

United States Environmental Protection Agency
Region 2
RCRA Outreach Program

EPA-902-B-94-001
Revised May, 1994



**TECHNICAL ASSISTANCE DOCUMENT
FOR COMPLYING WITH THE TC RULE
AND IMPLEMENTING THE TOXICITY
CHARACTERISTIC LEACHING
PROCEDURE (TCLP)**

TECHNICAL ASSISTANCE DOCUMENT FOR
COMPLYING WITH THE TC RULE AND
IMPLEMENTING THE TOXICITY
CHARACTERISTIC LEACHING PROCEDURE (TCLP)

The following individuals prepared Chapter 1:

John Hansen
Hazardous Waste Compliance Branch
Air and Waste Management Division
USEPA Region 2
26 Federal Plaza
New York, New York 10278

Claudette Reed
Hazardous Waste Compliance Branch
Air and Waste Management Division
USEPA Region 2
26 Federal Plaza
New York, New York 10278

Michael Scudese
TRC Environmental Corporation
18 World's Fair Drive
Somerset, New Jersey 08873

Edited by: Frank Langone, IBM Corporation
Route 134, Yorktown Heights, New York 10598

The following individuals prepared Chapters 2 to 6:

Leon Lazarus
Monitoring Management Branch
Environmental Services Division
USEPA Region 2
2890 Woodbridge Avenue
Edison, New Jersey 08837

Mitzi Miller
Environmental Quality Management
10801 Fox Park
Knoxville, Tennessee 37931

Edited by: Frank Langone, IBM Corporation
Route 134, Yorktown Heights, New York 10598

May 1994

References herein to any specific commercial product, process or service by trade name, manufacturer, or otherwise does not imply its endorsement or recommendation by EPA, TRC or EQM.

Acknowledgements

**The authors would like to thank the following individuals
for peer reviewing this document:**

Kate Anderson, USEPA Office of Waste Programs Enforcement

Dr. Bill Batchelor, Texas A&M University

Edwin Barth, USEPA Center for Environmental Research

Dr. Ila Cote, USEPA Health Effects Research Laboratory

Phil Flax, USEPA Region 2

Oliver Fordham, USEPA Office of Solid Waste

Kathleen Grimes, NJDEPE Bureau of Environmental Measurements
and Quality Assurance

Dr. Larry Jackson, Environmental Quality Management

Kevin Kubik, USEPA Region 2

Frances Liem, USEPA Office of Compliance Monitoring

Davis Jones, USEPA Office of Waste Programs Enforcement

Rose Lew, USEPA Office of Waste Programs Enforcement

Ken Peist, USEPA Region 2

Dr. Roger Spence, Oak Ridge National Laboratories

Gale Sutton, Galson Laboratories

Rock Vitale, Environmental Standards

Dr. Ken Wilkowski, USEPA Office of Research and Development

Dr. Lew Williams, USEPA Environmental Monitoring Systems Laboratory

Appreciation is also expressed for technical contributions from:

Jennifer Bramlett, SAIC Corporation

Dr. Mike Maskarinec, Oak Ridge National Laboratory

Carla Stout, TRC Environmental Corporation

Ted Varouxis, Associated Design and Manufacturing
the supplier of equipment and training tapes for the course

Document Introduction

The goal of this document is to assist the regulated community to make proper utilization of the Toxicity Characteristic Leaching Procedure (TCLP) to demonstrate compliance with the Toxicity Characteristic (TC) and Land Ban Regulations. The following issues will be discussed:

- ! What is TCLP?
- ! When must TCLP be performed?
- ! Which analyte lists should be used to demonstrate compliance with TC and Land Ban regulations?
- ! How should a sampling strategy be developed?
- ! How much QA/QC and analytical deliverables are appropriate?
- ! How should one use the USEPA Region 2 TCLP data validation criteria?
- ! How should sampling plans be developed for multi-phase and oily materials?

The following topics were added to the 1994 version of this document:

- ! Obtaining CAMU variances from the Land Ban regulations.
- ! Inappropriateness of TCLP method for risk assessments.
- ! Characterizing heterogeneous solid wastes.
- ! Characterizing building demolition debris containing lead based paint.
- ! Implications of classifying non-hazardous wastes as hazardous.
- ! Region 2 State TCLP policy guidances.

TABLE OF CONTENTS

Chapter		Page
1.0	COMPLYING WITH THE TC RULE	1-1
1.1	Introduction	1-2
1.2	RCRA OVERVIEW	1-3
1.2.1	Growth of Hazardous Waste in America: The Case of Love Canal	1-3
1.2.2	RCRA Cradle to Grave Concept	1-5
1.2.3	Definitions of Hazardous Waste	1-8
1.2.4	Making a Hazardous Waste Determination	1-10
1.3	THE TOXICITY CHARACTERISTIC RULE	1-11
1.3.1	EP Tox Test	1-11
1.3.2	TCLP Test	1-12
1.3.3	TC Rule's Effect Upon Generators and TSDFs	1-14
1.4	TC RULE'S EFFECT ON INDIVIDUAL RCRA REGULATIONS	1-18
1.4.1	General	1-18
1.4.2	Corrective Action and Closure	1-19
1.4.3	Land Disposal Restrictions (LDR)	1-20
1.4.4	Minimum Technology Requirements for Landfills and Surface Impoundments	1-21
1.4.5	Exemption for Tanks (Minimum Technology Requirements)	1-22
1.4.6	Mixture Rule Exemption	1-23
1.4.7	Previously Delisted Wastes	1-24
1.4.8	Special Waste Exemptions	1-25
1.4.9	Hazardous Waste Listings	1-26
1.4.10	"Mixture" and "Derived From" Rules	1-27
1.4.11	Excluded Wastes	1-28
1.5	IMPACT OF TC RULE ON OTHER EPA PROGRAMS	1-29
1.5.1	Underground Storage Tanks (USTs)	1-29
1.5.2	Comprehensive Environmental Response and Liability Act (CERCLA)	1-31
1.5.3	Clean Water Act (CWA)	1-32
1.5.4	Safe Drinking Water Act (SDWA)	1-34
1.5.5	Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)	1-37
1.5.6	Used Oil Recycling Act	1-38
1.5.7	Toxic Substances Control Act (TSCA)	1-39
1.6	POLLUTION PREVENTION	1-40
1.7	CONCLUSIONS	1-43

TABLE OF CONTENTS (Continued)

Chapter		Page
2.0	APPLICATIONS OF THE TCLP METHOD	2-1
2.1	What is TCLP?	2-4
2.2	When is the Use of TCLP Applicable?	2-3
2.3	When is the Use of TCLP Inappropriate?	2-9
2.4	Sampling and Analysis Design	2-12
3.0	TC AND TCLP PROJECT PLANNING	3-1
3.1	Data Quality Objectives	3-2
3.2	DQO Case Study: Cadmium Contaminated Fly Ash Waste	3-10
3.3	Sampling and Analysis Design	3-18
3.4	Analytical Method Selection	3-22
4.0	OVERVIEW OF THE TCLP METHOD	4-1
4.1	Preliminary Sample Preparation for Leaching	4-2
4.2	Leaching Procedure for Nonvolatiles	4-5
4.3	Leaching Procedure for Volatiles	4-11
4.4	TCLP Method Quality Control	4-15
5.0	DATA VALIDATION AND DELIVERABLES	5-1
5.1	Data Validation	5-2
5.2	Data Deliverables	5-6
6.0	ANALYZING AND ASSESSING MULTI-PHASIC AND OILY WASTES	6-1
6.1	Definition of Oily Waste	6-2
6.2	Problems/Issues	6-3
6.3	Suggestions	6-5
6.4	Most Commonly Asked TCLP Question	6-7
6.5	Analytical Options	6-14

TABLE OF CONTENTS (Continued)

TABLES

Table	Page
1-1 TC Rule Constituents	1-13
1-2 Permit Modifications	1-17
2-1 Toxicity Characteristic Constituents - Alphabetical	2-10
3-1 TCLP Holding Times	3-20
3-2 TC Analytes and Their Regulatory Levels	3-23
3-3 Metals Analysis Method By ICP	3-25
3-4 Metals Analysis Methods by GFAA and Mercury by CVAA	3-25
3-5 Pesticide and Herbicide Quantitation Limits by SW 846 and CLP	3-26
3-6 Quantitation Limits for Volatile TC Constituents	3-27
3-7 Quantitation Limits for Semivolatile TC Constituents	3-28
4-1 Volume of Extract Required for One Nonvolatile Analysis	4-7

TABLE OF CONTENTS (Continued)

FIGURES

Figure	Page
3-1 Overview of the Data Quality Objectives Planning Process	3-5
3-2 Decision Performance Curve for Cadmium Fly-Ash Waste Example	3-17
4-1 TCLP Preliminary Determinations	4-4
4-2 Nonvolatile Extraction	4-6
4-3 Volatiles by ZHE	4-12
4-4 Volatiles by ZHE Continued	4-13
4-5 Standard Addition Plot	4-17

TABLE OF CONTENTS (Continued)

APPENDICES

Appendix

- I TCLP Method 1311 (July 1992, Revision 0)
- II 40 CFR 268 Subpart D Land Ban Treatment Standards
- III Associated Design and Larry Jackson's TCLP Bench Sheets and Calculations
- IV USEPA Region 2 Organic, Inorganic and TCLP Data Validation SOPs
- V References for Multi-phasic and Oily Waste
- VI Office of Solid Waste Management Methods Section Memoranda #35, #36
- VII Recommendations and Rationale for Analysis of Contaminant Release by the Environmental Engineering Committee, Science Advisory Board, October 1991
- VIII USEPA Region 2 Special Analytical Services Request
- IX Required Uses of SW 846
- X Stabilization/Solidification: Is It Always Appropriate? and Stabilization/Solidification of Wastes Containing Volatile Organic Compounds in Commercial Cementitious Waste Forms from: Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes, Second Volume, ASTM STP 1123
- XI Army Waste Classification Guidance for Building Demolition Debris Containing Lead Based Paint
- XII 1992 Workshop on Characterizing Heterogeneous Materials
- XIII Improper Hazardous Waste Characterizations: Financial and Compliance Implications
- XIV Region 2 State TCLP Guidances
- XV Risk Assessment for Disposal of Solidified/Stabilized Waste and Contaminated Soil
- XVI Barbara Metzger's 1992 Speech on Environmental Data Use, "Meeting the Customer's Need"

List of Abbreviations and Acronyms

AC	Alternating Current
ARARs	Applicable or Relevant and Appropriate Requirements
ASTM	American Society of Testing and Materials
BDAT	Best Demonstrated Available Technology
BNA	Base, Neutral and Acid Extractable Organics
CAMU	Corrective Action Management Unit
CBEC	Concentration Based Exemption Criteria
CCWE	Constituent Concentrations in Waste Extracts
CERCLA	Comprehensive Environmental Response Compensation and Liability Act of 1980
CESQG	Conditionally Exempt Small Quantity Generator
CFR	Code of Federal Regulations
CLP	Contract Laboratory Program
COC	Chain of Custody
CRDL	Contract Required Detection Limits
CTRL	Chronic Toxicity Reference Levels
CVAA	Cold Vapor Atomic Adsorption
CWA	Clean Water Act
DAF	Dilution Attenuation Factor
DC	Direct Current
DQO	Data Quality Objectives
DQOPP	Data Quality Objectives Planning Process
FAA	Flame Atomic Adsorption
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
EP Tox	Extraction Procedure Toxicity
EQL	Estimated Quantitation Limit
GFAA	Graphite Furnace Atomic Absorption
HAZWRAP	Hazardous Waste Remedial Action Program
HSWA	Hazardous Solid Waste Amendments
HWN	Hazardous Waste Numbers
	P designates Acute Toxicity
	U designates Toxic Waste
	K designates Process Waste
	F designates Generic Source Waste
	D designates Characteristic Waste
ICP	Inductively Coupled Plasma
LDR	Land Disposal Restrictions
LQG	Large Quantity Generator
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goals
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NIPDWS	National Interim Primary Drinking Water Standards
NPDES	National Pollutant Discharge Elimination System
PCB	Polychlorinated Biphenyls
POHC	Principal Organic Hazardous Constituent
POTWs	Publicly Owned Treatment Works
PPIC	Pollution Prevention Information Clearinghouse
PPIES	Pollution Prevention Information Exchange System
PQL	Practical Quantitation Limit
QA	Quality Assurance
QAMS	Quality Assurance Management Staff
QC	Quality Control
RA	Regional Administrator

List of Abbreviations and Acronyms (Continued)

RCRA	Resource Conservation and Recovery Act
RFI	RCRA Facility Investigation
RSD	Risk Specific Doses
RfD	Referenced Doses
SDWA	Safe Drinking Water Act
SQG	Small Quantity Generator
SW-846	Solid Waste Procedures
TC	Toxicity Characteristic
TCLP	Toxicity Characteristic Leaching Procedure
TIC	Tentatively Identified Compound
TSCA	Toxic Substances Control Act
TSDF	Treatment Storage and Disposal Facility
UIC	Underground Injection Control
USDW	Underground Sources of Drinking Water
UST	Underground Storage Tank
VOA	Volatile Organic Analysis
ZHE	Zero Headspace Extraction

Chapter 1

COMPLYING WITH THE TC RULE

Introduction

RCRA Overview

The Toxicity Characteristic Rule

TC Rule's Effect on Individual RCRA Regulations

Impact on Other RCRA Programs

Pollution Prevention

Conclusions

1.0 COMPLYING WITH THE TOXICITY CHARACTERISTIC RULE

The purpose of this chapter is to provide an understanding of the Toxicity Characteristic (TC) Rule, as it relates to hazardous waste management under the Resource Conservation and Recovery Act (RCRA). The development of hazardous waste issues in the United States is discussed first, giving the example of Love Canal, which is a case study of an uncontrolled hazardous waste site. Then an overview of RCRA is presented, with a comparison of the Extraction Procedure Toxicity (EP Tox) Test and the TC Rule, including the Toxicity Characteristic Leaching Procedure (TCLP) is presented. Finally, the impact of the TC Rule on RCRA and non-RCRA regulations is discussed.

1.1 Introduction

- ! Hazardous waste growth in America.
- ! RCRA system to control hazardous waste disposal.
- ! Determination of hazardous waste by testing.
- ! Changes to the testing procedure for hazardous waste. TC Rule replaces the EP Tox Test.
- ! Purpose of the manual.

- ! In America, about 500,000 companies generate approximately 170,000 metric tons of hazardous waste annually.
- ! In 1976, the Resource Conservation and Recovery Act (RCRA) was passed for proper management of hazardous waste to protect human health and the environment.
- ! The extraction procedure toxicity (EP Tox) test was one of the analytical methods used to ascertain if a waste was hazardous.
- ! The Toxicity Characteristic Leaching Procedure (TCLP) replaced the EP Tox test when determining if a solid waste is hazardous because it exhibits the toxicity characteristic.

1.2 RCRA OVERVIEW

1.2.1 Growth of Hazardous Waste in America: The Case of Love Canal

- ! America in the 1890s.
- ! The invention of electricity.
- ! New chemicals.
- ! Clustering of industries around power sources.
- ! Building of Love Canal to connect the lower and upper parts of Niagara Falls.
- ! DC power versus AC power.

! America in the 1890s was undergoing industrialization. With the invention of electric power, new chemicals were developed. A widely used chemical process was the electrolysis of sodium chloride (salt) to yield sodium hydroxide (lye), chlorine and hydrogen. Lye was mixed with waste animal fat from slaughter houses to produce soap. Ivory soap is still made this way. Chlorine, originally a useless byproduct, eventually was utilized as a raw material in the production of chlorinated solvents and pesticides. These chemicals had toxic effects which were not then understood.

! Direct current (DC) electricity was used for this electrolysis process. Industries in the 1890s which used significant quantities of electricity had to cluster around their DC power sources because DC electricity does not travel efficiently.

! In Niagara Falls, a hydroelectric dam generated low cost electrical energy. Industries were clustered in the area to obtain inexpensive DC power. Construction commenced on the Love Canal industrial transportation network to connect the lower and upper parts of the Niagara Falls area.

! However, when alternating current (AC) electricity was invented, electricity travelled much further over power lines. Thus, it was no longer necessary to cluster industries around the Niagara Falls area, and the Love Canal project was abandoned. Love Canal was subsequently used by industry as a hazardous waste dump, and leached toxic contaminants into the surrounding ground water and soil. Even after Love Canal was capped and closed, toxic chemicals continued to leach out.

! Most of the discarded hazardous chemicals were contained in the clay-lined Love Canal until school and highway construction ruptured the walls. This fracturing of the walls caused chemicals to contaminate local homes and the school built directly over the dump site. People living in the area started to experience health problems, including miscarriages, stillbirths, and chromosome damage.

- ! In 1980, President Jimmy Carter evacuated approximately 700 families out of the Love Canal area to protect their health.
- ! The purpose of RCRA is to prevent this type of inadequate hazardous waste management.

1.2.2 RCRA Cradle to Grave Concept

- ! RCRA tracks hazardous waste from cradle to grave:
 - the manifest system.

- ! Components:
 - generator
 - transporter
 - treatment storage and disposal facility (TSDF).

- ! Anyone generating hazardous waste must notify EPA:
 - generator definition.

- ! RCRA is considered a "cradle to grave" system because it regulates the handling of hazardous waste from creation to disposal. This ensures that hazardous waste is handled properly, and does not contaminate the environment.

- ! There are three hazardous waste handler classifications: the generator, who creates the hazardous waste; the transporter, who transports the hazardous waste to the ultimate disposal site; and the ultimate disposal site, which is called a treatment, storage and disposal facility (TSDF). Final disposition of hazardous waste often occurs after interim storage/treatment/recycling operations at several sites.

- ! Facilities that generate solid waste must determine if their solid waste is a hazardous waste.

- ! Facilities that generate hazardous waste must notify EPA or the authorized State agency, and obtain an EPA facility identification number (EPA ID number).

- ! The EPA or an authorized state agency issues an EPA ID number to make unique identification of each TSDF which handles hazardous waste.

- ! Hazardous waste generators must manage hazardous waste according to RCRA regulations. The generator must dispose of hazardous waste properly, and must complete a manifest enumerating the contents of the waste.

- ! The generator is responsible for using authorized transporters and disposal facilities.

- ! The generator can usually store hazardous waste on site for up to 90 days without a storage permit.

- ! Generator responsibilities:
 - Determination of hazardous waste
 - Notify EPA
 - Obtain EPA ID number
 - Prepare manifest
 - Dispose of waste using an authorized transporter and an authorized TSDf
 - Accumulation time
 - Annual reports
 - Contingency plans/Training requirements

! Generator categories - CESQG/SQG/LQG

- ! RCRA enforcement:
 - State versus Federal

! The generator must file bi-annual reports detailing the amount of waste disposed.

! EPA generator categories (many states have different generator categories):

- LQG - Large quantity generators (LQG) generate more than 1000 kilograms (kg) of hazardous waste/month or more than 1 kg of acutely hazardous waste/month. LQGs are fully regulated and must comply with all generator requirements indicated above.
- SQG - Small quantity generators (SQG) are generators which:
 - Generate between 100 and 1,000 kg/month of hazardous waste.
 - Accumulate no more than 6,000 kg of hazardous waste on site at any one time.
 - Accumulate hazardous waste on site for up to 180 days or 270 days if the disposal site for the waste is over 200 miles away.
 - Provide notification of hazardous waste activities, use manifests to dispose of hazardous waste, and dispose of hazardous waste at TSDFs, but do not file annual reports.

- CESQG - Conditionally exempt small quantity generators (CESQG) are generators which:
 - Generate less than 100 kg/month non-acute hazardous waste per calendar month or;
 - Generate less than 1 kg/month acutely hazardous waste (P-waste code). There are also several acutely hazardous F-listed wastes.
 - May never accumulate more than 1,000 kg of hazardous waste or greater than 1 kg of acutely hazardous waste at any time. If they do, they will be regulated as a SQG.
 - Are subject to reduced requirements. SQGs do not need to notify EPA or State agencies, use manifests, or dispose of their hazardous waste in a TSD (they may use a municipal or industrial landfill).

