely get cursory coverage, at best.

CHROMATOGRAPHY

GC covered 70% schools in SWAP survey, average 0.8 lecture periods.

LC covered 60% schools in SWAP survey, average 0.8 lecture periods

GREEN ANALYTICAL APPROACHES:

SAMPLE PREPARATION

Not even part of SWAP survey. Most schools likely cover solvent extraction, but not newer (greener) techniques like SFE, SPME, etc.

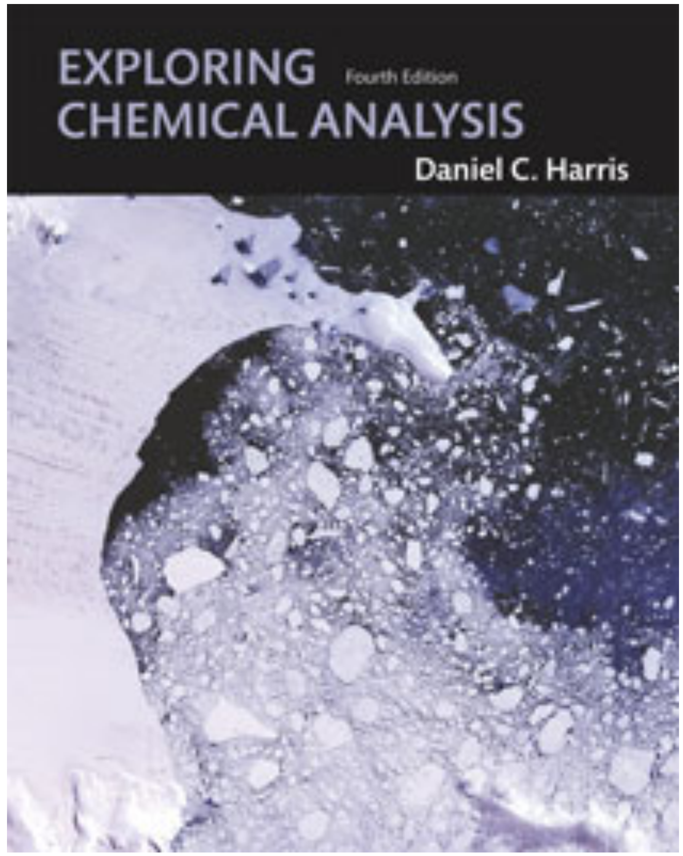
FIELD ANALYSIS/PROCESS ANALYSIS

Not even part of SWAP survey, not likely covered by most schools.

Exploring Chemical Analysis, 4th Edition

Daniel C. Harris

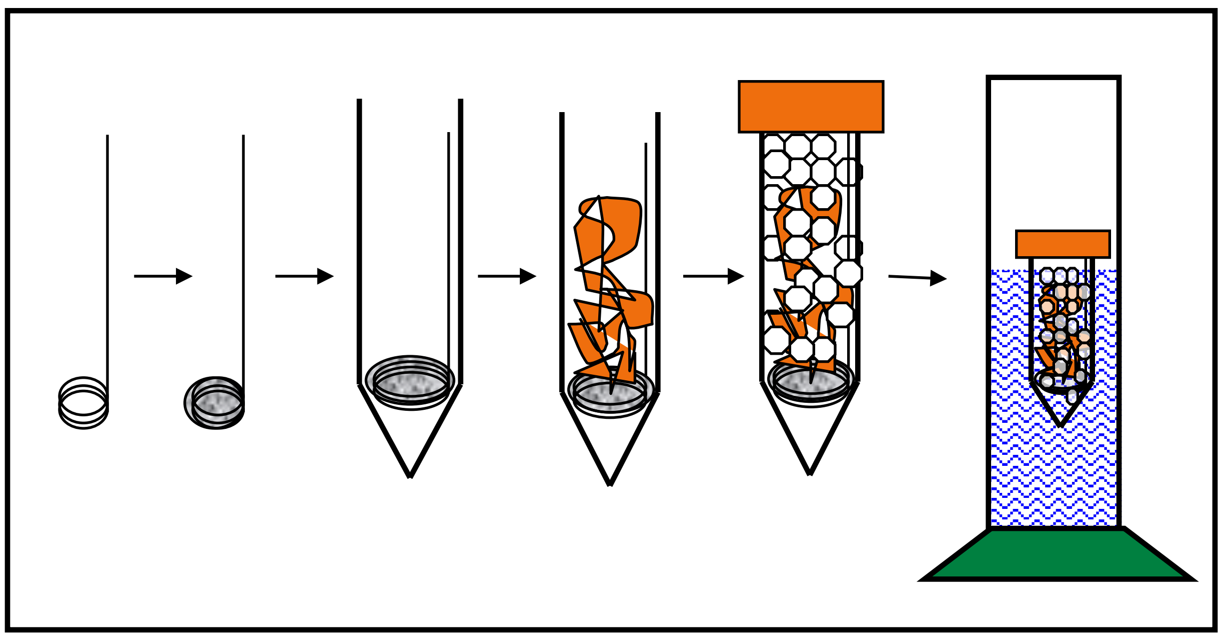
W. H. Freeman



ISBN: 1-4292-0147-9
ISBN-13: 978-1-429-20147-6

LIQUID CO_2 EXTRACTION

- Modified for Instrumental Analysis
- Lemon gives half dozen peaks in GC
- Teaches…instrument development



