

THE GREENING OF PCB ANALYTICAL METHODS NOV 14 1995

OS 11

MITCHELL D. ERICKSON, JORGE S. ALVARADO, JOSEPH H. ALDSTADT,
FREDERICK R. LEMLEY, KENT A. ORLANDINI, JAMES SILZER

Environmental Research Division,
Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439-4837
(Phone: 708-252-7772; FAX: 708-252-9594)

Abstract

Green chemistry incorporates waste minimization, pollution prevention and solvent substitution. The primary focus of green chemistry over the past decade has been within the chemical industry; adoption by routine environmental laboratories has been slow because "regulatory standard methods must be followed." A related paradigm, microscale chemistry has gained acceptance in undergraduate teaching laboratories, but has not been broadly applied to routine environmental analytical chemistry.

We are developing green and microscale techniques for routine polychlorinated biphenyl (PCB) analyses as an example of the overall potential within the environmental analytical community. Initial work has focused on adaptation of commonly used routine EPA methods for soils and oils.

Results of our method development and validation demonstrate that:

- Solvent substitution can achieve comparable results and eliminate environmentally less-desirable solvents,
- Microscale extractions can cut the scale of the analysis by at least a factor of ten,
- We can better match the amount of sample used with the amount needed for the GC determination step,
- The volume of waste generated can be cut by at least a factor of ten,
- Costs are reduced significantly in apparatus, reagent consumption, and labor.

Introduction

Green chemistry is an umbrella term addressing such related terms as waste minimization, pollution prevention, solvent substitution, environmentally conscious manufacturing, maximum atom utilization, technologies for a sustainable future, environmental security, and industrial ecology. The primary focus of green chemistry over the past decade has been within the chemical industry; adoption by routine environmental laboratories has been slow because "regulatory standard methods must be followed." A related paradigm, microscale chemistry may be defined as the application of chemical principles and apparatus at a scale much smaller than currently employed by most bench chemists, reducing volumes of reagents and products by several orders

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

MASTER 1

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DLE

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

of magnitude. Although it is gaining acceptance in undergraduate teaching laboratories, microscale chemistry has *not* been applied to routine environmental analytical chemistry. Green/microscale methods are increasingly necessary for the environmental analytical community as regulations tighten, waste disposal costs escalate, and public scrutiny increases. It is incumbent on the analytical chemists to become less introverted and “to take a lead towards the preserving of our environment rather than to [merely] measure its deterioration” (de la Guardia and Ruzicka, 1995).

We are developing green and microscale techniques for routine polychlorinated biphenyl (PCB) analyses as an example of the overall potential within the environmental analytical community. Here we report on the adaptation of commonly used routine EPA methods for water, solids, and oils. Necessary practical techniques and methods for implementation in the routine environmental laboratory community have been considered.

Results

Solvent substitution can achieve comparable results and eliminate environmentally less-desirable solvents, as illustrated in Table 1.

A wide variety of solvents are used as extractants (Erickson, 1986), generally without significant comparative evaluations among potential solvent systems. Technically, acceptable solvents are those which yield quantitative extraction of the analyte (as measured by a spiked sample); solubility of the PCBs and wetting of the soil matrix are contributing factors to the efficacy of a solvent. Our results indicate that many common solvents or solvent mixtures can yield quantitative extractions.

Microscale extractions can cut the scale of the analysis by at least a factor of ten, as illustrated in Tables 2 and 3.