! RCRA enforcement:

- EPA has delegated RCRA enforcement authority to many states. In those states, the hazardous waste regulations may not be less strict than EPA's regulations. Some states have regulations which are more stringent than EPA's.
- EPA however, retains overall jurisdiction over all state RCRA programs.

1.2.3 Definitions of Hazardous Waste

- ! Only wastes classified as "solid wastes" may be characterized as "hazardous wastes".
- ! The definition of hazardous waste has four parts:
 - "Statutory definition"
 - "Listed waste" - Four lists: F, K, U, P
 - "Mixture rule" - Defines hazardous waste as being a mixture of a hazardous waste and a non-hazardous waste.
 - "Characteristic waste"
 - Ignitable
 - Corrosive
 - Reactive
 - Toxic - (TC Rule)

- ! Only wastes classified as "solid wastes" may be characterized as "hazardous wastes." Definition of solid waste:

"The term solid waste means any garbage, refuse, or sludge, from a waste treatment plant, water supply treatment plant, or air pollution control facility; and other discarded material, including solid, liquid, semisolid, or contained gaseous material resulting from industrial, commercial, mining, and agricultural operations, and from community activities, but does not include solid or dissolved materials in irrigation return flows or industrial discharges which are point sources subject to permits under Section 402 of the Federal Water Pollution Control Act, as amended Statute 880; or source, special nuclear, or byproduct material as defined by the Atomic Energy Act of 1954, as amended (68 Statute 923)."¹

- ! Definition of hazardous waste:

"The term 'hazardous waste' means a solid waste, or combination of solid wastes, which because of its quantity, concentration, or physical, chemical or infectious characteristics may:

- (A) *cause, or significantly contribute to an increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness; or*
- (B) *pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed."²*

¹ 42 United States Code (USC) 6903, Section 1004(27)

² - Ibid, (5)

Regulatory Definitions:

! Listed hazardous waste - Wastes classified as hazardous because of how they were produced. There are four lists of hazardous waste: F, K, U, and P.

Four types of listed waste:

- F Waste - List of waste from non-specific sources
- K Waste - List of waste from specific sources
- U Waste - List of discarded chemical products
- P Waste - List of acutely toxic discarded chemical products

! Mixture rule - Any mixture of a listed hazardous waste and a non-hazardous waste is considered hazardous.

! Derived from rule - See 40 CFR 261.3c.

! Characteristic waste - Four characteristics are utilized to determine if a solid waste, which is not a listed hazardous waste, is classified as a hazardous waste.

! Characteristic of ignitability:

- A flashpoint of $< 140^{\circ}\text{F}$
- For non-liquids - if the waste, when ignited, can burn spontaneously
- An ignitable compressed gas
- An oxidizer as defined in 49 CFR 173.151

! Characteristic of corrosivity:

- The waste is aqueous and $\text{pH} \leq 2$ or ≥ 12.5 .
- The waste corrodes steel at a rate of ≥ 6.35 millimeters/year.

! Characteristic of reactivity:

- The waste is unstable and undergoes violent reaction.
- The waste reacts violently with water.
- The waste, when heated, is explosive.
- The waste, when mixed with water, releases toxic gases.
- The waste contains cyanide or a sulfide, and releases toxic gases when exposed to pH conditions between 2 and 12.5.
- The waste can explode if shocked or heated.
- The waste is defined as an explosive by U.S. Department of Transportation regulations.

! Characteristic of toxicity - A waste exhibits the characteristic of toxicity if the concentration of one or more of the 39 toxicity characteristic analytes in the TCLP aqueous extract exceeds regulatory action levels. This is known as the TC Rule. This replaces the EP Tox Test, which contained 8 inorganic and 6 organic constituents.

Note: If wastes are listed solely because they exhibit a characteristic, and the resulting mixture no longer exhibits a characteristic, the material is no longer a hazardous waste.

1.2.4 Making a Hazardous Waste Determination

- ! Does the waste meet the definition of solid and hazardous waste?
- ! Is the waste excluded?
- ! Is the waste listed?
- ! Does the waste exhibit a characteristic of hazardous waste?

Hazardous Waste Determination

- ! Is the waste a solid waste?
- ! Is the solid waste excluded from the RCRA regulations?
- ! If the solid waste is not excluded from the hazardous waste regulations, is it a listed waste? By definition, listed wastes are hazardous wastes.
- ! If neither excluded nor listed, does this solid waste exhibit any of the characteristics of hazardous waste? If so, it is a hazardous waste.

Note: Solid waste is determined to be hazardous waste by:

- The generator's reasonable knowledge of the characteristics of the waste, or
- The generator's testing of the waste.

Listed hazardous waste is hazardous regardless of analyte concentrations in TCLP extract.

1.3 THE TOXICITY CHARACTERISTIC RULE

1.3.1 EP Tox Test

- ! What is the Extraction Procedure Toxicity (EP Tox) Test?
- ! What is the EP Tox Test based on?
 - Landfill leaching,
 - 14 metals and organics form the basis of the EP Tox Test.
- ! Contaminant levels of the EP Tox Test
 - Relationship to drinking water standards,
 - Dilution attenuation factor (DAF).

! EP Tox Test was utilized prior to TCLP to ascertain if a waste exhibited the characteristic of toxicity. The EP Tox Test analyzed waste extracts for 14 specified chemical constituents.

! EP Tox Test was based on the assumption that chemicals placed in a landfill will leach at a uniform rate into the ground water.

! EP Tox regulatory action levels are based upon drinking water standards:

- (allowable drinking water level) X 100 = EP Tox regulatory level (assumes that toxic chemicals leaching out of landfill will be diluted by a factor of 100);
- The factor of 100 is termed a dilution attenuation factor (DAF).
- The 14 metals and organic chemicals regulated by the drinking water program were assigned EP Tox regulatory levels.
- 8 metals Arsenic
 Barium
 Cadmium
 Chromium
 Lead
 Mercury
 Selenium
 Silver
- 4 insecticides Endrin
 Lindane
 Methoxychlor
 Toxaphene
- 2 herbicides 2,4 - D
 2,4,5 - TP (silvex)

1.3.2 TCLP Test

- ! Why replace the EP Tox Test with the TC Rule?
- ! How is TC different than EP Tox?
- ! How regulatory limits are determined for the TC Rule.
 - Regulatory level = CTRL X DAF

! The EP Tox Test was replaced by the TC Rule because of a Congressional mandate for aggressive regulation of additional toxic constituents.

! The original EP Tox Test was not capable of leaching volatile organic compounds without unacceptable losses during the leach test.

! Major changes:

- 25 additional organic chemicals
- different leaching medium
- procedural modifications for leaching volatile compounds

! The regulatory limit for the TCLP constituents was determined by multiplying the Chronic Toxicity Reference Level (CTRL) times the Dilution Attenuation Factor (DAF):

$$\text{Regulatory limit} = \text{CTRL} \times \text{DAF}$$

The CTRL is a level below which health effects are not expected to occur. The CTRL is based on: drinking water standards maximum contaminant level (MCL); or for carcinogens, the risk specific dose (RSD); or for non-carcinogens, the reference dose (RfD).

TABLE 1-1 - TC RULE CONSTITUENTS

EPA WASTE NUMBER	HAZARDOUS CONSTITUENT ¹	Level (mg/l)	EPA WASTE NUMBER	HAZARDOUS CONSTITUENT ²	Level (mg/l)	EPA WASTE NUMBER	HAZARDOUS CONSTITUENT ²	Level (mg/l)
D004	Arsenic	5.0	D018	Benzene	0.5	D031	Heptachlor (& epoxide)	0.008
D005	Barium	100.0	D019	Carbon tetrachloride	0.5	D032	Hexachlorobenzene	0.13
D006	Cadmium	1.0	D020	Chlordane	0.03	D033	Hexachloro-1,3-butadiene	0.5
D007	Chromium	5.0	D021	Chlorobenzene	100.0	D034	Hexachloroethane	3.0
D008	Lead	5.0	D022	Chloroform	6.0	D035	Methyl ethyl ketone	200.0
D009	Mercury	0.2	D023	o-Cresol	200.0	D036	Nitrobenzene	2.0
D010	Selenium	1.0	D024	m-Cresol	200.0	D037	Pentachlorophenol	100.0
D011	Silver	5.0	D025	p-Cresol	200.0	D038	Pyridine	5.0
D012	Endrin	0.02	D026	Cresol (total)	200.0	D039	Tetrachloroethylene	0.7
D013	Lindane	0.4	D027	1,4-Dichlorobenzene	7.5	D040	Trichloroethylene	0.5
D014	Methoxychlor	10.0	D028	1,2-Dichloroethane	0.5	D041	2,3,5-Trichlorophenol	400.0
D015	Toxaphene	0.5	D029	1,1-Dichloroethylene	0.7	D042	2,4,6-Trichlorophenol	2.0
D016	2,4-D	10.0	D030	2,4-Dinitrotoluene	0.13	D043	Vinyl chloride	0.2
D017	2,4,5-TP (Silvex)	1.0						

¹ Original EP Tox constituents.

² Chemical constituent added by TC Rule (shaded areas).

1.3.3 TC Rule's Effect Upon Generators and TSDFs

- ! Generators
 - Notification
 - Manifests
 - Annual report
 - LDR

- ! In addition to the above requirements, TSDFs must
 - Obtain a new permit
 - Modify an existing permit
 - Close prior to obtaining a permit
 - Obtain interim status
 - Make changes to interim status
 - Meet minimum technology requirements for pretreatment

! Generators which produce newly regulated TC hazardous waste not previously regulated, must submit notification, use manifests, etc., as required by their generator status. Generator responsibilities are discussed in Section 1.2.2. If the waste was previously regulated under EP Tox, no additional requirements are applicable.

! Options for TSDFs

- Obtain a new permit
 - Land disposal facilities newly regulated by the TC Rule are required to comply with minimum technology requirements when new units are added, existing units are replaced, or existing units are laterally expanded.
 - New permit requirements are enumerated in 40 CFR 270.
- Modify an existing permit (see Table 1-2)
 - The three classes of permit modifications are based on the significance of the modification. This three-tiered process, which replaces the two-tiered major/minor process, is used by the permittee to initiate a permit change. In contrast, EPA uses the old major/minor process if it initiates a permit change.
 - Class 1 - modifications for routine changes;
 - Class 2 - modifications for changes of moderate complexity that allow the facility to respond to changing conditions; and
 - Class 3 - modifications for substantial facility alterations.

- If waste at a permitted Subtitle C facility exhibits the TC for constituents that were previously identified as EP toxic, the facility continues to comply with its permit. No permit modification is needed.
- Permitted Subtitle C facilities/units handling newly regulated TC wastes must submit permit modifications to incorporate:
 - new TC Rule wastes
 - new regulated units managing TC Rule wastes

TSDF Options

- Close the facility prior to obtaining a permit.
- Obtain interim status by submitting a Part A application as an interim permitted TSDF.
- Changes to interim status
 - Change the conditions of the Part A interim status permit application to reflect the new hazardous waste.
 - EPA's new procedures for interim status are listed in 40 CFR 270.72 (a)(1)
 - No prior approval is required for adding newly regulated units to Part A permit applications if:
 - Units were managing new wastes (e.g., TC wastes) on or before effective date.
 - Amended Part A was submitted by effective date.
 - Prior to March 7, 1989, new units received approval from EPA.
 - These new units are not subject to the reconstruction limit, which restricts cumulative interim status facility changes to less than 50% of the capital costs of a comparable new facility.
- Changes to interim status - Facilities with Surface Impoundments
 - Implementation of the TC Rule may cause some facilities to alter their management practices to avoid regulation of certain units under Subtitle C of RCRA.
 - Retrofitting surface impoundments to accept TC wastes entails adding liners and leachate collection systems not installed when the impoundment was constructed.
- Changes to interim status - Land Disposal Units
 - New land disposal units should have submitted certification of compliance with ground water monitoring and financial responsibility requirements by September 25, 1991.

- Land Ban Requirements
 - Land disposal restrictions refer to restrictions on the land disposal of hazardous wastes. Restricted wastes must be treated as specified in the LDR regulations, otherwise they are banned from disposal on land.
 - Any TC Rule wastes regulated by the LDR regulations would be prohibited from land disposal.
- Minimum Technology Requirements - Surface Impoundments
- Surface impoundments which were newly regulated as a result of the TC Rule were required to meet minimum technology standards by March 29, 1994.

TABLE 1-2 - PERMIT MODIFICATIONS

Type of Unit Involved	Permit Change Needed	Modification Class
Tank or Container	Addition of waste codes or units that will not require additional or different management practices than specified in the permit.	2
	Addition of waste codes or units that will require additional or different management practices than specified in the permit.	3
Surface Impoundment, Landfill, Waste Pile, or Land Treatment	Addition of waste codes or units that will not require additional or different management practices than specified in the permit.	2
	Addition of waste codes or units that will require additional or different management practices than specified in the permit.	3
	Addition of units .	3
Incinerator	If waste does not contain a principal organic hazardous constituent (POHC) that is more difficult to incinerate and no additional performance standards are needed.	2
	If waste contains POHC that is more difficult to incinerate.	3
	If different performance standards are needed in the permit.	3

1.4 TC RULE'S EFFECT ON INDIVIDUAL RCRA REGULATIONS

1.4.1 General

! The TC Rule has potential impact on other parts of the RCRA program.

- Regulations not impacted
- Regulations which are impacted

! The TC Rule will not affect wastes already considered hazardous. The following RCRA regulations are not affected by the TC Rule:

- Listed hazardous wastes (i.e., the F, K, P, and U lists)
- Wastes that are hazardous by the "Mixture" and "Derived From" rules
- Wastes already excluded from regulation

! The implementation of the TC Rule increases the categories and volume of solid waste classified as hazardous waste. The expanded definition causes additional solid waste to be classified as hazardous wastes. The following RCRA regulations are affected by the TC Rule:

- Corrective action and closure
- Land disposal restriction (LDR) regulations
- Minimum technology requirements for surface impoundments and landfills
- Mixture rule exemptions
- Previously delisted wastes
- Special waste exclusions

1.4.2 Corrective Action and Closure

- ! TC increased the universe of regulated facilities.

Number of Subtitle C permitted and interim status facilities subject to corrective action increased.
 - Number of regulated units within permitted or interim status facilities undergoing closure increased.
- ! Excavated material from corrective action and closure that exhibits the TC must be managed as hazardous waste.
- ! TC levels are *not* used to set clean-up levels for corrective actions or clean closures.

- ! The TC Rule added more wastes of concern and brought more facilities under the RCRA program as hazardous waste management facilities. Therefore, additional facilities are newly subject to the Subtitle C corrective action and closure requirements.
 - Previously unregulated TSDFs managing TC Rule wastes were subject to RCRA requirements if they did not close or change management practices (e.g., exempt tanks) before the TC Rule became effective.
 - Existing RCRA facilities may have to amend their closure plans to reflect newly regulated units as the TC Rule expands the number of regulated units.
- ! Excavated materials, which did not previously exhibit the toxicity characteristic, may now have to be managed as hazardous waste because of the addition of newly added constituents to the regulated list.
- ! The Subtitle C corrective action program addresses remediation of hazardous waste releases from facilities subject to RCRA permitting. The TC Rule levels are neither action levels nor cleanup standards, both of which are developed from site-specific information gathered during the investigatory and evaluation phases of the remediation process.

1.4.3 Land Disposal Restrictions (LDR)

- ! LDR standards will continue to affect the 14 wastes previously regulated under the EP Tox Test.
- ! No LDR standards are currently promulgated for the 25 new TC constituents.
- ! LDR treatment standards are based on the best demonstrated available technology (BDAT) standards. The characteristic (regulatory) levels were developed using a risk-based approach.
- ! For some constituents, LDR treatment standards are set at the regulatory level.

! HSWA requires EPA to make an LDR determination for all newly listed wastes within six months of publication in the *Federal Register*, or by the effective date of the TC Rule ruling. Newly listed or identified wastes were not automatically prohibited from land disposal under LDRs if EPA failed to make this determination within six months (i.e., no "hammer" provisions).

- EPA set LDR standards for the 14 original EP characteristic constituents, which EPA does not consider newly identified. These 14 constituents had to meet LDR treatment standards before land disposal on the effective date of the TC Rule.
- The 25 additional organics identified by the TC Rule are considered newly identified, and as such have not yet been affected by LDR regulations.

! EPA is reviewing the treatability of each TC Rule constituent independently to determine LDR treatment standards for TC Rule wastes. These standards may differ from standards set for spent solvent wastes (F001-F005) based on differences in treatability.

! LDR treatment standards are based entirely on technology-based standards expressed as BDAT. While TC Rule levels are based upon health-based allowable concentration levels and dilution/attenuation factors, they are not the same as LDR treatment standards. However, for many TC wastes, EPA has set the LDR treatment standards at the regulatory level.

! This issue is being litigated. Therefore, the LDR treatment standards for TC Rule wastes may change.

1.4.4 Minimum Technology Requirements for Landfills and Surface Impoundments

- ! Landfills and surface impoundments newly regulated under RCRA because of the TC need to comply with minimum technology requirements
- ! HSWA requires that:
 - Interim status waste piles, landfills, and surface impoundments must meet certain minimum technology requirements
 - Surface impoundments must be retrofitted to meet minimum technology requirements

- ! Existing land disposal units, except surface impoundments, that already contained TC Rule wastes will not require retrofitting unless they are expanding, replacing units or continuing to place TC Rule wastes in these units.
- ! The minimum technology requirements (liners and leachate collection systems) for interim status surface impoundments are found in 40 CFR 265.221.
- ! Surface impoundments that become regulated under Subtitle C because of the TC Rule must have met the minimum technology requirements by March 29, 1994. This extension applied to those impoundments that contain the newly identified or characteristic wastes.

1.4.5 Exemption for Tanks (Minimum Technology Requirements)

- ! TC wastes treated in wastewater treatment tanks are exempt from hazardous waste management standards under 40 CFR 264.1(g) and 265.1(c).
- ! Generators that manage TC wastewaters in on-site surface impoundments may switch to exempt tanks in order to avoid Subtitle C requirements.
- ! However, generators and handlers should have converted their surface impoundments to tanks *prior* to effective date of the final rule to maintain the exemption.
- ! Facilities managing TC wastes after the effective date, even unintentionally, are subject to interim status requirements.

- ! 40 CFR 264.1(g) and 265.1(c) exempt wastewater treatment units containing hazardous waste from Subtitle C regulation.
- ! Generators that continue managing wastewaters in on-site surface impoundments or non-wastewaters on site will require either interim status or a RCRA permit modification/change during interim status, depending on whether the facility is currently a Subtitle C TSDF.

1.4.6 Mixture Rule Exemption

- ! The mixture rule exemption was not modified by the TC rule; mixtures of wastewaters and certain listed spent solvents are exempt from Subtitle C regulations unless the wastewaters:
 - Exhibit hazardous waste characteristic; or
 - Contain listed hazardous wastes not specified in the exemption.
- ! TC Rule may regulate currently exempted wastewaters under Subtitle C.

- ! The mixture rule under 40 CFR 261.3(a)(2)(iv) provides an exemption from RCRA Subtitle C requirements for mixtures of wastewaters and certain listed spent solvents in low concentrations.
- ! The mixture rule exemption only addresses hazardous waste listings. Therefore, the mixture rule exemption does not affect the TC Rule.
- ! The mixture rule exemption precludes mixtures of wastewaters and specific listed spent solvents from hazardous waste regulations, unless they exhibit a characteristic of hazardous waste.
- ! EPA proposed modifying the mixture rule exemption to make it more consistent with current risk information.
- ! The TC Rule regulatory levels are based on state-of-the-art toxicological data and risk assessment methodologies. In contrast, the mixture rule exemption levels are based upon less current risk information.

1.4.7 Previously Delisted Wastes

- ! A waste previously "excluded" under Subtitle C regulation may no longer be delisted if it exhibits a hazardous characteristic (e.g., the characteristic of toxicity).
- ! TC rule applies to already delisted wastes that now exhibit TC characteristics.
 - These wastes are no longer considered "not hazardous"
 - These wastes must now be managed under Subtitle C
- ! Because delisting levels are generally more stringent than the final TC levels, the impact of TC rule on previously delisted wastes is expected to be minimal.