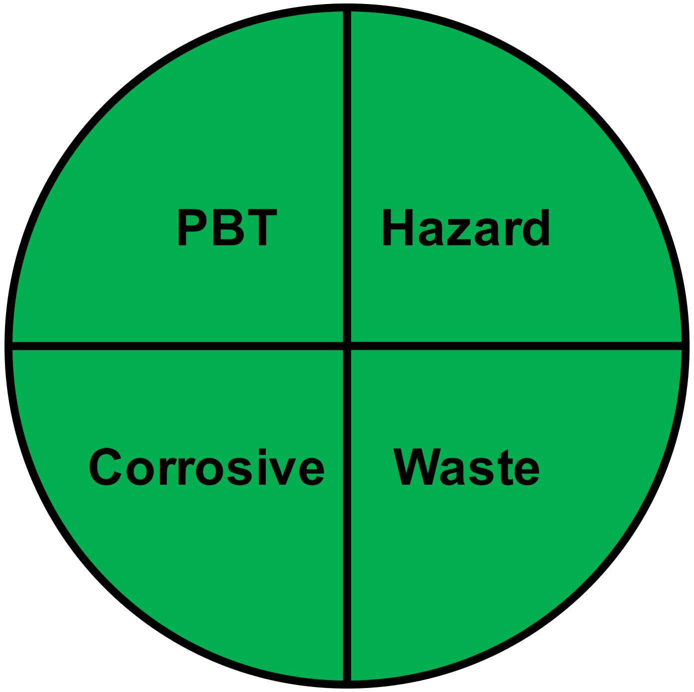
GREENNESS PROFILE

- Developed and applied to methods in NEMI database
  - ✓ ACS GCI and 25 environmental method experts from 5 agencies
- www.nemi.gov
- Profile criteria:
  - ✓ PBT – persistent, bioaccumulative, toxic as defined by EPA Toxic Release Inventory (TRI)
  - ✓ Toxic – listed on TRI or RCRA
  - ✓ Corrosive – pH < 2 or pH > 12
  - ✓ Waste – greater than 50 grams
  - ✓ Energy – considered, but no consistent means to evaluate

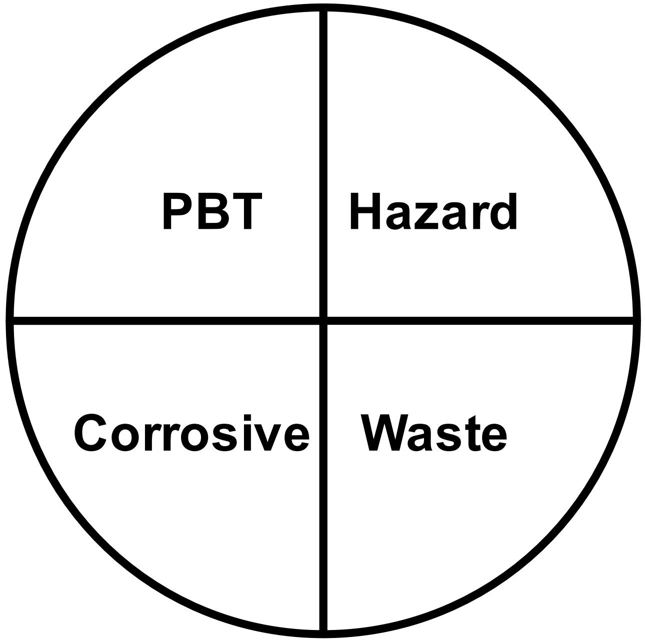
*Keith, L. H.; Gron, L. U.; Young, J. L. *Chem. Rev.* 2007, **107**, 695-708.

GREENNESS PROFILE
Comparison of Textbook Experiments to Environmental Methods

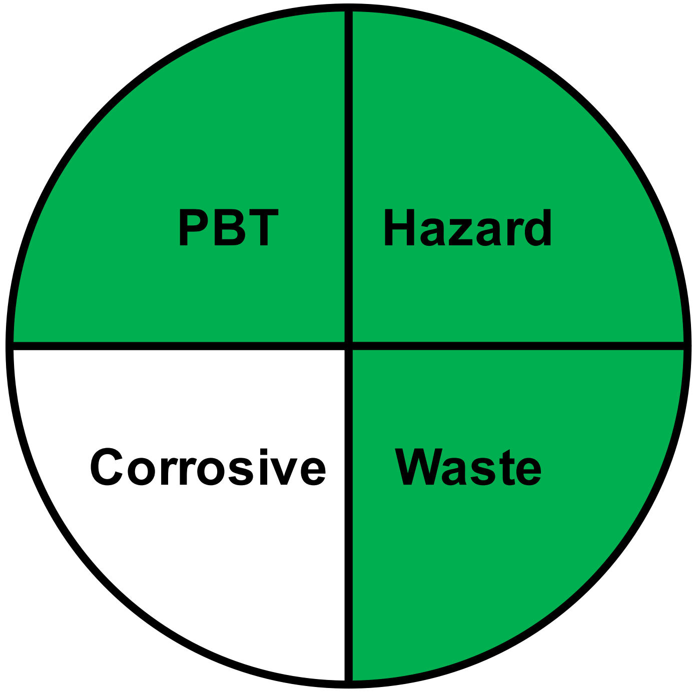
	NEMI Database	Harris Experiments
Hazard	about 50%	27%
Waste	about 67%	84%
Corrosion	20%	76%
PBT	5%	27%