Table 1 — Solvent Recoveries Using Soxhlet Extraction in Soil

Extraction Solvent	Aroclor 1254
Hexane	101
Acetone	101
1:1 Hexane/Acetone	105
3:1 Hexane/Acetone	109
3:1 Acetone/Hexane	94
Methylene Chloride	89
1:1 Methylene Chloride/Acetone	104
9:1 Hexane/Methylene Chloride	99
10:1 Toluene/Methanol	101

Table 2 - Table of Comparisons of Soxhlet/ Micro Soxhlet/ Shakeout

Parameters	Soxhlet	Micro Soxhlet	Shakeout
Sample Size (g)	10	1	0.5
Sodium Sulfate used (g)	10	1	0.5
Extraction Solvent Volume (mL)	300	15	15 ^a
Extraction Time	16-24 hrs	5 hrs	15 min
Concentration Technique	Kuderna-Danish	Nitrogen Blowdown	Nitrogen Blowdown
Concentration Time (min.)	10-20	10 - 20	10 - 20
Florisil used for clean-up (g)	20	1	1
Solvent used for clean-up	Methylene Chloride	Hexane	Hexane
Final Concentration Volume (mL)	10	1	1
Waste Volume (mL) ^b	610	25	24
Apparatus Cost (\$) ^c	2.50	1.40	0.19
Reagent Cost (\$) ^d	12.76	2.76	2.76

^aThe 15 mL consisted of three 5 mL extractions each lasting 5 min.

^bAssumes no recycling at this point. Does not include gloves and other ancillary waste.

^cBased on manufacturer's catalog prices or actual purchase requisitions. Soxhlet and micro soxhlet amortized over 100 uses (i.e., Soxhlet investment= \$250).

^dBased on manufacturer's catalog prices or actual purchase requisitions; assumes complete consumption of amount purchased for sodium sulfate, florisil, and solvent.

**Table 3 - Florisil Extraction of PCBs from Motor Oil -
Macroscale and Microscale (SPE)**

REAGENT	MACROSCALE	MICROSCALE
Florisil (g)	20	1
Hexane (mL)	280	25
Oil Sample (g)	1.5	0.2
TOTAL WASTE(mL) ^a	~ 300	~ 26
TIME (min)		
Dilution/Clean-Up	120	20
Eluate Concentration ^b	50	50
GC Analysis Time	45	45
TOTAL	215	115
COST (\$)		
Florisil	2.61	2.37 (SPE syringe)
Hexane	3.28	.29
Apparatus ^c	0.52	-
TOTAL ^d	6.41	2.66
YIELD		
% Yield	100	100

^aAssumes no recycling. Does not include gloves and other ancillary waste.

^bNitrogen Blowdown technique used for concentration of eluate. Time required is based on volume of solvent evaporated.

^cGlass chromatography column with reservoir amortized over 100 uses (i.e., column investment = \$52) for the macroscale procedure. Microscale requires no comparable apparatus.

^dBased on manufacturer's catalog prices or actual purchase requisitions. Assumes complete consumption of amount purchased.

Matching sample to determination size requirements. We can better match the amount of sample used with the amount needed for the GC determination step, as illustrated in Table 4.

Table 4 - Scaling Chemistries to What is Needed for the Determination Step (PCB Example)

Problem	Solution	Result
1 μ L/injection	Use of an internal recovery standard	Smaller initial sample
Currently 10 ⁻³ to 10 ⁻⁴ of sample injected	Final (small) inexact volume compensated	Fewer reagents

Waste volume reduction. The volume of waste generated can be cut by at least a factor of ten, as shown in Table 2 and 3. This is increasingly important as we move toward full cost-accounting including waste disposal costs, in the analytical chemistry laboratory.

Cost considerations. Costs are reduced significantly in apparatus, reagent consumption, and labor. The apparatus and reagent cost reduction are illustrated in Tables 2 and 3. The labor costs were not quantified, but can be inferred directly from several rows of both tables. There will be a cost impact during transition: new glassware will be purchased, method validation will require some overhead time (see next section), training will require some down-time, and some efficiencies will be seen only after a break-in period. Laboratories are advised to plan transitions such that they do not occur during a crisis period and phase in changes in methods over a period of time.

Quality assurance. Any adaptation of a method requires some sort of internal validation. The changes discussed here are no different. Any laboratory adapting their routine methods to green/microscale techniques needs to validate the changes with the appropriate quality control samples to demonstrate that the laboratory is providing data of known and consistent quality. In addition, quality control measures need to be modified as necessary to clearly monitor the performance of the analyses.