- ! Wastes "excluded" from Subtitle C regulation under the delisting program may nevertheless be hazardous if they exhibit a hazardous characteristic (see 40 CFR 260.22). Hazardous waste characteristic levels are those above which a waste is hazardous due to a particular property; delisting levels are those below which a waste is not hazardous for any reason. Thus, it is reasonable that these two levels do not coincide.
- ! Although the TC Rule applies to delisted wastes, EPA does not, in general, expect that such wastes will become hazardous because of application of the revised TC Rule. However, if a previously delisted waste exhibits the TC Rule, it will again be subject to Subtitle C requirements, and the facility will have to notify EPA of its activity.

1.4.8 Special Waste Exemptions

! RCRA defines four special waste categories exempted from Subtitle C regulation:

- Mining wastes
- Mineral processing wastes
- Oil and gas wastes
- Domestic sewage

! Subtitle C regulations may apply to these special wastes on a case-by-case basis.

! Special waste exclusions are being reevaluated as mandated by Congress.

! If EPA determines that any special waste should be regulated under RCRA Subtitle C, the Agency will determine the applicability of the TC Rule to such wastes.

! After completing the studies required by RCRA Section 8002, EPA may determine that one or more special wastes should be regulated under RCRA Subtitle C. Such wastes would then be listed or the generators required to determine whether the wastes exhibit a hazardous characteristic, including those specified in the TC Rule.

! The TC Rule will have no direct effect on the following types of wastes:

- Listed hazardous waste.
- Wastes classified as hazardous by the "mixture" and "derived from" rules.
- Wastes already excluded from regulation under 40 CFR 261.4

1.4.9 Listed Hazardous Waste

- ! TC rule has no effect on listings of hazardous waste
 - Wastes already *listed* as hazardous are always considered hazardous, unless they are delisted.

- ! Hazardous waste listings will continue to supplement the revised TC Rule. The TC Rule revisions do not eliminate any hazardous waste listings.
- ! Listed hazardous wastes continue to be hazardous even if they contain TC Rule constituents in concentrations below TC regulatory levels.
- ! TC Rule regulatory levels are not designed to identify the full range of wastes that may be toxic to human beings. Instead, the characteristic levels were established to protect human health.
- ! Listed wastes that do not exhibit the toxicity characteristic may nevertheless be hazardous because:
 - They contain listed hazardous waste constituents; or
 - They contain hazardous constituents that are not covered by the TC Rule.
- ! Listed wastes frequently contain hazardous constituents other than the ones cited in Appendix VII of 40 CFR Part 261. These additional hazardous constituents present in a waste may not be TC Rule constituents. Removing wastes from a hazardous waste listing without evaluating additional constituents would be inconsistent with the intent of RCRA §3001(f).

1.4.10 "Mixture" and "Derived From" Rules

- ! TC has no effect on the regulatory status of waste "mixtures" or "derived from" wastes:
 - Mixtures of listed wastes and solid wastes, and residues derived from listed wastes, are still hazardous until delisted.
- ! TC alone is not adequate to regulate mixtures and treatment residues.
- ! Problems may result by applying "mixture" and "derived from" rules.

- ! The "mixture" rule (40 CFR 261.2(a)(2)(iv)) states that any mixture of a listed hazardous waste and a solid waste is a RCRA hazardous waste.
- ! The "derived from" rule (40 CFR 261.3(c)) states that any waste derived from the treatment, storage, or disposal of a listed hazardous waste is hazardous.
- ! The "mixture" and "derived from" rules creates inequities in the classification of certain dilute wastes. For example, very low constituent concentrations in listed wastes may still be considered hazardous even after treatment.

1.4.11 Excluded Wastes

- ! TC Rule does not apply to wastes that are already excluded from Subtitle C regulations under 40 CFR 261.4:
 - For example, household hazardous waste is excluded from Subtitle C; it remains excluded after the TC effective date.
- ! TC Rule does not add any exclusions to the applicability of previously promulgated hazardous waste characteristics.

! Wastes described in 40 CFR 261.4(b) that are already excluded from Subtitle C regulations will continue to be exempt from regulation as hazardous wastes, even if they exhibit the TC Rule.

! EPA does not at this time intend to expand the list of exemptions under 40 CFR 261.4(b) to include creosote- and pentachlorophenol-treated wood.

! Other wastes that are excluded from Subtitle C in 40 CFR 261.4(b) include:

- Household hazardous wastes
- Certain mining wastes
- Certain solid wastes generated from farming or raising animals
- Certain wastes generated from the combustion of coal or other fossil fuels
- Wastes associated with the production of crude oil and natural gas
- Some chromium containing wastes
- Solid waste from extraction and processing of ores and minerals
- Cement kiln dust wastes
- Certain wood products

1.5 IMPACT OF TC RULE ON OTHER EPA PROGRAMS

1.5.1 Underground Storage Tanks (USTs)

- ! Two programs currently regulate underground storage tanks (USTs).
 - Subtitle C (tanks containing hazardous wastes) or Subtitle D (tanks containing non-hazardous solid wastes),
 - Subtitle I (tanks containing petroleum product or hazardous substance products).
- ! The TC Rule may increase the number of tanks regulated under Subtitle C.
- ! Product (petroleum, hazardous substance) that leaks may become a hazardous waste and may also exhibit TC.

! Petroleum contains several TC constituents. Therefore, it is likely that some petroleum-contaminated media will exhibit the TC.

! The management of any petroleum-contaminated media exhibiting TC would normally be subject to Subtitle C requirements for hazardous waste management. However, EPA believes further study of these impacts is necessary before imposing TC requirements on media and debris contaminated solely by petroleum from USTs.

! EPA has insufficient information on the impact of the TC Rule on UST cleanups; therefore, EPA has deferred a final decision on the application of the TC Rule to media and debris contaminated with petroleum from USTs exhibiting the D018-D043 waste characteristics that are subject to the 40 CFR Part 280 requirements.

! EPA believes deferral of a final decision concerning the application of the TC Rule to UST cleanups is necessary. Imposition of the Subtitle C requirements is likely to significantly delay cleanups and severely discourage the self-monitoring and voluntary reporting essential to implementing the UST program.

- ! Subtitle I and Subtitle C potentially overlap if a substance exhibits the TC characteristic and the origin of substance is not known.
- ! The contents of a tank determines which regulatory program (i.e., Subtitle C or Subtitle I) applies:
 - Subtitle C regulates hazardous wastes
 - Subtitle I regulates hazardous products and petroleum

- ! Hazardous product that leaks may become hazardous waste.
- ! Petroleum and hazardous product may exhibit the TC but may not be regulated under Subtitle C.
- ! Corrective action under Subtitle I addresses releases of product.
- ! Old releases of product not subject to Subtitle I may have occurred:
 - Via inactive tanks
 - In areas considered as RCRA solid waste management units
- ! If wastes exhibit the TC for D004-D017, RCRA standards may apply to these old releases.
- ! TC Rule excludes D018-D043 wastes from RCRA regulation if they are covered under Subtitle I Corrective Action:
 - Petroleum-contaminated soil and ground water
 - Petroleum-contaminated debris (tanks)
- ! EPA is studying impacts of Subtitle C regulation on petroleum-contaminated areas.
- ! Note: Petroleum contaminated media from aboveground storage tanks are also excluded from TCLP testing requirements where a state has an adequate treatment mechanism in place.

1.5.2 Comprehensive Environmental Response and Liability Act (CERCLA)

- ! CERCLA response actions must comply with all applicable, or relevant and appropriate requirements (ARARs), including RCRA regulations.
 - TC will cause more Superfund wastes to be classified as RCRA hazardous wastes.
 - Thus, more Superfund cleanups will be subject to RCRA regulations.
- ! TC will not, however, affect CERCLA clean-up levels.

- ! Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) addresses remediation of inactive waste sites.
- ! ARARs are "applicable or relevant and appropriate requirements." CERCLA must meet other Federal or State environmental requirements whenever they are applicable or relevant and appropriate to CERCLA actions.
- ! The primary effect of TC Rule on Superfund will be to regulate many organic constituents found at Superfund sites as RCRA hazardous wastes.
 - A current problem at many Superfund sites is determining if an organic constituent is from a listed RCRA hazardous waste.
 - There is often little evidence about the source of contamination that exists at Superfund sites to prove a waste is a listed waste. Therefore, a waste may not be managed under RCRA (but it will be handled in a protective manner according to risk assessment).
 - Under the TC regulation, if tetrachloroethylene is found above the TC regulatory level, the waste is hazardous regardless of its origin.
- ! As in RCRA corrective actions, Superfund response personnel will not use the TC to determine whether to undertake a clean-up action. The TC will affect decisions concerning the management of wastes generated during cleanup activities (i.e., hazardous wastes generated during cleanup must be managed in accordance with Subtitle C). For a lower cost Superfund cleanup option, please read the CAMU Rule discussion in Chapter 2.

1.5.3 Clean Water Act (CWA)

- ! The CWA regulates discharges of pollutants to surface waters and to publicly owned treatment works (POTWs).
- ! Regulatory levels of TC are consistent with those of the CWA:
 - NPDES effluent guidelines
 - Pretreatment standards
- ! Treated wastewaters that exhibit the TC Rule.

- ! The Clean Water Act (CWA) regulates discharges of hazardous substances to surface waters through the National Pollutant Discharge Elimination System (NPDES) permit program, and pretreatment standards for POTWs.
- ! EPA believes TC levels and CWA standards are consistent.
- ! Thus, CWA discharges are exempt from RCRA regulation under 40 CFR Part 261.
- ! Treated wastewaters exhibiting TC are regulated under RCRA unless:
 - discharged under NPDES permit
 - treated in POTW

! Objectives of the Clean Water Act

! Impact of the Clean Water Act

! Objectives of the CWA are:

- To restore and maintain the chemical, physical, and biological integrity of the nation's waters;
- To eliminate the discharge of pollutants into surface waters;
- To attain water quality that provides for the protection and propagation of fish, shellfish, and wildlife, and provides for recreation in and on the water.

! Impact of the Clean Water Act:

- In lieu of retrofitting and obtaining permits for existing surface impoundments to meet RCRA requirements, hazardous waste management facilities may utilize tank treatment and storage of hazardous wastewater. NPDES treatment tanks are exempt from RCRA permitting requirements.
- Wastewater treatment facilities using surface impoundments to treat TC waste may be subject to RCRA regulations.
 - The Agency expects many owner/operators to replace surface impoundments with wastewater treatment tanks.
 - Wastewater treatment tanks are exempt from Subtitle C regulation under 40 CFR 264.1(g)(6) and 265.1(c).
- If a POTW sludge (from wastewater treatment) exhibits TC, the owner/operator must treat the sludge to remove the characteristic.
 - Treatment may be through a pre-treatment program (i.e., before POTW receives discharge); or
 - After sludge is produced.

1.5.4 Safe Drinking Water Act (SDWA)

- ! Safe Drinking Water Act (SDWA) establishes maximum levels of contaminants acceptable in public drinking water supplies.
 - Maximum Contaminant Levels (MCLs)
 - Maximum Contaminant Level Goals (MCLGs)
- ! TC fate and transport models assume ingesting contaminated drinking water, and uses MCLs as the basis for setting regulatory levels for many TC constituents.

! SDWA protects human health from contaminants in drinking water.

! The specific objectives are:

- To assure that all people served by public water systems be provided with a high quality water;
- To remove contaminants found in water supplies to protect human health; and
- To establish programs to protect underground sources of drinking water from contamination.

! SDWA primary drinking water regulations include MCLs for specific contaminants.

! Many TC levels are based on SDWA MCLs.

! Underground injection control (UIC) program regulates injection of fluids to protect underground sources of drinking water (USDWs).

! Five classes of wells are regulated under the UIC program:

- Class I - municipal or industrial waste discharged beneath USDWs
- Class II - oil and gas production
- Class III - mineral recovery
- Class IV - hazardous or radioactive waste into or above USDWs
- Class V - all other wells used for injection of fluids, including septic tanks and sumps.

! Class I wells are often used by generators of hazardous waste or owner/operators of hazardous waste management facilities to inject hazardous waste below USDWs. The largest user of hazardous waste Class I wells is the chemical industry. Class I is the smallest class of wells with 554 reported in 1989. There are no Class I hazardous wells in Region 2.

! Class IV wells are banned with the exception of wells used for remediation of aquifers contaminated with hazardous wastes (40 CFR 144.13).

! The largest group of injection wells is Class V, with approximately 180,000 wells. The second largest group of wells is the Class II group with approximately 150,000 wells, followed by Class III wells with about 20,000 wells.

! The Agency is enforcing the ban on shallow injection of hazardous wastes. The Agency is also developing guidance on best management practices to reduce the amount and toxicity of wastes injected into Class V wells (40 CFR 144.24).

! The TC Rule may increase the number of Class I wells accepting TC waste, and bring newly identified hazardous Class I wells into the Subtitle C program.

! Some Class V wells may be illegally accepting hazardous wastes; the number may increase as a result of the TC Rule.

! Class V wells that may receive TC wastes:

- Agricultural drainage wells;
- Industrial drainage wells;
- Experimental technology wells;
- Industrial process water and waste disposal wells;
- Automobile service station wells; and
- Aquifer remediation-related wells.

- ! Wastes injected into some Class V wells are exempted from regulation as a hazardous waste. For example: geothermal electric and direct heat re-injection wells, several of the domestic wastewater disposal wells, most of the mineral and fossil fuel recovery-related wells, and certain experimental technology wells.
- ! Many of the facilities that operate Class V wells (e.g., auto service stations) also generate listed hazardous waste, such as solvents. It is possible that some facilities are not managing their listed wastes properly, and that hazardous wastes are entering Class V wells. Of course, when hazardous wastes are injected into Class V wells, they become Class IV wells.
- ! It is unclear at this time what effects TC will have on the UIC program because the Class V program is very new.

1.5.5 Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)

- ! FIFRA regulates the sale, distribution, and use of all pesticide products.
- ! RCRA regulates listed wastes, including pesticide product wastes.
- ! TC Rule:
 - adds one pesticide to the list of TC constituents; and
 - regulates more "multiple active ingredient" formulations.
- ! Other TC constituents may be ingredients in pesticides.
- ! If pesticide wastes exhibit TC, they are subject to Subtitle C regulation unless they are exempt.

- ! The following pesticide users are exempt from RCRA requirements:
 - Household pesticide users.
 - Farmers who triple rinse their containers, dispose of the containers on their own farm, and follow the pesticide manufacturer's label instruction for disposal.
 - Small quantity generators following reduced requirements. Many pesticide users are small quantity generators.
 - Properly emptied containers may be exempted from further RCRA requirements under 40 CFR 261.7. Many pesticide containers, therefore, may not be subject to regulation as hazardous waste.
- ! There is no change in listed pesticide wastes that are either pure, technical grade, or sole active ingredient *product* wastes; they will continue to be regulated under Subtitle C (P and U listings).
 - The exemption for arsenic-treated wood was not expanded in the TC Rule.
 - This exemption may be reevaluated in the future.
- ! Multiple active ingredient *products* are usually not regulated as RCRA Subtitle C wastes, but are instead regulated under RCRA Subtitle D or FIFRA.
- ! TC increases the potential for multiple active ingredient product wastes to be hazardous.
- ! Adding new pesticide constituents to the TC Rule will primarily affect commercial applicators, such as aerial applicators and pest control operators. If they use large quantities of multiple active ingredient pesticide products that have not previously been regulated, such applicators may be newly subject to RCRA Subtitle C requirements.
- ! Wastes from multiple active ingredient products that do not exhibit a hazardous waste characteristic will still be regulated under applicable FIFRA and RCRA Subtitle D requirements.

1.5.6 Used Oil Recycling Act

- ! Some used oil exhibits TC or ignitability characteristic.
- ! TC will affect used oil that is
 - used for road oiling;
 - that is dumped;
 - disposed in solid waste landfills and incinerators.
- ! TC will *not* affect used oil that is:
 - Managed by *do-it-yourselfers* (exempt as household hazardous waste);
 - Recycled through energy recovery (40 CFR Part 279 regulates this activity);
 - Recycled in any other manner (regulated under 40 CFR 279).

- ! Used oil may exhibit the toxicity or ignitability characteristic.
- ! *Disposed* used oil which exhibits the toxicity characteristic is subject to full RCRA Subtitle C regulation (40 CFR 279.80).
- ! However, oil that is *burned* for energy recovery is not regulated as a hazardous waste.
 - Used oil generated by household do-it-yourselfers is exempt from RCRA under 40 CFR 279.20(a)(1).
 - Used oil that exhibits one or more of the characteristics of hazardous wastes but is recycled in some other manner than being burned for energy recovery is exempt under 261.6(a)(43).
- ! Significant quantities of used oil may exhibit EP toxicity for metals, but little used oil is currently recognized as EP toxic.
- ! Shifts in used oil management practices may result from the TC Rule. Management practices may shift away from road oiling, dumping, and disposal in solid waste facilities to burning as fuel, recycling, and disposal in Subtitle C facilities.
- ! Standards for regulating used oil that is recycled were promulgated in the Federal Register on September 10, 1992 (FR 41566).

1.5.7 Toxic Substances Control Act (TSCA)

- ! TSCA addresses manufacturing, processing, and distributing hazardous substances such as PCBs.
- ! If TSCA-regulated *products* become wastes and contain D004-D017, they become RCRA regulated.
- ! If Polychlorinated Biphenyls (PCBs) are fully regulated under TSCA, TC rule exempts those PCB-wastes containing D018-D043 from RCRA regulations; not all PCB wastes are fully regulated under TSCA (D004-D017).
- ! Exempt wastes include PCB-containing dielectric fluids removed from:
 - Electrical transformers; and
 - Capacitors.

- ! Toxic Substances Control Act (TSCA) regulates toxic substances and specifically addresses PCB management and disposal.
- ! Dielectric fluids from electrical transformers, capacitors and associated PCB-contaminated electrical equipment could exhibit the TC because they may contain chlorinated benzenes.
 - These wastes exhibiting TC are *exempted* from Subtitle C management standards if they exhibit waste codes D018-D043.
 - The exemption applies only to certain wastes noted above that are fully regulated under TSCA, not to all PCB wastes.
- ! PCB wastes exhibiting D004-D017 characteristics (i.e., those hazardous under EP toxicity) remain regulated under RCRA if they are a D004-D017 waste under TC (i.e., contain other constituents).

1.6 POLLUTION PREVENTION

- ! Defining pollution prevention.
- ! Pollution prevention as a national priority for managing hazardous waste.
- ! Priorities of pollution prevention:
 - Source Reduction
 - Source Reduction exclusions
- ! Implementation.

- ! The Pollution Prevention Act of 1990 encourages waste reduction at the source rather than the management of waste already produced.
- ! An integral component of EPA's RCRA program is pollution prevention through waste minimization.
- ! Therefore, EPA's encourages hazardous waste source reduction rather than "end-of-pipe" controls.
- ! EPA has produced industry-specific outreach materials to assist industry in their waste minimization efforts (source reduction, process modifications, recycling, and the use of less toxic materials).
- ! Pollution prevention allows industry to:
 - Reduce costs of raw materials, hazardous waste treatment and disposal;
 - Minimize regulatory burdens of compliance;
 - Minimize liability for environmental problems and occupational safety problems;
 - Enhance efficiency and product quality.
- ! EPA encourages industries affected by this ruling to consider achieving compliance through pollution prevention.

! Source reduction is:

- A practice that reduces the amount of any hazardous waste entering a waste stream or the environment that occurs prior to recycling, treatment, or disposal;
- A practice that reduces hazards to public health and the environment due to release of hazardous substances, pollutants, or contaminants.

! Source reduction includes:

- Equipment/technology modifications;
- Process/procedure modifications;
- Reformulations/redesign of products;
- Substitution of raw materials;
- Improvements in housekeeping, maintenance, training.

! Source reduction does not include:

- Practices that alter the physical, chemical, biological characteristics or volume of a hazardous substance, pollutant, or contaminant through process or activity that, itself, is not integral to and necessary for the production of the product or service.