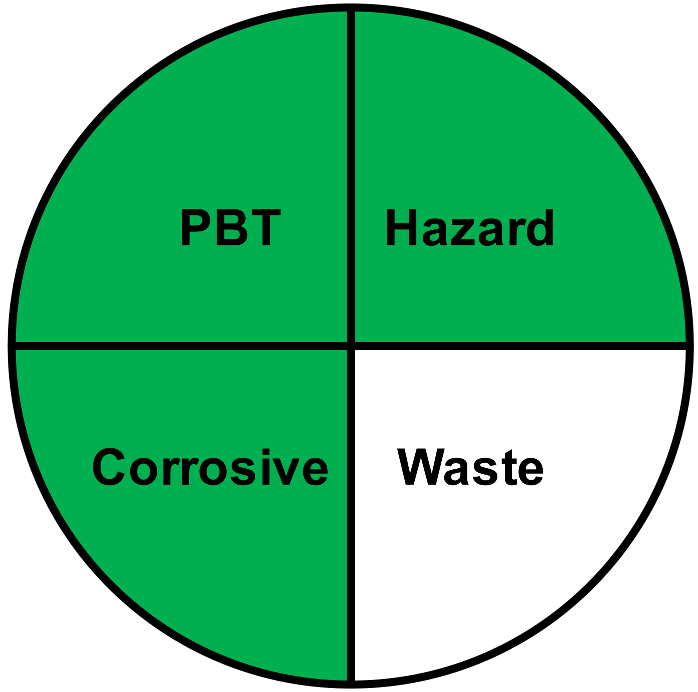
- Calibration of Volumetric Glassware
- Penny Statistics
- Measuring Carbon Dioxide in Automobile Exhaust by Gas Chromatography
- DNA Composition by High-Performance Liquid Chromatography
- Carbon Dioxide Extraction of Lemon Peel Oil



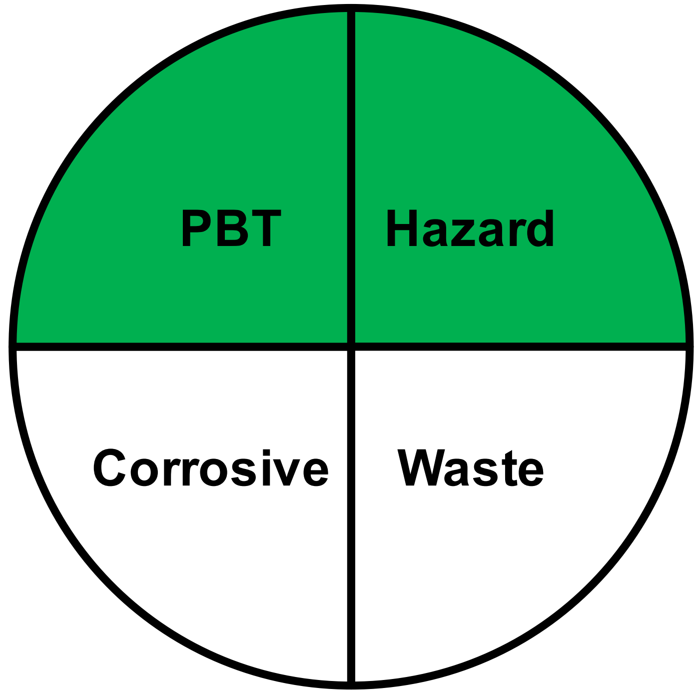
- Gravimetric Determination of Iron as Fe_2O_3
- Analysis of a Mixture of Carbonate and Bicarbonate
- Iodimetric Titration of Vitamin C
- Potentiometric Halide Titration with Ag^+
- Electrogravimetric Analysis of Copper
- Polarographic Measurement of an Equilibrium Constant
- Coulometric Titration of Cyclohexene with Bromine
- Spectrophotometric Determination of an Equilibrium Constant: The Scatchard Plot
- Measuring Manganese in Steel by Atomic Absorption Using a Calibration Curve



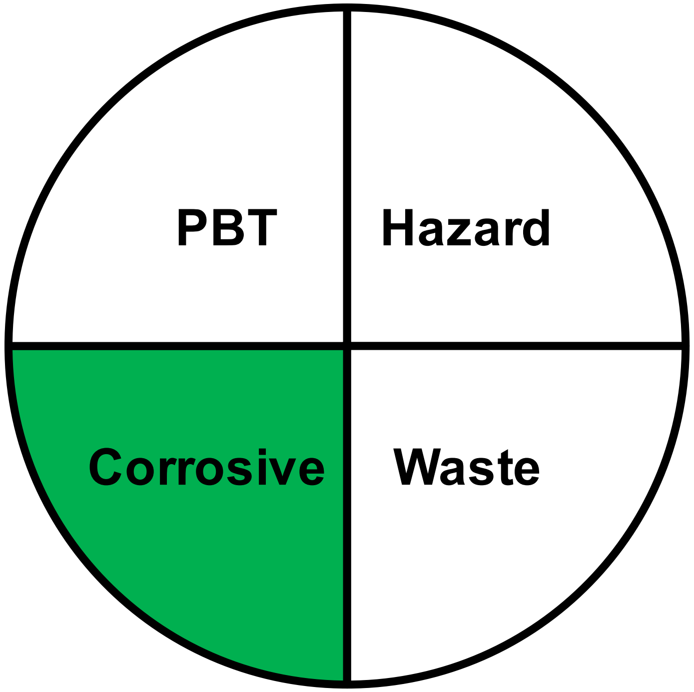
•Anion Content of Drinking Water by Capillary Electrophoresis



- Spectrophotometric Analysis of a Mixture:
  Caffeine and Benzoic Acid in Soft Drink
- Mn^{2+} Standardization by EDTA Titration
- Analysis of Analgesic Tablets by High-Performance
  Liquid Chromatography