Regulatory considerations. PCB analyses are most often conducted to comply with regulatory guidance under several statutes, notably TSCA. Except in specific instances, TSCA rules do not specify the analytical methods to be used. Dozens of standard methods have been issued (Erickson, 1986). Among the more broadly applied is EPA's "Test Methods for Evaluating Solid Waste" (EPA, 1986 and any newer updates, editions, or revisions), which has document number SW-846 and is commonly referenced by that alphanumeric shorthand. This multi-volume document contains methods to be applied under the Resource Conservation and Recovery Act (RCRA), but is widely applied beyond the regulatory requirements. For most applications, SW-846 is a guidance document and **analyses using reasonable adaptations of the published procedures are permitted.** Except for four specific federal applications and any imposed by states or other authorities, the manual is a "guidance document setting forth acceptable, though not required, methods to be implemented by the user, as appropriate, in responding to RCRA-related sampling and analysis requirements" (58 FR 46041, August 31, 1993) and "any reliable analytical method may be used to meet other requirements under Subtitle C of RCRA" (Abstract of SW-846, Revision 1, July 1992). Lesnik (1992) clearly amplifies this by stating that "the manual is intended to be a collection of flexible methods, suitable for adaptation to cover the wide range of analytical applications and matrices required by the RCRA regulations...Examples of this flexibility include

adjusting sample sizes to fit the optimum analytical range of methods, or using alternate glassware or equipment provided that method performance is not compromised." The Disclaimer in the manual states "SW-846 methods are designed to be used with equipment from any manufacturer that results in suitable method performance (as assessed by accuracy, precision, detection limits, and matrix compatibility)" (Disclaimer of SW-846, Revision 0, July 1992). Similar text is found in Chapter 2 (Section 2.1.2, Rev. 2, Nov., 1992): "...glassware and supplies...specified in these methods *may be replaced by any similar types* as long as this substitution does not affect the overall quality of the analyses [emphasis added]." Thus, contrary to beliefs of many requesting or conducting analyses, PCB analysis according to verbatim SW-846 procedures is not required for many applications and reasonable adaptations are permitted.

Conclusions

We have demonstrated the potential of green chemistry in the laboratory through the adaptation of commonly used routine EPA methods for soils and oils. We have developed miniature extractions and cleanups feeding into standard GC analysis. The "green chemistries" applied include:

- Substitute other solvents for methylene chloride
- Minimize reagent consumption
- Reduce apparatus costs with microscale glassware
- Reduce energy consumption.

The methods developed here have direct applicability to the routine PCB analysis laboratory, such as those used by the utility industry. The applications presented here can be applied now without awaiting regulatory approval.

The results reported here are but a few steps along the path toward green analytical chemistry; much more remains to be done.

Acknowledgments

Work supported by the U.S. Department of Energy, Assistant Secretary for Environmental Management, Office of Technology Development, under contract W-310109-Eng-38. We wish to thank Ella Mulford (DOE-Chicago) for her support of this project and Jim Thuot (ANL-Environmental and Waste Minimization) for encouragement and helpful suggestions. Pam Postlethwait and Amrit Boparai are thanked for assistance in the chemical analyses.

References

1. de la Guardia, M. and J. Ruzicka, "Towards Environmentally Conscientious Analytical Chemistry through Miniaturization, Containment, and Reagent Replacement," *Analyst* 120: 17N (1995).
2. Environmental Protection Agency. "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods, SW-846, 3rd Edition," Office of Solid Waste and Emergency Response, Washington, DC (November 1986).
3. Erickson, M. D., *Analytical Chemistry of PCBs*, Butterworths Publishers, Boston, MA, 506 pp. (1986); reprinted by Lewis Publishers, Chelsea, MI (1992); second edition in preparation.
4. Lesnik, B. "Perspectives on SW-846," *American Environmental Laboratory* 4(4): 26-27 (1992).