! EPA is implementing the strategy by:

- Creating incentives for industry;
- Building pollution prevention into their decision-making processes;
- Making technical information available to help firms reduce waste generation through the use of:
 - The Pollution Prevention Information Clearinghouse (PPIC), a nationwide network of people and resources with direct experience in waste reduction strategies in many industries (202-260-1023);
 - The Pollution Prevention Information Exchange System (PPIES), a computer electronic bulletin board (703-506-1025) which contains a database of bulletins, programs, contacts, and reports related to pollution prevention.
- Supporting the development of state programs to assist generators in their waste reduction efforts;
- Initiating specific new regulatory requirements for generators to:
 - Certify on their hazardous waste manifests and annual permit reports that are reducing the volume or toxicity of their hazardous wastes as much as possible;

- Describe on their RCRA biennial reports the efforts undertaken during the year to reduce the volume and toxicity of their hazardous waste and compare the efforts to those in previous years;
- To require waste minimization/pollution prevention in RCRA permits for TSDFs that generate hazardous waste.

! EPA recommends owners/operators implementing waste minimization programs at the plant level:

- Conduct a waste minimization assessment by selecting a few processes or waste streams for source reduction or recycling. Accurate records on the rate of generation and the cost of management should be retained;
- Identify waste minimization techniques;
- Practice inventory management (substitute less toxic source materials);
- Modify equipment (upgrading the performance of process equipment, reducing leaks and malfunctions, installing conditioning or recovery systems);
- Initiate production process changes; and
- Recycle and reuse.

! Contact the Pollution Prevention Office, U.S. EPA, 401 M Street, SW, Washington, D.C. 20460 to obtain information or to offer suggestions on how the Agency might facilitate waste reduction efforts.

! Role of the TC Rule in the Pollution Prevention strategy:

- By subjecting a larger number of toxic compounds to the RCRA regulations, it increases the costs to generators of managing solid wastes.
- In effect, the TC forces waste managers to rethink their solid waste management practices due to the high cost of compliance with RCRA Subtitle C requirements.
- The TC will alter the management of previously disposed wastes that might leach toxic contaminants by restricting their management in land-based units (surface impoundments, waste piles, lagoons, etc.).

1.7 CONCLUSIONS

- ! The TC Rule expands the definition of hazardous waste.
- ! The TC Rule adds 25 additional organic analytes.
- ! The TC Rule should encourage facilities to utilize less hazardous chemicals, to avoid the increased disposal costs associated with the TC Rule.

- ! By expanding the number of toxicity characteristic constituents from 14 to 39, EPA has expanded the definition of hazardous waste, and brought more wastes under the RCRA jurisdiction. This will keep additional wastes within the RCRA "cradle to grave" system and prevent them from harming human health or the environment.
- ! By adding organics to the EP Tox inorganics, the TC Rule addresses the potential harm these substances could cause in the environment.
- ! By increasing the costs of disposal for facilities which are now handling hazardous wastes which were formerly not regulated, facilities are encouraged to find substitutes or otherwise avoid chemicals which are hazardous.

Chapter 2

APPLICATIONS OF THE TCLP METHOD

What is TCLP?

When is the Use of TCLP Applicable?

When is the Use of TCLP Inappropriate?

Sampling and Analysis Design

2.0 APPLICATIONS OF THE TCLP METHOD

Discussions in this chapter include:

- ! What is TCLP?
- ! When is the use of TCLP applicable?

2.1 What is TCLP?

- ! An analytical method to simulate leaching through a landfill. The leachate is analyzed for appropriate analytes.
- ! TCLP is comprised of four fundamental procedures:
 - sample preparation for leaching
 - sample leaching
 - preparation of leachate for analysis
 - leachate analysis
- ! The Toxicity Characteristic does *not* equal TCLP.

The toxicity characteristic leaching procedure is located in:

- ! Test Methods for Evaluating Solid Wastes, SW-846 Method 1311, July 1992.

Appendix I of this document contains the July 1992 version of Method 1311. When regulations specify the use of TCLP, approval to deviate from the method must be obtained from the State or EPA Region.

The Toxicity Characteristic (TC) is utilized to determine whether a solid waste is classified as a hazardous waste because it exhibits the characteristic of toxicity. The TC of a waste material is established by determining the levels of 8 metals and 31 organic chemicals in the TCLP extract of the waste. TC utilizes the TCLP method to generate leachate under controlled conditions. The regulatory levels of TC constituents in the TCLP leachate are listed in Table 2-1.

2.2 When is the Use of TCLP Applicable?

The most common reasons for performing the TCLP are:

- ! Determining if an unknown waste is hazardous according to 40 CFR 261.24.
- ! Determining what type of disposal (hazardous waste or solid waste) is appropriate. Solid wastes *are not necessarily* Hazardous.
- ! Demonstrating the effectiveness of treatment processes to comply with Land Disposal Restrictions (LDR) or "Land Ban" requirements.
- ! Fulfilling shipping or transportation requirements.

Determining if a Waste is Hazardous

The toxicity characteristic regulations require generators to determine whether a solid waste is a regulated hazardous waste. Generators of potentially hazardous waste can determine if a waste is hazardous by one of the following methods:

- ! If a waste is excluded from regulation (40 CFR 261.4), no further determination is necessary.
- ! If the waste is listed per 40 CFR 261.30-261.35. Listings may be industry and process-specific (K-wastes) or may encompass all wastes from non-specific processes (F-wastes). Listings also include commercial chemical and off-specification products (P and U wastes).
- ! If a waste is not excluded or not listed as a hazardous waste, the generator must ascertain whether the waste exhibits any hazardous waste characteristic: toxicity, ignitability, corrosivity, or reactivity.
- ! A solid waste is classified as a hazardous waste because of characteristics, knowledge, or testing.
- ! If the waste is not listed, and there is not enough information to determine whether the Toxic Characteristic constituents are present above regulatory action levels, the TCLP test must be performed.
- ! The waste generator must certify in writing that the waste is not hazardous and must maintain records to demonstrate exclusion from RCRA requirements by knowledge or testing results.

Characterizing Waste for Disposal

- ! The RCRA regulations specify how listed and characteristic hazardous waste must be treated or disposed.
- ! Hazardous waste disposal facilities are permitted to accept specific categories of hazardous waste. Hazardous waste disposal facilities cannot accept hazardous waste without a manifest which lists the constituents or characteristics of the hazardous waste. TCLP waste characterization may be required by some disposal facilities.
- ! Disposal facilities may require initial waste testing. After analytical data are collected from a waste, process knowledge may be used instead of testing.

The Land Disposal Restrictions (LDR) regulate hazardous waste treatment and subsequent disposal. The following is a synopsis of the LDR regulations and their CFR citations:

! **40 CFR Part 268 Subpart A**

The highlights are:

- Definitions of "waste water" (40 CFR 268.2).
- Material otherwise prohibited from land disposal may be treated in a surface impoundment if the residues from that treatment comply with applicable standards.
- Petitions to allow land disposal of 40 CFR Part 268 Subpart C prohibited wastes must include comprehensive waste and simulation model sampling and analysis. This typically includes TCLP and other analysis.
- Generators of restricted waste must either analyze their waste or its TCLP extract or use process knowledge to ascertain if the waste complies with 40 CFR Part 268 Subpart D treatment standards for land disposal. The generators must submit copies of the restricted waste's chemical analysis to the hazardous waste storage or disposal facility.
- Restricted wastes are subject to the treatment standards of 40 CFR Part 268 Subpart D. The generator must notify the disposal company of the restriction and must supply test data if available.

! **40 CFR Part 268 Subpart B**

This section outlines a timetable for waste disposal prohibitions and establishment of treatment standards.

! **40 CFR Part 268 Subpart C**

This section outlines waste disposal prohibitions. The following are examples of hazardous wastes that must meet LDR requirements:

- Solvent waste codes F001-F005, including waste from Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA) actions.
- Dioxin containing waste codes F020-F023 and F026-F028, including CERCLA waste.
- California List wastes, including hazardous waste that contain 1,000 mg/L (liquid) or 1,000 mg/kg (non-liquid) of certain halogenated organic compounds, liquid hazardous wastes that contain ≥ 50 ppm PCBs, and liquid hazardous wastes that contain ≥ 134 mg/L nickel or ≥ 130 mg/L thallium.
- SW-846 Method 9095 must be used to determine if a waste is liquid.
- The initial generator of a California List hazardous waste must test the waste (not an extract), or use knowledge of the waste, to determine if the concentration levels in the waste meet the regulatory levels for California listed waste.
- Prohibitions for wastes with D, K, P, and U hazardous waste codes are also listed with effective dates of prohibition.

40 CFR Part 268 Subpart D

This section outlines LDR treatment standards. 40 CFR Subpart D 268.41 lists treatment standards expressed as concentrations in the waste extract.

- A restricted waste may be land disposed only if the TCLP extract of a waste or waste treatment residue, does not exceed the values shown in Constituent Concentrations in Waste Extracts (CCWE) of 268.41 for any TC constituent. Some wastes require total constituent analysis instead of TCLP (see Appendix II).
- The regulation specifies waste/waste residue TCLP extract concentrations which may not be exceeded. The following Hazardous Waste Codes are exceptions: D004, D008 (lead), D031, K084, P010, P011, P012, P036, and U136 (all arsenic), K101 (o-nitroaniline, arsenic, cadmium, lead, and mercury), and K102 (o-nitrophenol, arsenic, cadmium, lead, and mercury).
- The arsenic and lead regulatory levels are based on the EP Tox Test, not TCLP. If waste/waste residue does not pass the TCLP test, the EP Tox Test may be used for these contaminants.

- LDR treatment standards are based entirely on technology-based standards expressed as Best Demonstrated Available Technology (BDAT). TC levels are based upon health-based allowable concentration levels and Dilution Attenuation Factors (DAFs). Therefore, the TC regulatory action levels are NOT the same as the LDR treatment standards in all cases. For many characteristic wastes, EPA has set the LDR treatment standards at the characteristic level. Note that EPA has not yet established LDR standards for D018 through D043 TC wastes.

LDR Records

! 40 CFR Part 268.7 requires hazardous waste generators and receivers to maintain the following records of process knowledge or data regarding:

- A determination that a restricted waste does *not* meet treatment standards.
- A determination that a restricted waste can be land disposed without further treatment.
- A determination that waste is exempt under 40 CFR Part 268.5, 268.6 or a nationwide capacity variance under Subpart C of 40 CFR Part 268.
- A determination to manage a prohibited waste in tanks or containers during waste treatment.

! The generator must certify that the waste is not hazardous either by knowledge of testing or by knowledge of process generation. While records are only required for hazardous waste, it is prudent to maintain records of non-hazardous waste classification.

! The generator must keep records on site for five years from the date that the waste was last sent to on-site or off-site treatment, storage, or disposal. The record retention time is extended if an enforcement action occurs within five years of waste generation.

! In general, the types of information required in all of the aforementioned records include:

- Hazardous waste numbers
- Manifest numbers
- Waste analysis data if applicable
- Treatment standards (including codes for required treatment technologies.)
- Certification statements signed by the generator
- Any waste analysis plans

LDR Variances: CAMUs are Designed to Reduce the Cost of On-Site Remediation

- Corrective action management unit (CAMU) regulations are enumerated in 40CFR260.10 and 40CFR270.2. CAMU is an area within a facility designated by the Regional Administrator (RA) for implementing CERCLA or RCRA corrective action requirements. A CAMU may only be used for the management of remediation wastes pursuant to corrective action requirements at a facility.
- Placement of hazardous remediation waste into a CAMU will not automatically trigger LDRs. This variance from the LDRs can result in substantial cost reductions. CAMU boundaries are not confined to where contamination exists at the site; CAMU boundaries are based on where remediation waste will be managed.

Limitations and Conditions Applicable to CAMU Designations

- The CAMU shall facilitate the implementation of reliable, effective, protective, and cost-effective remedies;
- Waste management activities associated with the CAMU shall not create unacceptable risks to humans or to the environment resulting from exposure to hazardous wastes or hazardous constituents;
- The CAMU may only include uncontaminated areas of the facility if the incorporated area is more protective than management of such wastes at contaminated areas of the facility;
- Areas within the CAMU, where wastes remain in place after closure of the CAMU, shall be managed and contained so as to minimize future releases to the extent practicable;
- The CAMU shall expedite the timing of remedial activity implementation, when appropriate and practicable;
- The CAMU shall enable the use, when appropriate, of treatment technologies (including innovative technologies) to enhance the long-term effectiveness of remedial actions by reducing the toxicity, mobility, or volume of wastes that will remain in place after closure of the CAMU; and
- The CAMU shall, to the extent practicable, minimize the land area of the facility upon which wastes will remain in place after closure of the CAMU.

2.3 When is the Use of TCLP Inappropriate?

Risk Assessments

The TCLP model assesses risk to ground water when potentially hazardous TC waste is co-disposed with garbage into sanitary landfills. The TCLP model does not assess risk when potentially TC waste is disposed in any other matrix. If a waste is hazardous because it exhibits the toxicity characteristic for mercury, the hazardous waste generator could attempt stabilization by adding cement and water to the waste, in a tank, and the resultant concrete may become non-hazardous. In this example, the concentration of mercury in the concrete's TCLP extract demonstrates that the waste is not a risk to the ground water beneath a sanitary landfill. Therefore, according to Federal regulations, this non-hazardous concrete can now be emplaced at the disposal site. The resultant concrete may only be emplaced on the disposal site if it does not exhibit the toxicity characteristic for mercury, unless a CAMU is obtained. The TCLP model discloses no information about potential risks to groundwater at the factory site where the mercury immobilized in the concrete is emplaced. EPA is designing site specific risk assessment models, but these will not be promulgated for several years.

When determining whether to use the TCLP for risk assessment, it is important to remember that TCLP simulates worst case management of hazardous waste in a landfill. Much caution must be used before TCLP data are used in risk assessment because the TCLP conditions rarely reflect actual site conditions. EPA's Science Advisory Board Report outlines many limitations of using TCLP for risk assessment at industrial sites. The Board recommends developing leach tests which are appropriate to site conditions. There are several excellent discussions on the inadequacies of TCLP organic analysis of solidified waste in "Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes, ASTM, 1992, edited by T. Gilliam and C. Wiles (Appendix X of this document).

EPA's 1991 Science Advisory Board report on Leachability Phenomena (Appendix VII of this document) concluded that:

1. Many of the proposed uses of the EP and TCLP test have been inappropriate because the waste management scenarios of concern were not within the range of conditions used in the development of the tests themselves. In most cases of inappropriate use of the EP or TCLP tests, the justification given was that it was necessary to cite "standard" or "approved" methods. Even if it is acknowledged that the tests cannot be applied without significant change in test protocol itself, the need to use a previously "approved" test has been cited (page 3).
2. A variety of contaminant release tests and test conditions which incorporate adequate understanding of the important parameters that affect leaching should be developed and used to assess the potential release of contaminants from sources of concern. In scientific terms, no "universal" test procedure is likely to be developed that will always produce credible and relevant data for input to all decision making exercises (pages 7-8).

3. Leach test conditions appropriate to the situations being evaluated should be used for assessing long-term contaminant release potential. The best way to estimate the extent of contaminant release from a waste matrix of interest is to have a test that reflects realistic field conditions (page 13).
4. To facilitate the evaluation of risk implications of environmental releases, the EPA should coordinate the development of leach tests and the development of models in which the release terms are used (page 17).

The TCLP test cannot predict the potential for toxic chemicals to leach from oily waste, through soil, to contaminate ground water. This applies to both sanitary landfills and industrial sites. EPA and the American Society of Testing and Materials (ASTM) have formed a work group to develop a site-specific risk assessment model for oily waste. At a minimum, the model will incorporate physical and chemical characteristics of the oily waste and the soil. However, this model is not expected to be approved by EPA for several years. Until EPA approves this site-specific model for oily waste risk assessments, oily waste site assessments should be based on total constituent analysis, not TCLP extract analysis.

A percent reduction in organic contaminant concentrations between the original waste and a TCLP extract of stabilized/solidified waste yields very limited information. In fact, organic TCLP extract data from stabilized/solidified waste is not realistic because stabilization/solidification is not an appropriate treatment for organic wastes. Appendix X lists several papers that describe the problems with measuring organics in stabilized/solidified wastes. VOA data from stabilized/solidified waste is particularly ineffectual because concrete curing and concrete particle size reduction (hammering concrete into small pebbles) both produce heat, which evaporates volatiles from stabilized/solidified waste. Therefore, all or most of the volatiles will evaporate before analysis of the stabilized/solidified waste TCLP extract. This stabilization/solidification treatment will therefore appear to be very effective because of analyte evaporation. The semivolatile organic data in the TCLP extract of stabilized/solidified waste is of very limited value because the organic compounds are not very soluble in the TCLP extraction fluid. This usually results in comparable TCLP extract analyte concentrations between the original waste and the stabilized/solidified waste.

If waste is hazardous because it exhibits the toxicity characteristic for both benzene and mercury, adding cement and water will bind the mercury, and evaporate the benzene. At the present time, the LDR regulations do not specify how toxicity characteristic waste must be treated.

Appendix XV discusses risk assessment for disposal of solidified/stabilized waste and contaminated soils.

! **Unnecessary Hazardous Waste Determinations:**

- Generator's knowledge of waste (e.g. chocolate ice cream).
- Exempt waste (e.g. household garbage).
- Material is not a solid waste (e.g. clean sand, laundry detergent).
- Generator's testing of waste (total constituent analysis).
- The solid waste is a listed hazardous waste.

! **Unnecessary Land Ban Determinations:**

- Some LDRs are for total constituents, not TCLP extract concentrations.
- Generator's testing of waste (total constituent analysis).
- Pure liquid waste samples (waste is TCLP extract; waste would fail paint filter test).

! **Determination of Corrective Action Clean-up Levels and Clean Closures**

TC levels are not used to set clean up levels for corrective actions or clean closures. Clean up levels are developed from site-specific information.

2.4 Sampling and Analysis Design

The following issues discussed in this section are critical in sampling and analysis design:

- ! Total constituents versus TCLP
- ! Specifying sample collection procedures

Total constituents versus TCLP - EPA Memorandum

EPA has several memoranda which address issues such as Characterizing Heterogeneous Material and Total Analysis Versus TCLP. These are presented in Appendix VI. The Office of Solid Waste - Methods Section, Notes on RCRA Methods and QA Activities, Memorandum #36, January 12, 1993, is helpful in delineating sampling design related to the analysis of samples for total constituents versus leachable constituents. The consequential portions of Memorandum #36 and a discussion of their significance follows.

Office of Solid Waste Memorandum - Methods Section #36, January 12, 1993

Page 10 Characterizing Heterogeneous Materials

Characterization of a solid waste is essential for determining whether a waste is hazardous or for developing management and treatment standards for hazardous materials. Current EPA regulations for characterizing waste includes determining the average property of the "universe or whole." This task is difficult when applied to heterogeneous wastes because conventional sampling and compositing techniques are often inadequate in providing a "representative sample" of the waste. As a result, analytical results are often biased and imprecise, making compliance decisions difficult.

The above paragraph means that all of the samples collected from a heterogeneous waste do not have to be below the regulatory action level for the waste to be considered non-hazardous. What percent of the samples are allowed to be above regulatory action levels without classifying the waste as hazardous? Chapter 9 of SW-846 recommends utilizing the student "t" test to determine an appropriate percentage of samples that may be above regulatory action levels without classifying a solid waste as "hazardous."

Please be aware that the above discussion is only for heterogenous wastes with no obvious "hot spots" of highly concentrated hazardous wastes. Whenever regulatory agencies collect samples to determine compliance with the TC regulations, only the most contaminated media will be sampled. For example, if there is a one-acre mercury waste pile surrounded by ninety-nine acres of clean sand, TC inspectors will not collect samples of the clean sand.

The RCRA definition of "average property" is very different than the definition of "average" which was taught in elementary school. For example, if the TCLP extract regulatory action level is 50 mg/L, and our sample results are 80 mg/L and 0 mg/L, we can not compute the numerical average of analytical results as 40 mg/L, and affirm that the waste is not hazardous. To make proper characterization of the above waste, we would declare the waste hazardous because 50% of the samples were above regulatory action levels. Appendix XI discusses characterization of heterogeneous waste.