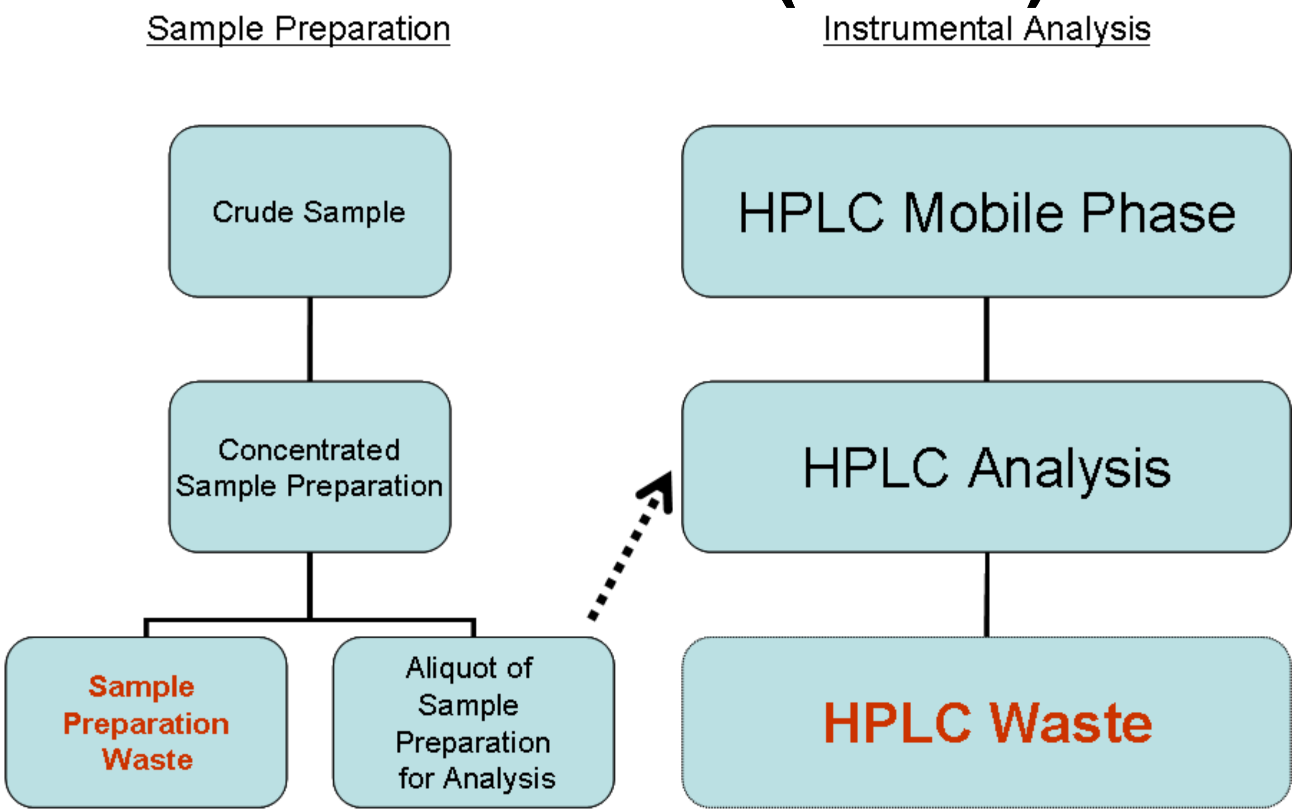


- Gravimetric Determination of Calcium as $CaC_2O_4 \cdot H_2O$
- Statistical Evaluation of Acid-Base Indicators
- Preparing Standard Acid and Base
- Using a pH Electrotrode for an Acid-Base Titration
- Analysis of an Acid-Base Titration Curve: The Gran Plot
- Fitting a Titration Curve with Excel SOLVER©
- Kjeldahl Nitrogen Analysis
- EDTA Titration of Ca^{2+} and Mg^{2+} in Natural Waters
- Synthesis and Analysis of Ammonium Decavanadate
- Measuring Ammonia in an Aquarium with an Ion-Selective Electrode
- Measuring Vitamin C in Fruit Juice by Voltammetry with Standard Addition
- Spectrophotometric Determination of Iron in Vitamin Tablets
- Microscale Spectrophotometric Measurement of Iron in Foods by Standard Addition
- Spectrophotometric Determination of Nitrite in Aquarium Water
- Measuring Manganese in Steel by Spectrophotometry with Standard Addition
- Properties of an Ion-Exchange Resin
- Analysis of Sulfur in Coal by Ion Chromatography
- Amino Acid Analysis by Capillary Electrophoresis



•**Preparation and Iodometric Analysis of High-Temperature Semiconductor**

MERCK ANALYTICAL METHOD VOLUME INTENSITY (AMVI)



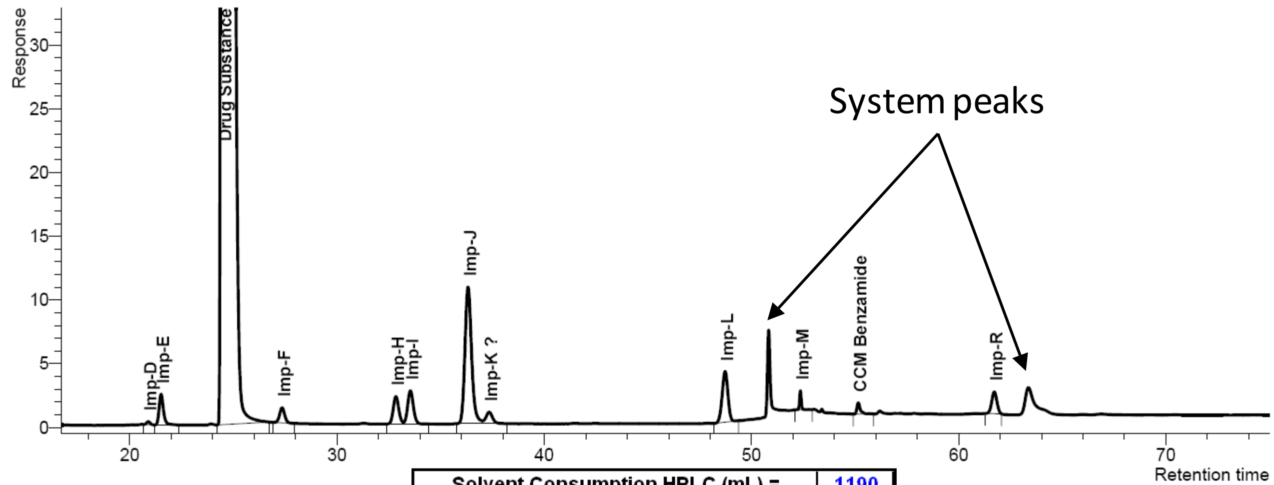
AMVI = Total Solvent Consumption/Peak Number