Pages 19-21 Totals Analysis Versus TCLP

Over the past year, the Agency has received a number of questions concerning the issue of total constituent analysis with respect to the TCLP. Section 1.2 of the TCLP allows for a compositional (total) analysis in lieu of the TCLP when the constituent of concern is absent from the waste, or if present, is at such a low concentration that the appropriate regulatory level could not be exceeded. A number of persons have contacted the MICE Service and have requested clarification on this issue with respect to a number of waste testing scenarios.

Wastes that contain less than 0.5% dry solids do not require extraction. The waste, after filtration, is defined as the TCLP extract. The filtered extract is then analyzed and the resulting concentrations are compared directly to the appropriate regulatory concentration.

For wastes that are 100% solid as defined by the TCLP, the maximum theoretical leachate concentration can be calculated by dividing the total concentration of the constituent by 20. The dilution factor of 20 reflects the liquid to solid ratio employed in the extraction procedure. This value then can be compared to the appropriate regulatory concentration. If this value is below the regulatory concentration, the TCLP need not be performed. If the value is above the regulatory concentration, the waste may then be subjected to the TCLP to determine its regulatory status.

The same principal applies to wastes that are less than 100% solid (i.e., wastes that have filterable liquid). In this case however, both the liquid and solid portion of the waste are analyzed for total constituency and the results are combined to determine the maximum leachable concentration of the waste. The following equation may be used to calculate this value:

$$\frac{[AxB + [CxD]]}{B + [20L/kg \times D]} = E$$

where: A = concentration of the analyte in liquid portion of the sample (mg/L)

B = Volume of the liquid portion of the sample (L)

C = Concentration of analyte in the solid portion of the sample (mg/kg)

D = Weight of the solid portion of the sample (kg)

E = Maximum theoretical concentration in leachate (mg/L)

To illustrate this point, the following example is provided:

An analyst wishes to determine if a lead processing sludge could fail the TC for lead. The sludge is reported to have a low concentration of lead, and the analyst decides to perform a compositional analysis of the waste instead of the TCLP. A preliminary percent solids determination as described in the TCLP is performed. The percent solids is found to be 75%. Thus, for each 100 grams of this waste filtered, 25 grams of liquid and 75 grams of solid are obtained. It is assumed for the purposes of this calculation that the density of the filterable liquid is equal to one. The liquid and solid portion of the sample are then analyzed for total lead. The following data are generated:

Percent solids = 75%

Concentration of lead in the liquid phase = 0.023 mg/L

Volume of filtered liquid = 0.025 L

Concentration of lead in the solid phase = 85 mg/kg (wet weight)

Weight of the solid phase = 0.075 kg.

The calculated concentration is as follows:

$$\frac{[0.023 \text{ mg/L} \times .025\text{L}] + [85 \text{ mg/kg} \times .075\text{kg}]}{.025 \text{ L} + [20 \text{ L/kg} \times .075\text{kg}]} = 4.18 \text{ mg/L}$$

In this case, the maximum leachable concentration is below the 5 mg/L regulatory concentration for lead, and the TCLP need not be performed.

Non-aqueous based wastes (i.e., oily waste) may be calculated in the same manner as described above, except the concentration of constituents from the liquid portion of the waste (A in the above formula) are expressed in mg/kg units. Volumes also would be converted to weight units (kg). The final leachate concentration is expressed in mg/kg unit.

This memorandum should significantly reduce the number of TCLP samples analyzed to demonstrate compliance with the TC regulations. The profound regulatory impact of Notes on RCRA Methods and QA Activities Memorandum #36, pages 19-21, are most easily comprehended with the following uncomplicated monophasic examples. These examples explain how the calculations are made and evaluated to determine whether to analyze the total constituents or perform the TCLP.

Example 1. The TCLP Extract Regulatory Action Level for cadmium is 1 mg/L. A soil (with no liquid phase) contains 10 mg/kg of cadmium. Is the TCLP required?

The TCLP test for a solid matrix leaches one part of waste with twenty parts of an acetic acid buffer. Therefore, even if all of the cadmium was leached from the soil to the solvent, the maximum concentration in the TCLP extract would be 0.5 mg/L. Consequently, TCLP is not required.

Example 2. The TCLP Extract Regulatory Action Level for cadmium is 1 mg/kg. A soil (with no liquid phase) contains 100 mg/kg of cadmium. Is the TCLP required?

The TCLP test for a solid matrix leaches one part of waste with twenty parts of acetic acid buffer. Therefore, if all of the cadmium was leached from the soil to the solvent, the maximum concentration in the TCLP extract would be 5 mg/L. Consequently, TCLP is required.

Example 3. The TCLP Extract Regulatory Action Level for cadmium is 1 mg/L. A liquid with no solid phase contains 0.5 mg/L cadmium. Is the TCLP required?

The TCLP test for a liquid with no solid phase consists of filtration. The filtrate is the TCLP extract. Therefore, even if all of the cadmium passed through the filter, the maximum concentration of cadmium in the TCLP extract would 0.5 mg/L. Consequently, TCLP extraction is not required.

Example 4. The TCLP Extract Regulatory Action Level for cadmium is 1 mg/L. A liquid (with no solid phase) contains 5 mg/L cadmium. Is the TCLP extraction required?

The TCLP test for a liquid with no solid phase consists of filtration. The filtrate is the TCLP extract. Therefore, if all of the cadmium passed through the filter, the maximum concentration of cadmium in the TCLP extract would be 5 mg/L. Since the filtrate equals the TCLP extract, the waste exceeds the TC level for cadmium and is a hazardous waste. Therefore, the TCLP extraction is not required.

The following abstract and introduction of a research paper on the relationship between total mercury and TCLP mercury at Oak Ridge National Lab illustrates how difficult it is to estimate the mercury concentration in the TCLP extract from the mercury concentration in the soil.

Chapter 3

TC AND TCLP PROJECT PLANNING

Data Quality Objectives

DQO Case Study: Cadmium Contaminated Fly Ash Waste

Sampling and Analysis Design

Analytical Method Selection

3.0 TC AND TCLP PROJECT PLANNING

Planning a project prior to sampling and analysis promotes successful implementation. The conclusion of the planning process should result in an efficient sampling and analysis design which allows the collection of appropriate data. The data should promote making a correct decision on the storage, treatment or disposal of the waste. This chapter provides information in the following areas which are critical to project planning.

- ! Data Quality Objectives (DQOs)
- ! Sampling and analysis design
 - Sample containers, preservation, and storage
 - Sample volumes
 - Sample decontamination
 - Holding times
 - Field QC
 - Documentation

Barbara Metzger's 1992 speech on Environmental Data Use: "Meeting the Customer's Need", (Appendix XVI) - illustrates how site-specific Data Quality Objectives (DQOs) are utilized in environmental projects.

3.1 Data Quality Objectives

Environmental samples are often collected and analyzed without proper planning. The data collected may not allow a correct decision to be made. In response to this problem, EPA has developed a planning process to facilitate clear definition of the decision to be made and the data required to make these decisions. This process is the Data Quality Objective (DQO) process. Prior to initiating sampling, the questions to be answered should be listed, prioritized and one primary question identified. These should be agreed upon by all parties, including the regulatory agencies and TSDFs, the site owners and operators/generators, and the technical staff.

The DQO Process should identify:

- ! What question will the data resolve?
- ! Why is a specific type, quantity and quality of data needed?
- ! How will the customer use the data to make a defensible decision?
- ! How much data are required?
- ! What resources are needed?

The information included in the DQO section describes the following information:

- ! DQO definition
- ! DQO Planning Process (DQO-PP) description
- ! Value of DQO-PP
- ! Example of DQO-PP implementation

The American Society of Testing and Materials (ASTM) Committee D34.02.10 is working with Quality Assurance Management Staff (QAMS) and the Office of Solid Waste to produce an ASTM Standard Practice which describes the DQO Planning Process (DQO-PP). Additional guidance is available from the Office of Emergency and Remedial Response, US EPA, Washington, D.C. 20460 in a document titled: "Data Quality Objectives Process for Superfund, Interim Final Guidance, EPA/540/G-93/071, Publication 9355.9-01, September 1993.

Many of the following flow charts, definitions and information are derived from these documents and from the draft ASTM document.

DQOs are defined by the ASTM document as:

Qualitative and quantitative statements derived from the DQO-PP describing the problems, decision rules, and the uncertainty of the decisions stated within the context of the problem.

The DQO Planning Process is:

A Total Quality Management tool developed by the US EPA to facilitate the planning of environmental data collection activities. The DQO Planning Process asks planners to focus their efforts by specifying the use of the data (the decision), the decision criteria, and their tolerance to accept an incorrect decision based on the data.

Incorrect decisions can result from many causes. One cause of making incorrect decisions is insufficient or inadequate data to address the problem. The DQO-PP provides a method to allow the decision makers and technical specialists to assure that sufficient data of appropriate quality is collected at the proper time. In order to make the best decisions, the chance of making an incorrect decision must be understood. In order to examine the probability of making an incorrect decision, it must be understood that all measurements have error. Measurement error results from heterogeneity of the waste, errors in sampling methods and laboratory error. Measurement error is cumulative. The laboratory error is a small component in the overall measurement error. Decision makers must understand that there is a balance between resources and decision error. Decision makers must make informed decisions as to the cost versus the decision error and ultimately the measurement error.

The goal of this document is to assist the regulated community comply with the TC and TCLP Rules in a cost effective manner. Therefore, it is essential for the regulated community to understand the importance of obtaining the most cost effective sampling and analysis design which provides the appropriate decision error. If an appropriate sampling and analysis design is not utilized, the data may not allow a waste generator to accurately determine if a solid waste is a hazardous waste. The DQO-PP is essential for preparing a sampling and analysis design which balances the resources with the chance of making an incorrect decision.

What is the value of using the DQO-PP?

The DQO-PP:

- ! Helps users determine the amount, frequency, and quality of data needed.
- ! Saves resources by making data collection operations more efficient.
- ! Encourages communication between the data users, technical experts, and decision makers.
- ! Helps focus studies by clarifying vague objectives and narrowing the questions to the essential issues.
- ! Helps provide a logical process which facilitates documentation.

Additional critical information about the DQO-PP

- ! A statistical design, which may result from the DQO-PP, allows the uncertainty in the data and ultimately the decision uncertainty to be quantified. Chapter 9 of SW-846 outlines strategies for statistical design. The statistical design must be carefully applied to assure that the correct assumptions are made and that the assumptions address the question(s) related to the objectives.
- ! The DQO-PP is iterative. Projects should focus on essential questions and take a phased approach to answering these questions. This allows reevaluation of the DQOs as the data collection is completed. This iteration allows the resources to be efficiently used.
- ! The term "decision maker" used in this document may include owners and managers of facilities and regulators. Prior to undertaking large projects, the owners and managers may choose to involve the regulators to assure consensus is reached in the planning phase.

The following discussion presents summary information about each of the seven steps within the DQO Planning Process shown in Figure 3-1.

Figure 3-1

The DQO Planning Process has a logical problem solving structure which includes the following seven steps:

1. State the problem
2. Identify the decision(s)
3. Identify inputs to the decision(s)
4. Define the study boundaries
5. Develop decision rule(s)
6. Specify acceptable limits on decision error
7. Optimize the design

1. State the problem

The essential goal of this step is to focus the decision makers and the technical team on one or more problems. These problems should be as narrowly stated as possible. For waste generators, these problems may focus on whether a particular waste is hazardous.

2. Identify the decision

Clear and concise potential decision(s) should be agreed upon by the decision makers and the technical team. One or more decisions should be presented for each problem.

3. Identify the inputs to the decision

The goal is to list the data which are needed to make the decision. Questions such as whether metals or organic data must be generated should be addressed. Production or process data may be required if the task is related to a waste generator. Additionally, knowledge about the homogeneity of the material to be sampled may need to be determined. This data should also include any time factors, physical limitations, process data, and resources which may effect the sampling and analysis. The environmental characteristics such as analytes, method, and process knowledge required should also be listed.

4. Define the study boundaries

The boundaries are the limitations on the study. Examples include time and budget constraints, permit requirements, disposal requirements, and exposure levels. Any physical boundaries such as drum or container size is considered a spatial boundary. Sampling depth may be considered a boundary. Any changes in the waste concentration over time must be considered as a temporal boundary. This step is often performed simultaneously with the previous step.

5. Develop decision rule(s)

This is a statement which describes how the data will be summarized, collected, and compared to the decision. The statement should include actions which will be based on criteria and conclusions from the sampling and analysis. The statement should be an "if...then..." statement that incorporates the action limits. The statement should include the parameter to be measured, the mode of comparison (greater than, less than, average, etc.), action levels and actions to be taken. An example statement: If the average concentration in drum is greater than 1 mg/L of cadmium, the material will be disposed of as a hazardous waste.

Instead of statements, a decision logic diagram may be used to present the decisions and actions, and criteria. When complex decisions are required or when multiple criteria must be considered, the decision logic diagram is often more easily followed and understood.

6. Specify acceptable limits on decision error

The decision maker should understand that results of all studies have uncertainty and error. The goal is to quantitate the amount of uncertainty that the decision maker is willing to accept in making the decision. The key step is to move from a qualitative "feeling" of uncertainty to a quantitative level of uncertainty. The process for establishing this, in the case of a hazardous waste determination, includes the following:

- i. Identify the consequences of incorrectly deciding the waste is not hazardous.
- ii. Identify the consequences of incorrectly deciding the waste is hazardous.
- iii. Rank these consequences by severity.
- iv. Estimate the health risk and financial risk associated with an incorrect result.
- v. Estimate how far below the regulatory limit one wants to be in order to decrease the consequence of an incorrect decision. Some statistical experience in assessing decision error and in assessing sampling and analysis design error is needed to make this assessment.

This information is incorporated into the decision rule. An example decision rule which incorporates the decision error is:

Three samples per drum are collected and the concentrations from each drum are averaged. If the within drum average concentration of cadmium is greater than 0.7 mg/L of cadmium, then the material will be disposed of as a hazardous waste.

7. Optimize the design

In order to characterize a site or waste successfully, a sampling and analysis design must be established. The sampling and analysis design includes development of statistical and observational design alternatives, and specifies sampling, handling, and analysis methods. The design indicates the number and locations of samples based on the acceptable decision error which was agreed on during the DQO development. The most important input from the DQO process is the degree of decision error which the decision maker will accept. When

preparing a sampling and analysis design, the time and budgetary constraints should be evaluated to balance their importance versus the decision error.

The preliminary design may contain the following information:

- ! Spatial areas of interest
- ! Hot spots versus average values of contamination
- ! Particular contaminants of concern
- ! Desired levels of detection
- ! Which matrices will be investigated
- ! Patterns of contamination
- ! Stratification of the contaminants
- ! Contaminant degradation
- ! Temporal considerations (changes of concentration over time)
- ! Quality control samples designed to allow estimation of precision and accuracy, and background contamination
- ! Health and safety issues

Designs must be practical and achievable. There is no one correct design but rather an optimum design which balances resources with the data required to make a decision. Technical staff must work carefully to present several designs to decision makers along with the probability of decision error, resources, and benefits of each design.

Other factors used to select the appropriate measurement methods include:

- ! DQOs,
- ! required regulatory or risk assessment levels,
- ! method precision and accuracy, and
- ! contaminants of interest.

Improved accuracy, precision, and lower detection limits usually result in higher sampling and analytical costs because larger numbers of samples, improved instrumentation, and more field/analytical expertise may be required. The improved accuracy may result in decreased decision error. If matrix specific accuracy and precision data are not available, preliminary precision and accuracy studies must be performed. These studies should measure total error from sample heterogeneity, sampling, and analytical methods. Regulatory agencies may review these studies prior to method approval.

Prior to sampling design implementation, the decision makers must approve the design. Several designs may be presented to the regulators and decision makers. The level of uncertainty, advantages and disadvantages, budgetary and time constraints, and other relevant factors must be presented for each design. This approach allows the decision makers to properly assess options and to agree upon the best sampling design. Sampling designs are implemented after approval by the decision makers.

The technical team must continually evaluate the proposed designs with respect to the DQOs, health and safety criteria, budget and time constraints. If the proposed design does not meet the criteria, it may be altered. In extreme cases, the DQOs may be unattainable and must be altered. The DQOs should only be changed after consultation with the decision makers and technical team members. The DQOs may need to be reevaluated if a decision cannot be made.

References for sampling design strategies are:

- ! U.S. EPA, Test Methods for Evaluating Solid Wastes, SW-846 Third Edition-Chapter 9. August 1993.
- ! Characterizing Heterogeneous Materials, July, 1992 (Appendix XII) .

Chapter 9 of SW 846 outlines several statistical design approaches. Many other design strategies exist and may be better suited for the situation at hand. It is wise to examine many statistical options and methods of evaluating the data during the planning phase.

An example of using the DQO-PP is presented in the following pages. This example demonstrates how to design a sampling program to determine whether fly ash from a municipal incinerator is a RCRA hazardous waste. This example is from a draft ASTM standard practice on the use of DQO-PP in waste management activities. The ASTM document was the product of a cooperative agreement between ASTM, US EPA Quality Assurance Management Staff and the Office of Solid Waste. The example was written by the ASTM D.34.02.10 committee.

3.2 DQO Case Study: Cadmium Contaminated Fly Ash Waste

Background

A municipal waste incineration facility located in the Midwest routinely removes "fly ash" from its flue gas scrubber system and disposes of it in a sanitary landfill. Previously, it was determined that the ash was "non-hazardous" under RCRA regulations. However, the incinerator has recently begun treating a new waste stream. As a result, a local environmental public interest group has asked that the ash be retested against RCRA standards before it is dumped. The group is primarily concerned that the ash could contain hazardous levels of cadmium from the new waste sources. The facility manager has agreed to test the ash and decides to employ the Data Quality Objectives process to help guide decision-making throughout the project.

The Code of Federal Regulations (CFR) Part 261 RCRA toxicity characteristic criteria for determining if a solid waste is hazardous requires collection of a "representative portion" of the waste and performance of Toxicity Characteristic Leaching Procedure (TCLP). During this process, the solid fly ash will be "extracted" or mixed in an acid solution for 18 hours. The extraction liquid will then be subjected to tests for specific metals.

Since the impact of the new waste stream is not known, a preliminary study was conducted to determine the variability of the concentration of the contaminants. Random samples were collected from the first 20 truck loads. Since process knowledge of the waste stream indicated that cadmium was the only toxicity characteristic (TC) constituent in the waste, these samples were analyzed individually for cadmium using the TCLP. The results were expressed as the average concentration along with the standard deviation.

DQO Development

The following is an example of the output from each step in the DQO process.

Assemble the Team -- The Plant Manager assembled a skeletal team consisting of himself and a representative of the current disposal facility staff. The two of them assembled the team with the responsibility to deal with this problem.

The decision makers evaluation team will include the incineration plant manager, a representative of the environmental public interest group, a representative of the community where the ash is currently being disposed of. The technical staff include a statistician, and a chemist with sampling experience.

1. State the Problem

The problem is to determine if any loads of fly ash are hazardous for cadmium under the RCRA TCLP. If so, those loads must be disposed of in a RCRA landfill.

2. Identify the Decision(s)

- i. *Decision* -- Determine whether the concentration of cadmium in the waste fly ash exceeds the regulatory RCRA standards.
- ii. *State the Actions That Could Result From the Decision* --
 - a) If the average concentration of cadmium is greater than the action level, then dispose of the waste fly ash in a RCRA landfill.
 - b) If the average concentration of cadmium is less than the action level, then dispose of the waste fly ash in a sanitary landfill.

3. Identify the Inputs Needed for the Decision

List the environmental variables or characteristics which are known from historical and regulatory information and information which must be obtained in order to make the decision.

Available Inputs

Preliminary Study Information -- Since the concern is with a new waste stream, the team ordered a pilot study of the fly ash to determine the variability in the concentration of cadmium between loads of fly-ash leaving the facility. They have determined that each load is fairly homogeneous. However, there is a high variability between loads due to the nature of the waste-stream. Most of the fly ash produced is not a RCRA hazardous waste and may be disposed of in a sanitary landfill. Because of this, the company has decided that testing each individual waste load before it leaves the facility would be the most economical. In that way, they could send loads of ash that exceeded the regulated cadmium concentrations to the higher cost RCRA landfills and continue to send the others to the sanitary landfill.

The study showed that the standard deviation of the cadmium concentration within a load was $S_w = 0.4$ mg/L and the standard deviation of the cadmium concentration between loads was $S_b = 1.4$ mg/L. Sample and quality control data indicates that a normal distribution can be assumed.

Identify Contaminants of Concern, Matrix, and Regulatory Limits -- The team identified the following factors critical to the problem:

- ! Contaminants of concern: cadmium soluble in the Toxic Characteristic Leaching Procedure (TCLP) extract.
- ! Sample Matrix: fly ash.
- ! Regulatory Threshold: 1 mg/L.

Specific Project Budget and Time Constraints -- The incinerator plant manager has requested that all stages of the operation be performed in a manner that minimizes the cost of sampling, chemical analysis and waste disposal. However, no formal cost constraints have been implemented.

The environmental public interest group has threatened to file a law suit for violation of environmental regulations if testing does not proceed within a "reasonable time-frame."

Contained in the trucks, the waste does not pose a threat to humans or the environment. Additionally, since the fly ash is not subject to change, disintegration or alteration, the chemical properties of the waste do not warrant any temporal constraints. However, in order to expedite decision making, the evaluation team has placed deadlines on sampling and reporting. The fly ash waste will be tested within 48 hours of being loaded on to waste hauling trailers. The analytical results from each sampling round should be completed and reported within 5 working days of sampling.

Identification of the testing methods -- In this case, 40 CFR Part 261, Appendix II specified the TCLP method SW 846 Method 1311. The leachate must be analyzed by an appropriate method. Potential methods of characterizing the leachate for cadmium include, but are not limited to, SW 846 methods 6010, 6020, 7130, or 7131.

Inputs To Be Determined

Method validation and QC -- The analytical method accuracy and precision and method detection limits in the fly ash matrix must be determined. The QC samples must be specified.

Identification of sampling procedure or devices -- The following must be determined:

- Number of samples
- Sampling methods for composite or grab samples of ash
- QC requirements for sampling

4. Define the Boundaries of the Study

Define a detailed description of the spatial and temporal boundaries of the decision; characteristics that define the environmental media, objects or people of interest; and any practical considerations for the study.

- i. *Specify the Characteristics that Define the Sample Matrix* -- The fly ash should not be mixed with any other constituents except the water used for dust control.
- ii. *Identify Spatial Boundaries* -- The variability between loads was greater than within a load therefore, decisions will be made on each load. The waste fly ash will be tested after it has been deposited in the trailer used by the waste hauler. Separate decisions about the toxicity of the fly ash will be made for each load of ash leaving the incinerator facility. Each load of ash should fill the waste trailer at least 70%. In cases where the trailer is filled less than 70%, the trailer must wait on-site until more ash is produced and can fill the trailer to the appropriate capacity.
- iii. *Identify Temporal Boundaries (The temporal boundaries of the study include the time frame over which the study should be conducted)*. -- The study will be conducted until at least 30 data points are collected and the action limits, number and frequency of samples will be reevaluated after that time.

5. Develop a Decision Rule

The arithmetic mean of sample results will be compared to the action level.

Decision Rule:

- a) If the average concentration of cadmium in a truck load is greater than the action level, then dispose of the waste fly ash in a RCRA landfill.
- b) If the average concentration of cadmium in a truck load is less than the action level, then dispose of the waste fly ash in a sanitary landfill.

Note that the team has decided that the action level will be less than the regulatory level in order to decrease decision error at the regulatory level of 1 mg/L.

Develop Decision Error Constraints

The decision makers specify acceptable decision errors based on the consequences of making an incorrect decision. Both error rates have negative consequences.

The team must make a baseline assumption. Based on the initial pilot study each load will be assumed to be less than the regulatory level and the burden of proof will be to prove that the load is above the action level. In this example, there are two types of error that the evaluation team could make:

- i. *false positive error* (declaring the load hazardous when it is not) -- If the true cadmium concentration is below 1 mg/L, but the average measured cadmium concentration is above the action level, the non-hazardous fly-ash waste will be sent to a RCRA landfill. The consequence of a false positive error is that the company will have to pay additional cost to dispose of the waste with a concentration between the action level and regulatory threshold at a RCRA facility as opposed to a less expensive method of disposal in a sanitary landfill.
- ii. *false negative error* (declaring the load non-hazardous when it is hazardous) -- If the true cadmium concentration is equal to or greater than 1 mg/L, but the average measured cadmium concentration is below the action level, the hazardous fly-ash waste will be sent to a sanitary landfill. The consequence of a false negative error is that the fly-ash waste may be disposed in a manner that will be harmful to human health or the environment. Legal consequences and subsequent remedial costs are also possible consequences.
- iii. *number of samples* -- The number of samples will depend on the uncertainty of estimating the true cadmium concentration for each load and the resources available to sample and to chemically analyze the samples.

The purpose of this stage of the process is to specify the probabilities of making an incorrect decision on either side of the "action level" that are acceptable to decision makers. The team must agree on which type of decision error is of greater concern, false positives or negatives and must target the level of false positives and negatives.

For this example, the project team is more concerned about false negatives because of the increased liability due to sending potentially hazardous waste to a sanitary landfill. The team set a target level of false negatives of 10% when the true concentration is 1 mg/L.

Decision Performance Curve

The Decision Performance Curve will be calculated to determine the action level and review the performance of the decision rule. To calculate the Decision Performance Curve, decision makers use the following steps:

Step 1: Number of samples are calculated with $L = 0.2$ mg/L, $\sigma = S_w = 0.4$ mg/L, and $\alpha = 0.05$ (or $Z_{\alpha/2} = 1.960$ for a 95% confidence level).

$$n = \left(\frac{1.960 \times 0.4}{0.2} \right)^2 \approx 16 .$$

where:

L = the limit of error on the average of 0.2 mg/L

S_w or standard deviation = 0.4 mg/L within a load

$Z_{\alpha/2} = 1.960$ for a 95% confidence level, the $\alpha/2$ percentile point of normal probability distribution e.g. $Z_{\alpha/2} = Z_{.0005}$. These are tabled values from a standard normal distribution at $Z_{.0005}$.

n = number of samples

Step 2: Calculate the action level (AL) from the specified false negative error of 10%. The probability calculations are based on an approximating normal probability distribution for the cadmium concentration measurements. This approximating normal probability has a mean = $RT = 1.0$ mg/L and a standard deviation = $S_w = 0.4$ mg/L. The 10% percentile point for the standardized normal probability distribution is $Z_{0.10} = 1.282$.

False Negative Error = $\Pr(\text{Average} < AL \text{ when the true concentration} = RT) = 0.10$.

or

$$\frac{AL - RT}{S_w / \sqrt{n}} = -Z_{0.10} ,$$

AL = Action Level

RT = Regulatory Threshold

$Z_{0.10}$ = Tabled Z-value from standard normal distribution at 0.10

$$AL = 1.0 \text{ mg/L} - (1.282)(0.4 \text{ mg/L}) / 4 = 1.0 \text{ mg/L} - 0.13 \text{ mg/L} ,$$

or

$$AL = 0.87 \text{ mg/L} .$$

Therefore, the decision rule is:

- a) If (average concentration of cadmium) ≥ 0.87 mg/L, then dispose of the waste fly ash in a RCRA landfill.
- b) If (average concentration of cadmium) < 0.87 mg/L, then dispose of the waste fly ash in a sanitary landfill.

The decision performance curve for this decision rule would have a probability of taking action (i.e., sending fly-ash waste to a RCRA landfill) of 0.90 at a possible true concentration value of $RT = 1.0$ mg/L.

Step 3: Calculate the true concentration (say, $\theta < RT$) that corresponds to an action level of $AL = 0.87$ mg/L and a false positive error of 20%. The probability calculations are based on an approximating normal probability distribution for the cadmium concentration measurements. This approximating normal probability has a mean = θ mg/L and a standard deviation = $S_w = 0.4$ mg/L. The 20% percentile point for the standardized normal probability distribution is $Z_{0.20} = 0.848$.

False Positive Error = $\Pr\{\text{Average} < AL \text{ when the true concentration} = \theta\} = 0.20$.

or

$$\frac{AL - \theta}{S_w / \sqrt{n}} = + Z_{0.20} ,$$

AL = Action Level

θ = True Value

$Z_{0.20}$ = Tabled Z-value from standard normal distribution at 0.10

$$\theta = 0.87 \text{ mg/L} - (0.848)(0.4 \text{ mg/L}) / 4 = 0.87 \text{ mg/L} - 0.08 \text{ mg/L} ,$$

or

$$\theta = 0.79 \text{ mg/L} .$$

The decision performance curve would have a probability of taking an action (i.e., sending fly-ash waste to a RCRA landfill) of 0.20 at a true cadmium concentration of $\theta = 0.79$ mg/L. The possible true cadmium concentration values in the interval (0.79 mg/L, 1.0 mg/L) represents values that cause the decision rule to send fly-ash waste to a RCRA landfill even though the true concentration is below the regulatory threshold. This interval can be reduced by increasing the number of samples, by changing the false negative error or by changing the false positive error.

Step 4: Draw the decision performance curve by using the standardized normal probability distribution. The standardized normal probability

distribution is defined as a normal probability distribution with mean = 0 and standard deviation = 1.0. There are many tables and computer programs that can be used to calculate probabilities for a standardized normal random variable, Z. A normal random variable, X, with mean = μ and standard deviation = σ can be transformed to a standardized normal random variable by $Z = (X - \mu)/\sigma$.

$\text{Prob}(\text{Action}) = \text{Pr}(\text{Average} \geq \text{AL when the true concentration} = \theta)$.

$$\text{Prob}(\text{Action}) = 1.0 - \text{Prob}\left(Z \leq \frac{\text{AL} - \theta}{S_w / \sqrt{n}}\right),$$

$$\text{Prob}(\text{Action}) = 1.0 - \text{Prob}\left(Z \leq \frac{0.87 - \theta}{0.1}\right).$$

Figure 3-2 plots the decision performance curve of $\text{Prob}(\text{Action})$ versus possible true concentration values θ .

7. OPTIMIZE THE DESIGN

The decision maker(s) will select the lowest cost sampling design that is expected to achieve the DQOs. The optimal design(s) for sampling the fly-ash waste will be generated by the statisticians on the evaluation team. The choice of sampling plan will be decided by consensus.

Figure 3-2 plots the probability of taking action (disposing of the waste in a RCRA landfill) versus different possible values for the true concentration in the TCLP extract. Note that various numbers of samples, n, are used to generate each curve. All of the curves meet the criteria of 10% false negatives at the regulatory threshold. The differences lie in the false positives versus the true concentration. If the true concentration value is equal to .87 mg/L (the action level) then the probability of taking action is .5 or 50% chance of taking action. The action level is below the regulatory threshold and does insure the agreed upon false negative rate of 10%. Note that if the regulatory level and the action level were equal, the likely chance of having a false negative would be 50% at 1 mg/L.

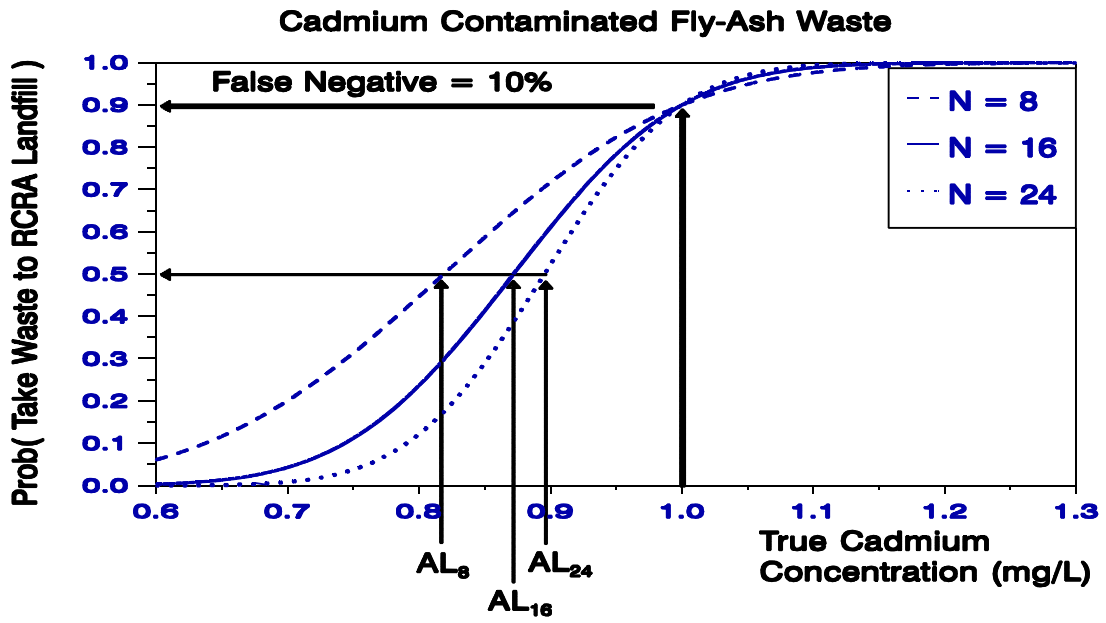


Figure 3-2. Design Performance Curve for Cadmium Example

Implementation -- After completion of the sampling and measurement process, the data assessment is performed. The concentration measurements from each load of fly-ash waste are averaged and compared to the action level. Any load with average concentrations less than the action level will be sent to a sanitary landfill, and those loads with average concentrations greater or equal to the action level will be sent to a RCRA landfill.

3.3 Sampling and Analysis Design

Specifying Sample Collection Procedures

- ! The methods and equipment used for sampling waste materials vary with the physical and chemical properties of the waste materials.
- ! 40 CFR Part 261, Appendix I lists several representative sampling methods. Unfortunately, for most matrices, selecting representative samples is an extremely difficult objective.
- ! The methods in the above reference are recommended. *No prior approval by EPA is required if alternate sampling methods are used.*
- ! All procedures for sampling should be documented and referenced.

Sample Containers, Preservation, and Storage

Prior to Extraction or Filtration

- ! No preservatives are added to the initial waste collected for TCLP filtration and extraction.
- ! Preservatives used after filtration and extraction are listed in Chapter 4 of this document.
- ! If organics are being analyzed, samples must be collected in glass containers with Teflon lid liners.
- ! Metals may be collected in polyethylene or glass containers.
- ! If practical, samples which will undergo Zero Headspace Extraction (ZHE) for volatiles should be collected in 40 mL glass Volatile Organic Analysis (VOA) vials with Teflon lids. Clay type soil samples, or other large particle size solid matrices which are difficult to put into narrow-mouth containers, should be collected in 250 mL wide mouth glass jars.
- ! Any sample which will undergo ZHE should be collected with minimal head space in the container.
- ! All samples should be stored at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ prior to extraction or filtration. Samples should be placed in coolers immediately after collection.

Sample Volumes

A discussion of required sample volume is presented in Chapter 4 which includes the following general points:

- ! A minimum of 100g of waste is needed to determine the percentage of solids, extraction fluid type, and particle size.

- ! A second aliquot of 100g is the minimum which must be extracted for non-volatiles. The amount of sample is dependent on the percent wet solids. The lower the percent wet solids, the greater the sample volume required for leaching.
- ! Another aliquot of at least 25g must be used for volatiles by ZHE. The amount of sample is dependent on the percent wet solids. The lower the percent wet solids, the more material which must be collected for leaching.
- ! If multiple phases are collected and the solids appear to be $\leq 0.5\%$, each phase may have to be analyzed individually. This is especially true of oily waste. If the oil will not pass through the filter, it will be considered a solid.
- ! Enough sample must be collected to allow for the matrix spike. Each matrix requires a spike. The same amount of material is required for the spike as for the sample.
- ! Extra sample volume may be needed if vessel leakage or breakage occurs. Multi-phasic samples require much larger sample volumes than monophasic samples.

Sampling Equipment Decontamination

Acceptable sampling equipment decontamination should be performed before sample collection. Decontamination may be required in the field if an adequate number of pieces of sampling equipment is not available to allow equipment to be dedicated to one sampling point.

Each EPA region and some states have special decontamination requirements. These decontamination requirements should be verified for compliance in a particular region or state. The RCRA decontamination procedures may differ from CERCLA decontamination procedures in some locations. For most TCLP sampling events, there are no sampling equipment decontamination criteria.

Paint or coatings on sampling equipment must be removed from any part of the equipment that may contact the sample.

The USEPA Region 2 decontamination procedure for CERCLA sampling and RCRA Facility Investigation (RFI) sampling is as follows:

- a. wash and scrub with low phosphate detergent
- b. tap water rinse
- c. rinse with 10% HNO₃, ultra pure
- d. tap water rinse
- e. an acetone-only rinse or a methanol followed by hexane rinse (solvents must be pesticide grade or better)
- f. thorough rinse with demonstrated analyte free water*
- g. air dry, and
- h. wrap in aluminum foil for transport

* The volume of water used during this rinse must be at least five times the volume of solvent used in Step e.

If metal samples are not being collected, the nitric acid rinse may be omitted. If organic samples are not being collected, the solvent rinse may be omitted.

Holding Times for TCLP

TCLP has three sets of holding times (see Table 3-1). The first holding time commences with sample collection and ends with TCLP extraction. The second holding time is from TCLP extraction to preparative extraction. The final holding time is from preparative extraction to analysis.

Table 3-1 - TCLP Holding Times

Analysis Type	Days From Field Collection to TCLP Extraction	Days From TCLP Extraction to Preparative Extraction	Days From Preparative Extraction to Determinative Analysis
Volatiles	14	NA	14
Semivolatiles*	14	7	40
Metals, except Mercury	180	NA	180
Mercury	28	NA	28

* Pesticides and herbicides are deemed semivolatiles.

Some regional and state agencies may alter these times. If Contract Laboratory Program (CLP) methods are used, the holding times from extraction to preparation and from preparation to determinative analysis will differ from the above times. However, to demonstrate compliance with the TC or Land Ban regulations, sample holding times may not exceed the holding times listed in the preceding table.

Field QC Samples

The following field QC samples may be collected during the sampling process:

Trip Blanks are aliquots of analyte-free water brought to the field in sealed containers and transported back to the lab with the sample containers. Trip blanks, which are only analyzed for volatiles, are especially useful when aqueous volatiles are collected. Trip blanks allow one to assess contamination from transport and storage.

Equipment Blanks are analyte-free water which is poured over the sampling equipment in the field after the final rinsing of equipment. Equipment blanks allow one to assess cross contamination and decontamination procedures.

Several key issues must be understood when evaluating the need for equipment blanks. Equipment blanks are analyzed for total constituents while waste undergoes extraction. The TCLP leaching process uses 20 grams of leaching fluid per gram of

wet weight sample. Therefore, TCLP equipment blanks may not be cost effective for some types of TCLP sampling. However, if sampling is being done for legal purposes, such as enforcement actions or potential litigation, equipment blanks should be collected to assure that the data are legally defensible.

- ! **Field Duplicates** are samples collected from the same location and waste source at the same time. The goal is to determine variability in the waste or sample matrix. The frequency of these depends on the sampling design. Most agencies recommend at least 5%. Duplicates provide information about sampling and analysis precision.
- ! **Laboratory Duplicates** are samples which have sufficient volume to allow the laboratory to homogenize the sample, split the sample and prepare and analyze both aliquots as separate samples. The purpose is to assess precision between two laboratory analyses on the matrix.

Enough sample volume must be collected for the lab to generate matrix spikes and laboratory duplicates. The frequency of these samples varies, and depends on the different types of waste collected, the time over which they are collected, and the regulatory requirements.