- Total Solvent Consumption = (Σsolvent sample prep + Σsolvent HPLC) *Replicates
- Peak Number = Σ analyte peaks specified in method

R. Helmy, R. Hartman, C. J. Welch, and M. Al-Sayah, *Green Chem.*, 2011, **13**, (934-939)

HPLC METHOD FROM JOINT VENTURE

(250 x 4.6 mm, 5 μm column)

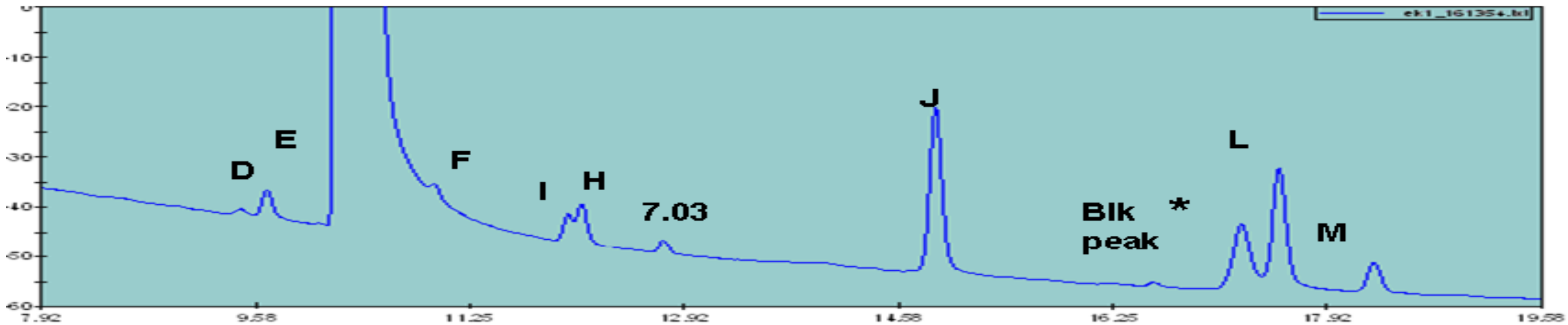


Solvent Consumption HPLC (mL) =	1190
Flow Rate	1.0
Total Run Time (run + post time)	85
Number of Inj for 1 full analysis (include all blanks, sys suit, std's, and sample inj's)	14
Number of potential analytes (only include analytes that are relevant to current process)	12
Solvent Consumption Sample Prep (mL) =	**500**
Standard Prep volume (mL)	100
Number of Std. preps	2
Sample Prep volume (mL)	100
Number of Sample Preps	2
System Suit volume (mL)	100
Number of System Suit Preps	1
Total Method Solvent Consumption =	**1690**
Analytical Method Volume Intensity =	**141**
% Consumption HPLC	70%
% Consumption Preparation	30%

R. Helmy, R. Hartman, C. J. Welch, and M. Al-Sayah, *Green Chem.,* 2011, **13**, (934-939)

GREENING SEPARATION USING CHIP-LC

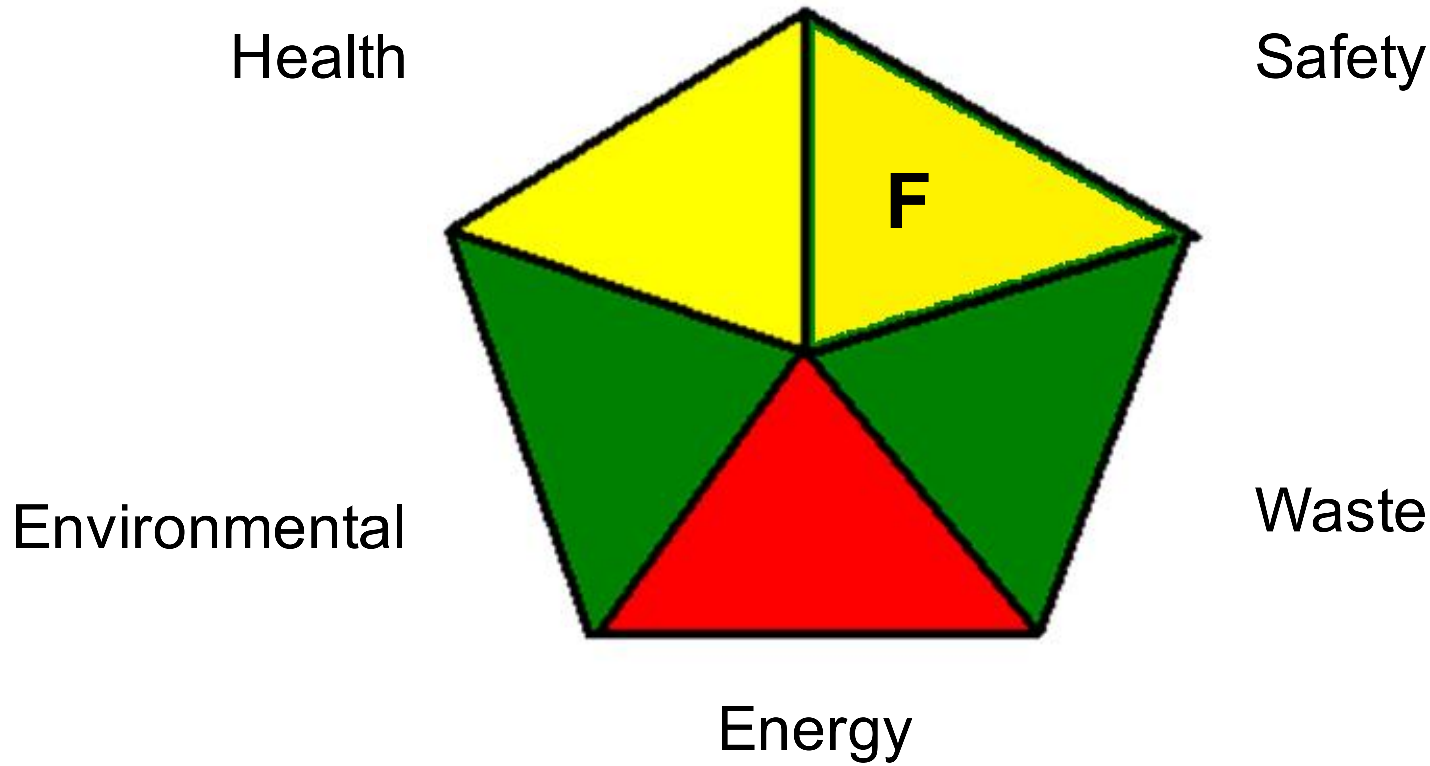
15 cm x 200 μm, 5 μm chip



Solvent Consumption HPLC (mL) =	**0.6**
Flow Rate	0.0015
Total Run Time (run + post time)	30
Number of Inj for 1 full analysis (include all blanks, sys suit, std's, and sample inj's)	14
Number of potential analytes (only include analytes that are relevant to current process)	10
Solvent Consumption Sample Prep (mL) =	**5**
Standard Prep volume (mL)	1
Number of Std. preps	2
Sample Prep volume (mL)	1
Number of Sample Preps	2
System Suit volume (mL)	1
Number of System Suit Preps	1
Total Method Solvent Consumption =	**6**
Analytical Method Volume Intensity =	**0.6**
% Consumption HPLC	11%
% Consumption Preparation	89%

R. Helmy, R. Hartman, C. J. Welch, and M. Al-Sayah, *Green Chem.*, 2011, **13**, (934-939)

GREEN ASSESSMENT PROFILE



D. E. Raynie and J. L. Driver 13th Green Chemistry and Engineering Conference, 2010, Washington, DC

ASSESSMENT WORKSHEET

Method Evaluation: EPA Method 550 Determination of PAH's in Drinking water by LLE and HPLC

Chemical	NFPA Health Rating*	NFPA Flammability Rating*	NFPA Instability Rating*	PBT, CAA, or CWA listed?*	Density (g/mL) if chemical is liquid*	Waste generated per sample (calculate amount if volumes are given in method)	
						Volume used to process one sample (mL)	Amount used to process one sample (g)
Methylene chloride	2	1	0	yes	1.33	60 + 60 + 60 + 20 + 1 + 2	270 g
Acetonitrile	2	3	0	yes	0.78	3 + 27	21 g
Reagent water						24	24 g
Sodium sulfate	1	0	1	no			20 g
Sodium Thiosulfate	1	0	0	no			
							Total: 335 g

* Information can be found on chemical's MSDS. (May need to look up a current MSDS for CAA and CWA listing information).

Extraction or analytical equipment or instrumentation	Watts listed on instrument	Approximate use time required for one sample (hours)	kWh
evaporate 200 mL CH_2Cl_2, warm water bath			
LC			

Summary

Method Health Rating: ________2________

Method Safety Rating: ________2F________ (Add letter 'F' if rating is for flammability, 'R' if rating is for reactivity/instability)

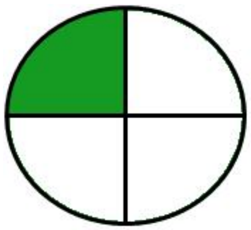
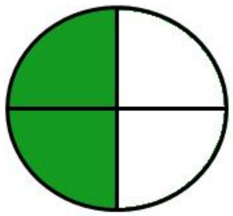
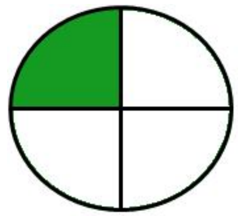
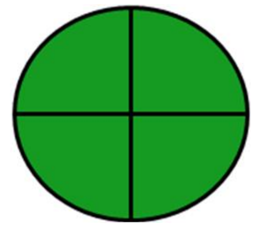
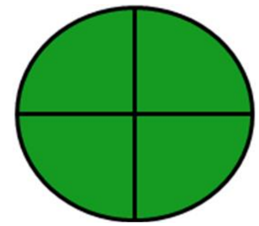
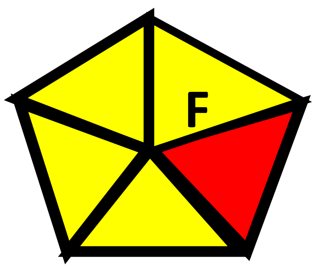
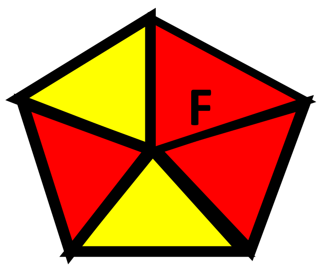
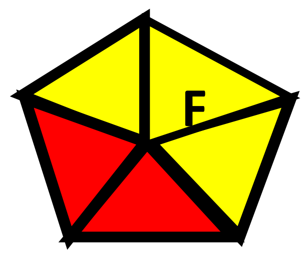
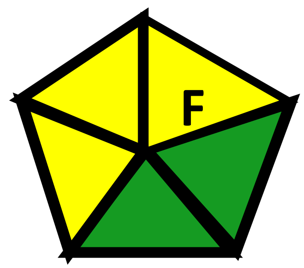
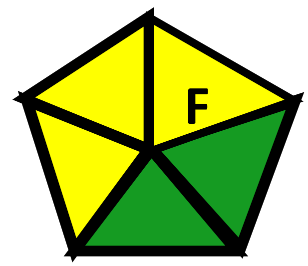
Method Environmental Rating: ________2________