Sampling Documentation

- ! All sample locations should be identified in a log book. Locations should be from a surveyed point when applicable. Both horizontal and vertical coordinates should be documented. Each sampling point should be assigned a unique number or other identifier.
- ! Unique sample numbers, collector, date and time of collection, container types, matrix and analysis required (including TCLP and the extract/filtrate analysis) should be documented in field log books, chain-of-custody (COC) forms, and on sample labels.
- ! In most cases, a COC should be used to document the collection and transport of samples to the laboratory. The chain of custody form should be signed and dated by individuals who collect, transport or receive the samples. Copies of COCs should be kept by sending and receiving parties.
- ! Any deviations from the sampling plan should be documented in the log books.
- ! The type of sampling equipment utilized must be documented in the log book.
- ! Ambient weather conditions at the sampling location(s) should be documented in the log book.

3.4 Analytical Method Selection

Strategy for Analytical Method Selection:

- ! Determine the analytes
- ! Determine the methods of analysis
- ! Specify detection limits and regulatory action levels
- ! Specify quality control samples and requirements

To specify appropriate analytes to demonstrate compliance with the TC regulations, the data requester needs to understand the basic groupings of analytes which are performed by each analytical method. The data requester also must understand the typical detection limits and the issues which revolve around not being able to achieve these limits. The following tables outline the TC constituent, the category of the analyte, and the potential methods of sample preparation and analysis. The current CLP contract required detection limits/quantitation limits and the SW-846 practical quantitation limits are also presented in this section.

The analytical method information should be used in conjunction with process knowledge and Table 3-2, which lists the TC constituents and regulatory levels, to plan the sampling and analysis.

TABLE 3-2 - TC ANALYTES AND THEIR REGULATORY LEVELS

Constituent ¹	Regulatory Level (mg/l)	Constituent ²	Regulatory Level (mg/l)	Constituent ²	Regulatory Level (mg/l)
Arsenic	5.0	Benzene	0.5	Heptachlor	0.008
Barium	100.0	Carbon tetrachloride	0.5	Hexachlorobenzene	0.13
Cadmium	1.0	Chlordane	0.03	Hexachloro-1,3-butadiene	0.5
Chromium	5.0	Chlorobenzene	100.0	Hexachloroethane	3.0
Lead	5.0	Chloroform	6.0	Methyl ethyl ketone	200.0
Mercury	0.2	o-Cresol	200.0	Nitrobenzene	2.0
Selenium	1.0	m-Cresol	200.0	Pentachlorophenol	100.0
Silver	5.0	p-Cresol	200.0	Pyridine	5.0
Endrin	0.02	Cresol (total)	200.0	Tetrachloroethylene	0.7
Lindane	0.4	1,4-Dichlorobenzene	7.5	Trichloroethylene	0.5
Methoxychlor	10.0	1,2-Dichloroethane	0.5	2,3,5-Trichlorophenol	400.0
Toxaphene	0.5	1,1-Dichloroethylene	0.7	2,4,6-Trichlorophenol	2.0
2,4-D	10.0	2,4-Dinitrotoluene	0.13	Vinyl chloride	0.2
2,4,5-TP (Silvex)	1.0				

¹ Original EP Tox constituents.

² Chemical constituent added by TC Rule (shaded areas).

General Method Information

There are two categories of permissible methods used to analyze TCLP extracts:

1. Many state environmental agencies mandate the use of SW-846 methods for hazardous waste determinations. SW-846 methods are sometimes also required to demonstrate compliance with the RCRA regulations. Several different SW-846 methods may be used to analyze TC analytes. Appendix IX explains when SW-846 methods are mandatory.
2. Any appropriate EPA approved method may be used to demonstrate compliance with the TC regulations. However, if the data are going to be validated, CLP methods are recommended. Two semi-volatile TC analytes (m-cresol, pyridine) are not included in the CLP target compound list of analytes. Therefore, the method must be slightly modified to incorporate these two compounds.

Specifying detection limits and regulatory action levels

- ! The method or contract detection limits must be evaluated versus the regulatory TC limits. The method or contract limits must be lower than the regulatory limits.
- ! There are three compounds which have quantitation limits that exceed the regulatory limits: 2,4-dinitrotoluene, hexachlorobenzene, and pyridine. In these cases, the quantitation limit becomes the regulatory limit.
- ! The EPA Region 2 TCLP SAS Request (Appendix VIII), shows recommended TC detection limits which are increased in order to minimize matrix effects.

Metals Analysis Information

- ! Metals analysis can be performed by three methods: Inductively Coupled Plasma (ICP), Flame Atomic Absorption (FAA) and Graphite Furnace Atomic Absorption (GFAA).
 - Laboratories usually analyze metals, except mercury, in the TCLP extract by ICP.
 - Mercury is usually analyzed by Cold Vapor Atomic Absorption (CVAA).
 - The GFAA generates lower detection limits than ICP method.
- ! The CLP Contract Required Detection Limits (CRDLs) are the same for both ICP and GFAA.

Table 3-3 Metals Analysis Method By ICP

Analyte	SW 846 Preparation/ Analysis	SW 846 PQL, mg/L(1)	CLP CRDLs, mg/L (2)
Arsenic	3010/6010	.05	.01
Barium	3010/6010	.002	.2
Cadmium	3010/6010	.004	.005
Chromium	3010/6010	.007	.01
Lead	3010/6010	.04	.003
Selenium	3010/6010	.07	.005
Silver	7760 (prep only)/6010	.007	.01

(1) PQL = Practical Quantitation Limit = EQL = Estimated Quantitation Limit

(2) Contract Laboratory Program, Statement of Work for Inorganic Analysis, ILM03.0

Table 3-4 Metals Analysis Methods by GFAA and Mercury by CVAA

Analyte	SW 846 Preparation/ Analysis	SW 846 PQL, mg/L(1)	CLP CRDLs, mg/L (2)
Arsenic	7060/7060	.001	.01
Barium	3020/7080	.1	.2
Cadmium	3020/7131	.001	.005
Chromium	3020/7191	.001	.01
Lead	3020/7421	.001	.003
Selenium	7740/7740	.002	.005
Silver	7760 (prep only)/7760	.01	.01
Mercury	7470	.0002	.0002

(1) PQL = Practical Quantitation Limit = EQL = Estimated Quantitation Limit

(2) Contract Laboratory Program, Statement of Work for Inorganic Analysis, ILM03.0

Table 3-5 Pesticide and Herbicide Quantitation Limits by SW 846 and CLP

Analyte	SW 846 Preparation/ Analysis	SW 846 PQL, ug/L (1)	CLP CRQL, ug/L (2)
Pesticides			
endrin	3510 or 3520/ 8080B	0.06	0.10
lindane (gamma BHC)	3510 or 3520/ 8080B	0.04	0.05
methoxychlor	3510 or 3520/ 8080B	1.76	0.05
heptachlor	3510 or 3520/ 8080B	0.03	0.05
toxaphene	3510 or 3520/ 8080B	2.4	5.0
chlordane (4)	3510 or 3520/ 8080B	0.14	0.05
Herbicides			
2,4-D	8150A	12	(3)
2,4,5-TP (Silvex)	8150A	2.0	(3)

- (1) PQL = Practical Quantitation Limit = EQL = Estimated Quantitation Limit
- (2) Contract Laboratory Program, Statement of Work for Organic Analysis, OLM01.8
- (3) No CLP methods exist for these compounds.
- (4) SW-846 quantitation limits are for "technical" chlordane. CLP quantitation limits are for alpha and gamma chlordane.

Table 3-6 Quantitation Limits for Volatile TC Constituents

Volatiles	SW 846 Preparation/ Analysis	SW846 8240 PQL, ug/L (1)	CLP CRQL, ug/L (3)
benzene	8240B or 8020B	5	10
carbon tetrachloride	8240B or 8010B	5	10
chloroform	8240B or 8010B	5	10
chlorobenzene	8240B or 8010 or 8020B	5	10
1,2-dichloroethane	8240B or 8010B	5	10
1,1-dichloroethylene (1,1-dichloroethene)	8240B or 8010B	5	10
methyl ethyl ketone (2-butanone)	8240B (2) or 8015	100	10
tetrachloroethylene (tetrachloroethene)	8240B or 8010B	5	10
trichloroethylene (trichloroethene)	8240B or 8010B	5	10
vinyl chloride	8240B or 8010B	10	10

- (1) PQL = Practical Quantitation Limit = EQL = Estimated Quantitation Limit
(2) Poor purging efficiency by this method produces a high detection limit.
(3) Contract Laboratory Program (CLP) Statement of Work for Organic Analysis, OLM01.8

Table 3-7 Quantitation Limits for Semivolatile TC Constituents

Semivolatiles (BNAs)	SW 846 Preparation/ Analysis	SW 846 PQL, ug/L (1)	CLP CRQL, ug/L (5)
o-cresol (2-methylphenol)	3510/8270B	10	10
m-cresol (3-methylphenol)	3510/8270B	10	(3)
p-cresol (4-methylphenol)	3510/8270B	10	10
1,4-dichlorobenzene	3510 or 3520/ 8270B	10	10
2,4-dinitrotoluene	3510 or 3520/ 8270B	10	10
hexachlorobutadiene (hexachloro-1,3-butadiene) (4)	3510 or 3520/ 8270B	10	10
hexachloroethane	3510 or 3520/ 8270B	10	10
hexachlorobenzene	3510 or 3520/ 8270B	10	10
nitrobenzene	3510 or 3520/ 8270B	10	10
pentachlorophenol	3510 or 3520/ 8270B	50	25
pyridine	3510 or 8270B	ND (2)	(3)
2,4,5-trichlorophenol	3510 or 3520/ 8270B	10	25
2,4,6-trichlorophenol	3510 or 3520/ 8270B	10	10

- (1) PQL = Practical Quantitation Limit = EQL = Estimated Quantitation Limit
(2) ND = Not Determined. If these methods are used, the method detection limits must be determined.
(3) These analytes are not routinely part of the CLP method. If required for TC, these analytes must be specially requested. The CLP 2/88 extraction procedure must be used for the TC semivolatile analytes if these analytes are desired.
(4) Other methods quantitate this in the volatile fraction.
(5) Contract Laboratory Program, Statement of Work for Organic Analysis, OLM01.8

Chapter 4

OVERVIEW OF THE TCLP METHOD

Preliminary Sample Preparation

Leaching Procedure for Non-Volatiles

Leaching Procedure for Volatiles

TCLP Method Quality Control

4.0 OVERVIEW OF THE TCLP METHOD

This chapter provides an overview of the TCLP method. Appendix I of this document includes a copy of the method and Appendix III provides worksheets which will be useful in understanding method calculations. The following topics are covered in this chapter:

- ! Preliminary sample preparation for leaching
- ! Leaching procedure for non-volatiles
- ! Leaching procedure for volatiles
- ! TCLP method QC

4.1 Preliminary Sample Preparation for Leaching

Prior to performing the leaching procedure, several preliminary determinations must be made. These include:

- ! Are there enough solids present for the leaching process?
- ! Is particle size reduction required?
- ! Are immiscible liquids present?
- ! Which leaching fluid should be used for non-volatile analytes?

Figure 4-1 provides a flow chart which delineates preliminary determinations. The first step is to take 100g of the waste, pass it through a 0.6 to 0.8 μm filter up to 50 psi and determine the percent solids. If the percent solids are greater than or equal to 0.5% on a dry weight basis, the solid must be leached. Any material which remains in the filtration apparatus is considered a solid. When liquids remain on the filtration apparatus because they are too viscous to pass through the filter, they are treated as solids. Any material which passes through the filter is the filtrate and considered a liquid. Therefore, viscous oils which do not pass through the filter are classified as solids. Oily waste will be discussed further at the end of this document. If the percent solids are less than 0.5%, the filtrate is the TCLP extract, and the laboratory analyzes the filtrate.

Particle Size

If the percent solids is $> 0.5\%$, the laboratory analyst must determine whether particle size reduction will be required.

- ! The requirement is *not* to measure the size. However, the surface area and particle size must conform with one of the following criteria:
 - The solid must have a surface area per gram of material equal to or greater than 3.1 square centimeters.
 - The solid must be smaller than 1 cm in its narrowest dimension (i.e., pass through a 9.5 mm (0.375 inch) standard sieve).
- ! If the particle size is too large, cutting, grinding, or crushing may be utilized to decrease particle size.

Choosing the Leaching Solution

Figure 4-1 shows the determination of the type of leaching fluid for use. If the solid content is greater than or equal to 0.5%, and if the sample is being analyzed for metals or semivolatiles, the type of leaching solution must be determined. Note that the leaching solution determination step requires a smaller (1 mm) particle size than the analytical method because the leaching solution determination allows much less contact time between the leaching solution and the sample.

After weighing a 5.0 g subsample of the solid, adding 96.5 mL of reagent water, and stirring for 5 minutes, the pH is measured. If the pH is ≤ 5.0 , fluid #1 is used. If the pH is > 5.0 , 3.5 mL of 1N HCl is added. The mixture is heated to 50°C for 10 minutes and cooled. If the measured pH is less than 5.0, fluid # 1 is used. If the pH is greater than 5.0, extraction fluid #2 is used.

The heating cycle is a critical step. After the sample has been heated, it should be cooled to room temperature. The pH must be measured immediately after the sample has reached room temperature. If the solid waste does not remain in contact with the acidic solution under specified time and temperature conditions, an erroneous pH may be measured.

The leaching fluid for all volatiles is fluid #1. Fluid #1 is an acetic acid and sodium hydroxide buffer of pH 4.93 ± 0.05 . Fluid #2 is an acetic acid solution of pH 2.88 ± 0.05 .

Figure 4-1

4.2 Leaching Procedure for Non-Volatiles

The non-volatiles include semivolatile organics, which are also called base, neutral, and acid extractables (BNAs), pesticides, herbicides, and metals. If the percent solids exceeds 0.5%, the solid is leached with the appropriate extraction fluid after any required particle size reduction. The following topics are discussed in this section:

- ! Determination of extraction fluid weight
- ! Sample and QC sample volumes
- ! Extract volumes required
- ! Issues when dealing with multi-phasic waste
- ! Initial filtrate versus TCLP leachate

The non-volatile extraction or leaching process is outlined in Figure 4-2. The extraction process includes placing the sample and appropriate fluid in the bottle extraction vessel and tumbling for 18 ± 2 hours and filtering the extract for subsequent analysis. The bottle extraction vessel is described in Section 4.2.2 of Method 1311, which is Appendix I of this document. In order to generate scientifically valid and legally defensible data, appropriate weights of environmental samples and leaching fluids must be used.

Figure 4-2

Determination of Extraction Fluid Weight

The following formula is used to compute the required weight of TCLP extraction fluid:

$$\text{Weight of Extraction Fluid} = 20 \times \frac{\% \text{Solids}}{100} \times \text{Weight of Waste Filtered}$$

The amount of extraction fluid required per extraction is 20 times the weight of wet filtered solids used in the extraction.

A minimum of 100g of waste material must be filtered to generate the solids utilized in the extraction. If the sample is 100% solids, a minimum of 100g must be used in the extraction. When aqueous environmental samples contain between one-half and ten percent solids, several kilograms of sample are required for analysis.

Sample and QC Sample Volumes

The generation of sufficient extract volume to perform all analysis is critical.

- ! The required volumes vary with the laboratory. *Check with the laboratory for actual volumes.*
- ! Depending on which metal analytes are selected, two or three digestions may be required.
- ! If matrix spikes or duplicates are performed, additional volume will be required. Labs may charge additional fees for these QC samples.

Table 4-1 Volume of Extract Required for One Nonvolatile Analysis

Analysis Type	Volume of TCLP Leachate Typically Required per Test
BNA	1 L
Chlorinated Pesticides	1 L
Herbicides	1 L
Metals	300 mL/digestion

The previous table outlines the "typical" volumes of extract or total leachate required for non-volatile analysis. *These volumes may vary with the laboratory. It is imperative that you check with the lab as to the amount of waste required for their analysis process.* The amount of waste varies with the percent solids. The lower the percent solids, the more waste will be needed for TCLP preliminary and final testing. If the waste sample is a filterable liquid with less than 0.5% solids, the volume listed in the previous table can be used as a guide for the minimum volume needed for the analysis.

Issues When Dealing with Multi-phasic Waste

- ! Subsampling stratified waste is difficult. Therefore, the analyst should consider calculating percent solids from the same sample container used for the TCLP extraction instead of compositing all the sample containers. This is the largest source of error in the TCLP leaching process. The laboratory must consider the amount of each phase present in each bottle and adjust the calculations accordingly.
- ! The particle size of multi-phasic material may be difficult to assess. The lab should identify procedures to classify multi-phasic samples which are not amenable to size measurement.
- ! Five grams of sample are usually used to determine the appropriate TCLP leaching fluid. If there is not enough volume of any individual phase, less material may be used.
- ! The pH of the filtrate should be recorded. This provides useful information when validating field or laboratory duplicates.
- ! The filtrate volume should also be measured. This information will be needed if the multiple phases must be mathematically combined.

Initial Filtrate Versus TCLP Leachate

Two liquids are generated when a multi-phasic waste is analyzed.

- ! Initial filtrate
- ! Leachate
- ! If the filtrate is miscible with the leachate, the two solutions are mixed prior to analysis.
- ! If the two solutions are not miscible, they are analyzed separately, and the results combined mathematically.

The mathematical calculations are performed via the following equation if the TCLP filtrate and extract are not miscible.

$$\text{Final analyte Concentration} = \frac{(V1) (C1) + (V2) (C2)}{V1 + V2}$$

where:

V1 = The volume of the first phase (L).

C1 = The concentration of the analyte of concern in the first phase (mg/L).

V2 = The volume of the second phase (L).

C2 = The concentration of the analyte of concern in the second phase (mg/L).

After generating the TCLP extract, the pH of the extract should be recorded. If the filtrate and TCLP extract are mixed, record the pH of the mixture as well as the original TCLP extract and filtrate. The TCLP extract or filtrate/extract mixture should be aliquoted for each analysis. Matrix spikes for all subsequent analyses must be added at this time.

The metals aliquot should be preserved to a pH<2 with nitric acid. Adjust the pH of a small portion of the TCLP extract or mixture prior to adjusting the entire metals aliquot. If a precipitate forms, do not adjust the pH of the sample extract. If nitric acid is not added, the sample should be analyzed as soon as possible after TCLP extraction. Metals analysis must include digestion prior to analysis. Aliquots for BNAs, herbicides and pesticides do not require chemical preservation. All aliquots must be stored at 4°C ± 2°C prior to analysis.

Example

The following example demonstrates how to calculate the weight of extraction fluid required to perform a TCLP extraction. In this example, the environmental sample contains 40% solids. Only metals will be analyzed since the waste is from a metals finishing shop.

In order to determine the total amount of waste required to generate 100g of solids, the following equation is used:

Amount of multi-phasic material = (10,000)/ (weight percent wet solids)

If 100g of original waste yields 40g of solid, the total amount of waste required to generate 100g of solid is 250g.

$$250\text{g of total waste required} = 10,000/40$$

Using the equation in Section 7.2.11 of Method 1311 (Appendix I):

Weight of extraction fluid = $20 \times \frac{\% \text{ solids}}{100} \times \text{weight of waste material filtered}$

$$20 \times \frac{40}{100} \times 250\text{g} = 2,000\text{g of extraction fluid}$$

Labs typically assume a density of 1 g/mL for the extraction fluid. Also, note that 40% is used, not 0.40, for the percent solids. Since 300 mL of extraction fluid is required for one complete metals digestion, using 250g of the multi-phasic waste will provide enough volume for the metals analysis. This allows enough volume to analyze one matrix spike. The use of matrix spikes will be discussed in the QC section of this chapter. The matrix spike sample size requirement is the same as for original environmental sample analysis.

If organic analysis were required, at least three times as much waste would have been used in the TCLP extraction. For matrix spikes analyses, a triple volume of TCLP leachate will be required. The terms analytical batch and waste type are not defined in the TCLP regulation. Most methods, including CLP and SW-846, indicate that a batch is the number of samples processed through preparation and analysis simultaneously, and should not exceed 20 samples of the same matrix. Most methods require that matrix spikes and matrix spike duplicates (MS/MSD) for organics be performed at 1 MS/MSD per processed batch, with a batch containing no more than 20 samples.

4.3 Leaching Procedure for Volatiles

Volatile organics are leached using different equipment than non-volatiles.