Method Waste Rating: ________3________

Method Energy Rating: ________2________

D. E. Raynie and J. L. Driver 13th Green Chemistry and Engineering Conference, 2010, Washington, DC

METHOD COMPARISON

550	610	525.2	70620	A00156/ A00157
				
				

D. E. Raynie and J. L. Driver 13th Green Chemistry and Engineering Conference, 2010, Washington, DC

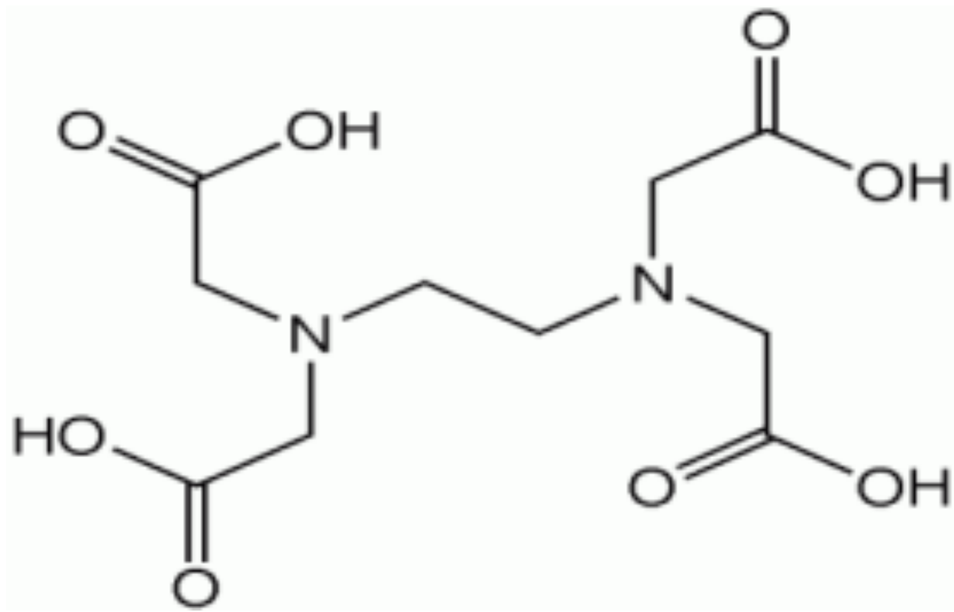
PFIZER MEDICINAL CHEMISTRY SOLVENT SELECTION GUIDE

Preferred	Usable	Undesirable
Water	Cyclohexane	Pentane
Acetone	Toluene	Hexane(s)
Ethanol	Methylcyclohexane	Di-isopropyl ether
2-Propanol	TBME	Diethyl ether
1-Propanol	Isooctane	Dichloromethane
Heptane	Acetonitrile	Dichloroethane
Ethyl acetate	2-Me THF	Chloroform
Isopropyl acetate	THF	NMP
Methanol	Xylenes	DMF
MEK	DMSO	Pyridine
1-Butanol	Acetic acid	DMAc
t-Butanol	Ethylene glycol	Dioxane
		Dimethoxyethane

PFIZER SOLVENT REPLACEMENT TABLE

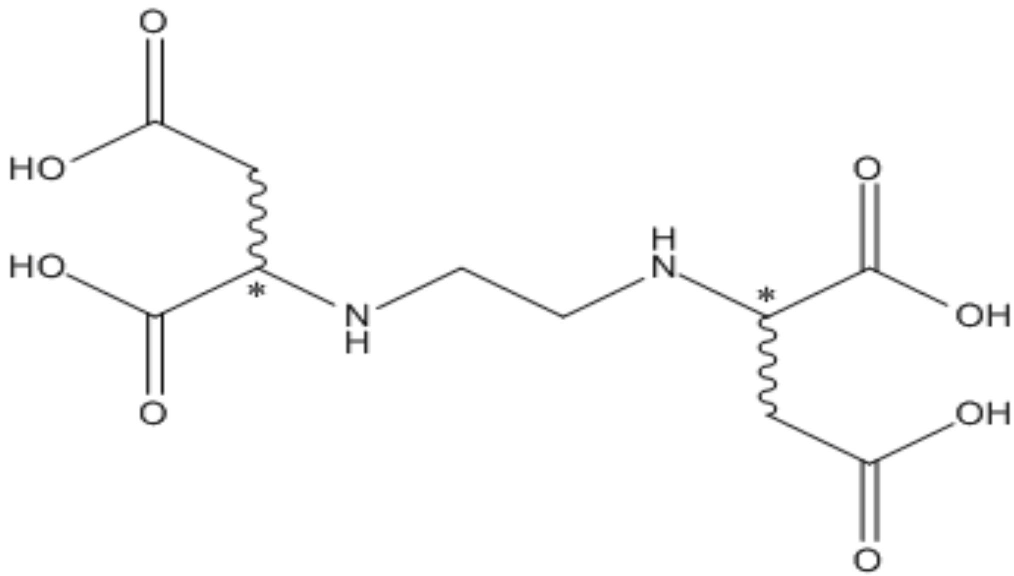
Red Solvents	**Alternative**
Pentane	Heptane
Hexane(s)	Heptane
Di-isopropyl ether or ether	2-MeTHF or *t*-Butyl methyl ether
Dioxane or dimethoxyethane	2-MeTHF or *t*-Butyl methyl ether
Chloroform, dichloroethane or carbon tetrachloride	DCM
DMF, NMP or DMAc	Acetonitrile
Pyridine	Et3N (if pyridine used as base)
DCM (extractions)	EtOAc, MTBE, toluene, 2-MeTHF
DCM (chromatography)	EtOAc/Heptanes
Benzene	Toluene

ETHYLENEDIAMINETETRAACETIC ACID



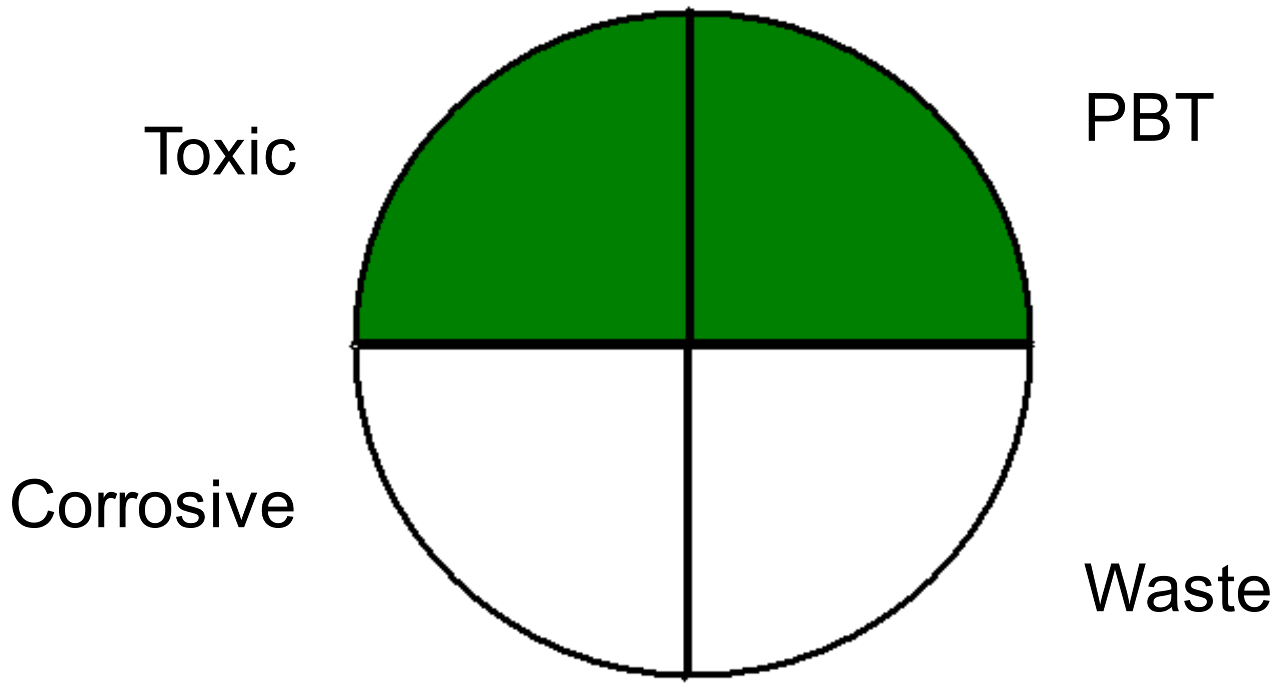
EDTA is a polyamino carboxylic acid which binds to metals through the two amino and four carboxylate groups. It does not easily degrade in the environment, allowing it to become environmentally persistent.

ETHYLENEDIAMINEDISUCCINIC ACID



EDDS is an isomer of EDTA with three stereoisomers. The most important one is the (S,S) isomer, which is easily biodegradable.

EPA Method for Total Water Hardness by EDTA Titration



- Measures Ca^{2+} and Mg^{2+} with EDTA
- Sample buffered at pH 10
- Eriochrome Black Indicator

TITRATION OF TAP WATER

	% Recovery with EDDS Titrant Relative to EDTA Titrant
Analyst #1	96.2% (2.7% RSD)
Analyst #2	108.1% (8.6% RSD)

TITRATION OF STANDARD Ca^{2+} SOLUTION

	EDTA Titrant	EDDS Titrant
Analyst #1	108.7% (2.2% RSD)	106.4% (2.1% RSD)
Analyst #2	98.7% (9.0% RSD)	101.0% (9.9% RSD)

TITRATION OF STANDARD Mg^{2+} SOLUTION

	EDTA Titrant	EDDS Titrant
Analyst #1	111.7% (1.8% RSD)	194.6% (7.7% RSD)
Analyst #2	111.8% (6.4% RSD)	149.3% (4.1% RSD)

TITRATION OF Ca^{2+} and Mg^{2+} STANDARDS

	% Recovery with EDDS Titrant Relative to EDTA Titrant
Ca^{2+}	102.3% (0.32% RSD)
Mg^{2+}, pH 9.0	96.5% (0.19% RSD)
Mg^{2+}, pH 10.0	96.9% (1.04% RSD)
Tap Water	105.88% (1.31% RSD)

TITRATION OF TAP WATER
GENERAL CHEMISTRY I LABORATORY

	Student Description	Ca^{2+} ppm
EDTA	495 students (>20 sections) 1485 data points	302.25 (15% RSD)
EDDS	56 student pairs (9 sections) 168 data points	346.05 (114.5% relative) (21% RSD)

TITRATION OF OTHER DIVALENT IONS

	% Recovery with EDDS Titrant Relative to EDTA Titrant
Mn^{2+}	115.3% (0.44% RSD)
Zn^{2+}	101.1% (0.19% RSD)
Pb^{2+} (UV-VIS Detection)	110.0% (1.11% RSD)

CONCLUSIONS:

- Both analytical chemistry and green chemistry are based on developing a way of thinking about how you perform chemistry and chemical experiments

- Green analytical chemistry is a convergence of these thought processes

- Good analytical chemistry is inherently green chemistry