Figures 4-3 and 4-4 are the flow charts describing the volatile leaching procedure using the Zero Headspace Extractor (ZHE). The ZHE must be used when leaching volatiles. In order to minimize evaporation of volatiles, the volatile leaching procedure is performed on a separate aliquot of waste. Once the percent solids has been determined in the preliminary sample preparation phase, a second aliquot of the waste is used to generate the volatile analysis extract. In all cases, no more than 25g of solids should be placed in the ZHE because the total volume of the ZHE is 500-600 mLs. In order to prevent the loss of volatile compounds, heating or excessive sample manipulation must be kept to a minimum. The samples and equipment used in the process should be cooled to 4°C when possible to prevent loss of volatiles.

If the sample contains less than 0.5% dry solids, the filtrate is defined as the TCLP extract. The solid is discarded in this instance. The filtrate is collected in either a Tedlar bag or a glass syringe which is described in the equipment section of the procedures in Appendix I of this document. This filtrate becomes the TCLP extract.

Weight of Waste Charged to the ZHE

If the solids are > 0.5% dry solids, the material must be extracted.

If the solids are > 0.5% and < 5.0 %, a 500 g subsample of the waste is weighed and recorded.

If the solids are > 5.0%, the following formula is used to determine the amount of waste to place in the ZHE:

$$\text{Weight of Waste Charged in ZHE} = \frac{25 \times 100}{\text{Percent wet solids}}$$

If the solids are greater than 0.5% and the sample is multi-phasic, any solids must be examined for particle size prior to filtration. The sieve is *not* used to verify particle size for the volatile sample. Particles are measured with a ruler and should be less than 1 cm diameter. Any particle size reduction should be done with minimal exposure to air and without heat production. All apparatus used in this process should be cooled to 4°C.

figure 4-3

Figure 4-4

All waste which remains in the ZHE after reaching a pressure of 50 pounds per square inch (psi) is considered solid phase and undergoes leaching. Any liquid which is removed during filtration is considered liquid phase filtrate. The filtrate is captured in either a Tedlar bag or glass syringe. The solids are leached with fluid #1.

If the percent solids is 100%, a 25g sample of the solid is placed in the ZHE after any necessary particle size reduction is performed. The particle size reduction follows the same protocol requirements as volatile extraction of waste with solids content greater than 0.5% but less than 100%. The extraction is similar to the TCLP extraction of multi-phasic material.

When performing TCLP extraction for volatile analysis, extraction fluid #1 is always used. The quantity of extraction fluid is 20 times the solid waste weight used in the extraction.

The extraction is performed by placing the ZHE in the rotary agitator at 30 ± 2 rpm for 18 ± 2 hours. The ambient temperature is maintained at $23 \pm 2^\circ\text{C}$ during agitation. At the end of the agitation period, the ZHE piston pressure must be measured to verify that pressure was maintained during the extraction. If pressure was not maintained, the extraction must be repeated after the ZHE is examined for mechanical problems. If the pressure was maintained, the material in the ZHE is separated into solid and liquid phases by pressure filtration. A small amount of the liquid extract should be examined for miscibility with the previously captured filtrate. If these fluids are miscible, the liquid extract and the filtrate may be stored in the same container (Tedlar bag or syringe) with minimal or no headspace. This mixture becomes the TCLP extract for volatile analysis. If the two fluids are not miscible, they are stored in separate containers with minimal or no headspace. The volatile analysis are performed separately and combined mathematically using the same equation as for the non-volatile analysis. All extracts and fluids are kept at $4^\circ\text{C} \pm 2^\circ\text{C}$ prior to analysis.

4.4 TCLP Method Quality Control

- ! TCLP extraction blank
- ! Method preparation blanks
- ! Calibration
- ! Matrix spikes

BIAS CORRECTION IS NO LONGER REQUIRED.

- ! Method of standard additions

TCLP Extraction Blanks

- ! A minimum of one TCLP extraction blank is generated for every 20 extractions processed in a given extraction vessel using the same fluid. Most labs have multiple extraction vessels. The common industry strategy is to generate one TCLP extraction blank for each group of samples processed simultaneously using the same batch of fluid.

Calibration

- ! Calibration should follow the respective method requirements. Typically a three to five point initial calibration followed by a single point continuing calibration is specified.

Method Preparation Blanks

- ! Preparation blanks performed for a specific analysis should follow the frequency and requirements of the method. Typical requirements are one per preparative batch from similar matrix for every 20 samples.

Matrix Spikes

- ! Matrix spikes are used to monitor the performance of the analytical methods on the matrix and to assess the presence of interferences.
- ! A matrix spike shall be performed for each waste type (waste water, soil, etc.) unless the result exceeds the regulatory level and the data are being used solely to indicate that the regulatory level is exceeded.
- ! A minimum of one sample from each "analytical batch" must be spiked. For spike samples, a double or triple volume of TCLP leachate will be required. The term analytical batch is not defined in the regulation. Most methods, such as CLP and SW846, indicate that a batch is no more than 20 samples of the same matrix

processed through preparation and analysis simultaneously. Based on this criteria, the minimal matrix spike frequency of analysis is one per 20 samples. However, many process batches may include from one to 19 samples and the frequency may increase with fewer samples processed. Some EPA Regions define each type of waste as a matrix, and require matrix spikes for each matrix.

- ! Matrix spikes (MS) are to be added after leaching and filtration but prior to preservation. Spikes are NOT to be added prior to the TCLP leaching.
- ! The spike should be added to the same nominal volume of TCLP extract as the unspiked sample.
- ! The spike concentration "should" be added at the regulatory level. If the expected concentration in the sample is as low as half the regulatory level, the spike concentration can be decreased to half the regulatory level. In all cases, the spike must be greater than 5 times the method detection limits.

- ! Matrix Spike Recoveries are calculated by:

$$\% \text{Recovery} = 100 \left(\frac{\text{Measured value for the spiked sample} - \text{measured value of the unspiked sample}}{\text{known value of the spike}} \right)$$

- ! When the matrix spike recovery falls below the expected analytical performance, alternate methods of analysis may be required to measure analyte concentration in the TCLP extract. The matrix spike recovery limits from the Contract Laboratory Protocol methods are used when the method is used.

If the matrix spike recoveries exceed limits, other analytical methods such as isotopic dilution may be used to deal with the matrix effects. Typically, the holding times will be exceeded or near the limits when this occurs. If possible, resampling of the waste may be required to assure that the appropriate method is used and holding times are met.

- ! *Bias correction is no longer required.*

Surrogate Spikes

Surrogates are compounds which are not expected to be in the samples but are chemically similar to those being determined. The concentrations and specific compounds are listed in the appropriate methods. The recovery of the compounds are monitored with specific criteria either being found in the method or determined by statistical quality control in the laboratory.

Method of Standard Addition

Four equal volume **pre-digestion** aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third

aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked standard should be the same.

In order to determine the concentration of analyte in the sample, the analytical value of each solution is determined and a plot or linear regression performed. On the vertical axis the analytical value is plotted versus the concentrations of the standards on the horizontal axis. An example plot is shown in Figure 4-5. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown.

Fig 4-5

When must Standard Addition be used?

The method of standard additions is used for metallic contaminant determinations if both of the following criteria are met:

1. The matrix spike recovery from the TCLP extract is less than 50% and the unspiked sample concentration is less than the regulatory level.
2. The contaminant measured in the sample is within 20% of the regulatory level.

For the method of standard additions to be correctly applied, the following limitations must be taken into consideration:

- ! The plot of sample and standards must be linear over the concentration range of concern. For best results, the slope of the line should be similar to that of a plot of the aqueous standard.
- ! The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

Holding Times

As previously discussed in Section 3, the holding times must be met. Sample data which exceed holding times are not acceptable for verifying that a waste does not exceed regulatory levels. However, if TCLP extract concentrations exceed regulatory action levels, and holding times are exceeded, the data are considered minimum values, and the data are considered valid.

Chapter 5

DATA VALIDATION AND DATA DELIVERABLES

5.0 DATA VALIDATION AND DELIVERABLES

This chapter addresses the following questions:

- ! What is data validation?
- ! When must TCLP data be validated in EPA Region 2?
- ! Which analytical deliverables are needed to validate TCLP data when utilizing the USEPA Region 2 Organic, Inorganic, and TCLP Data Validation Protocols?
- ! Which analytical deliverables are recommended for TCLP data which will not be validated?
- ! How should these deliverables be utilized to assess data quality and usability?

5.1 Data Validation

What is Data Validation?

"Data validation is a systematic process for reviewing a body of data against a set of criteria to provide assurance that the data are adequate for their intended use. Data validation consists of data editing, screening, checking, auditing, verifying, certifying and reviewing." (EPA Region 2 CERCLA QA Manual)

The most important criteria which the data reviewer evaluates are:

1. Holding times
2. Instrument tuning
3. Calibration and retention time windows
4. Blank contaminants
5. Surrogates (a measure of extraction efficiency)
6. Chromatographic performance (baseline, interference, retention time shift and peak resolution)
7. Emission interferences or spectral interference from other elements when reviewing metals data
8. Calculations
9. Transcription of numerical values to the required forms in the data package
10. Matrix effect errors; interference from the sample itself
11. Degradation of compounds during analysis

There is a substantial amount of uncertainty in all chemical data. In addition to lab error, there are field sampling errors, such as improper decontamination of field equipment, air bubbles in VOA vials, loss of samples, and failure to ship samples in a timely manner after collection. Different analytes have varying degrees of uncertainty.

TCLP data are expected to have significantly more inherent error than routine chemical analysis because additional procedures are performed by the laboratory analyst.

What is data qualification?

Qualifying data is a method of notifying the data user that some data have additional uncertainty. The Region 2 TCLP data validation protocol qualifies analytical data with the following flags:

- ! R Rejected (unusable)
- ! J Estimated
- ! UJ Estimated detection limit
- ! N Presumptively present (cannot positively identify an analyte)
- ! JN Presumptively present at an estimated concentration

The above qualification "flags" provide QC information to the data user. The Region 2 TCLP data validation protocol qualifies analytical data as unusable, estimated, presumptively present, or presumptively present at an estimated concentration.

Unusable data are rejected and qualified with an "R". When data are rejected, it doesn't mean that the analyte wasn't there - it means that either the test was not correctly performed or that the test was not appropriate for the matrix. Examples of reasons for rejecting data include: poor calibration, low surrogate recoveries, and air bubbles in volatile sample vials. If the data are needed, resampling and reanalysis must be performed. For example, the holding time for TCLP VOAs is 14 days from sampling until TCLP leaching, and then 14 days until analysis. If a sample is held for 30 days from collection until leaching, all non-detects and positive results below regulatory action levels will be rejected because analytes could have been present above regulatory action levels. Results above the regulatory action levels would be accepted. However, the site owner may still want resampling and reanalysis to assure that a false positive did not occur.

When data are qualified as estimated with a "J", it means that the data should be used with caution. The data are significantly imprecise, and the reported value given is little more than an estimate. Estimated means that the compound is present, but the exact concentration is uncertain.

When data are qualified with a "UJ", it means that the detection levels are uncertain. For example, this qualifier would be used when surrogate recoveries in organics are greater than 10% but not within the method criteria. The "UJ" notifies the data user that the detection limits are estimated.

When the analyte identity is uncertain, the qualifier "N" is used to indicate that it is presumptively present. This is used in data validation when a mass spectrum differs slightly from the required spectral criteria. Data validators use the qualifier "JN", presumptively present at an estimated concentration, much more often than the qualifier "N". The "JN" flag denotes both qualitative and quantitative uncertainty. This is typically used when tentatively identified compounds (TICs) from semivolatile gas chromatography/mass spectrometry analysis are presented. The concentration and identities of the TICs are uncertain and are flagged with "JN".

When Must TCLP Data Be Validated?

EPA Region 2 requires TCLP data for RCRA RFIs and many types of CERCLA sampling events to be validated. The RCRA program does not explicitly require the validation of routine TCLP analysis of waste materials to determine compliance with TC or LDR regulations.

Data validation reduces false negatives, false positives, and misquantitation in reported data. Misquantitation includes both laboratory arithmetic errors, and data qualified as estimated or presumptively present because of analytical problems. The costs for TCLP validation are quite variable, and depend specifically on which tasks the data user instructs the data validator to perform, and the quality of the laboratory analyzing the environmental samples. The cost of validating a single sample containing the 39 TC analytes is about \$300-\$500 per sample analyzed by a competent laboratory. In addition to the data validation cost, the laboratory will charge an additional fee, estimated at \$200-\$400 per sample, for generating analytical deliverables. The more a data user knows about a specific waste, the less useful data validation becomes. For example, if the data user knows which raw materials, final products, and by-products are in a waste, and has historical data that demonstrates that the TC analytes in the TCLP extract are far below regulatory action levels, TCLP validation would not be cost effective. Alternatively, when the data user has very limited knowledge of a waste's characteristics, decisions based on that data can result in significant disposal cost for management. Therefore, many businesses believe that it is prudent and cost effective to validate this type of TCLP data.

Some regulatory agencies, especially in the CERCLA program, do not allow laboratories to validate their own data. All laboratories review their own data for contractual compliance and analytical problems. Unfortunately, this assessment of contractual compliance may also be called data validation. Many laboratories now call their contractual compliance review "data review" to differentiate this review from data validation.

Contractual compliance is NOT the same as data validation. A lab can contractually fail and still produce technically valid data. An example of this occurrence is when contractual requirements for metals data indicated that results would be delivered to the client 40 days from receipt of the sample. If the laboratory did not deliver for 60 days, the laboratory failed the contract criteria, but the technical criteria were still met. Alternatively, a laboratory can contractually meet criteria but produce data which is not useable.

In order to validate TCLP data, the following must be ascertained:

- ! Are any specific data validation protocols required by a regulatory agency?
- ! What are the regulatory action levels?

The TC regulatory action levels are listed in Table 1. The Land Disposal Restrictions regulatory action levels are listed in Appendix II.

The EPA Region 2 TCLP, Inorganic and Organic Validation protocols are included in Appendix IV. If your region or state does not have a TCLP validation procedure, the Region 2 data validation protocol may be used. If the applicable sampling and analysis plan requires regulatory approval, the data user, lab and regulator must agree on validation criteria prior to sample collection.

Phenols

When validating TCLP phenols, the TCLP extraction fluid may cause a matrix effect. This matrix effect may lower surrogate and matrix spike recoveries for phenols. As long as the matrix spike and surrogate recoveries are above 10%, the data should not be rejected. If a matrix effect precludes acceptable pyridene or phenols surrogate and matrix spike recoveries, a facility should request a meeting with the appropriate regulatory agency to discuss alternate methods for determining whether a solid waste exhibits TC.

After determining whether the project will require validation, the appropriate deliverables must be specified to allow the validation to occur. For example, if the validation requires calibration verification, raw instrument calibration data must be present for the validation to be performed.

5.2 Data Deliverables

General TCLP Data Deliverables

In order to validate and assess TCLP data, appropriate deliverables must be specified. Deliverables will differ depending on whether validation is required. These analytical deliverables must be specified before samples are collected. The following topics are discussed:

- ! Deliverables when no validation is required
- ! Additional deliverables which may assist in review
- ! USEPA Region 2 analytical deliverables
- ! Specifying data deliverables

Deliverables When No Validation is Required

When TCLP data are not validated, we recommend that the laboratory furnish the data user the following deliverables:

1. Sample description and sample identification numbers.
2. Analytes, concentrations, and units.
3. Level of contaminant(s) in method and TCLP blanks.
4. Matrix spike, QC check sample when applicable, and surrogate recoveries.
5. A description of matrix problems and analytical problems observed during analysis, and an assessment of how those problems will affect data usability.
6. A certification that samples were analyzed within method holding times (from the date of sample collection). This certification must include the sampling date, TCLP extraction dates, preparatory extraction dates, and analysis dates.

The laboratory staff are not always familiar with data validation protocols or with data usability on a project specific level. Therefore, in addition to information about the QC supplied by the laboratory, it may be beneficial to work with a specialist in this area. Some firms specialize in validating and assessing data quality.

Additional Deliverables Which May Assist in Review

While the data is the key factor, some information is not always captured in the analytical result. For example, if a procedure is modified due to a matrix problem, the procedure must be documented and the validator provided this information. The following information may facilitate validation.

- ! Chain of Custody records
- ! Analytical procedures used by the laboratory
- ! An example of a data calculation

The data user must specify the information (analytical deliverables) desired from the laboratory. If this is not done, only the final result, or the final result plus a QC summary, will be provided.

Region 2 Analytical Deliverables

The following TCLP analytical deliverables are required by the Region 2 TCLP data validation protocol:

1. The TCLP and preparative extraction dates and analysis dates.
2. Selection of extraction fluid data.
3. A physical description of the samples.
4. The sample weights and the extraction fluids weights.
5. The final volume of TCLP extract and the volume of extract analyzed.
6. The data used to compute percent dry solids and the weight of the liquid phase (if applicable).
7. Extraction logs for each sample, indicating the volume and pH of acid added. Were inorganic sample extracts properly preserved?
8. A description of the materials of construction for extraction vessels, filtration devices, and ZHE extraction devices (i.e. glass, Teflon, PVC, stainless steel, etc.).
9. The data used to compute TCLP extract concentrations for multi-phasic samples.
10. When VOA samples consist of oily waste that cannot be filtered, describe how the TCLP aqueous extract is separate from the oily waste.
11. A copy of the sampling log or trip report.*
12. Any evidence of leakage in the ZHE device.

*Item 11, which requires the presentation of the sampling log, may not be available from the laboratory. The sampling team may supply this information.

In order to facilitate analysis and validation, Associated Design and Manufacturing Corporation and Dr. Larry Jackson have developed work sheets (Appendix III) which may be used by the analytical laboratory to generate the above listed analytical deliverables. Additional descriptions of requirements and deliverables for modification of CLP analysis of leachate is presented in Appendix VIII.

Specifying Data Deliverables

EPA Region 2 *requires* TCLP data to be validated for RCRA RFIs and many types of CERCLA sampling events.

Specific regulations, as noted in Appendix IX, require SW-846. Many state environmental agencies require the use of SW-846 methods for hazardous waste determinations. SW-846 methods cannot be validated by CLP validation criteria because SW-846 methods do not specify analytical deliverables, and have different QC criteria than CLP methods. Therefore, validation protocols must be prepared for non-CLP methods such as those in SW-846.

For non-CLP methods, data validation criteria must include:

- ! Holding times for sample preparation and analysis
- ! Preparation logs
- ! Calibration
- ! Method and instrument blank data review
- ! Calculations
- ! Matrix spike data
- ! Duplicate results

For organic analysis, the following additional items must be included:

- ! Instrument tuning if GC/MS is used
- ! Surrogate recoveries
- ! Chromatographic performance (baseline, interference, shift and peak resolution)
- ! Mass spectral interpretation or compound identification

For metals analysis, the following additional items must be included:

- ! Whether method of standard addition or serial dilution were needed and performed correctly. The November 24, 1992 modification to the TCLP procedure mandates the use of method of standard additions under certain circumstances.
- ! Post digestion spike recoveries versus pre-digestion spike recoveries.
- ! The frequency of analysis of QC samples must be validated.

Chapter 6

ANALYZING AND ASSESSING MULTI-PHASIC AND OILY WASTES

Definition of Oily Waste

Problems/Issues

Suggestions

Most Commonly Asked TCLP Question

Analytical Options

6.0 ANALYZING AND ASSESSING MULTI-PHASIC AND OILY WASTES

Analyzing and Assessing Multi-Phasic and Oily Wastes

This chapter provides strategies which may be beneficial in characterizing oily wastes. There is no single correct method to analyze these wastes.

- ! Definition of oily waste
- ! Problems/Issues
- ! Suggestions
- ! Most commonly asked TCLP question
- ! Analytical options

This chapter outlines the current issues and difficulties in performing TCLP on multiple phase and oily waste. This chapter is not meant to provide unequivocal answers, but to provide suggestions and strategies which may be successful. There is no single correct method in dealing with these materials. The initial discussion in this chapter provides references and information indicating that EPA understands the difficulties in applying the TCLP to multi-phasic and oily wastes. Subsequent discussions summarize possible strategies which may be used in leaching and analysis.

6.1 Definition of Oily Waste

Appendix VI contains several papers presented at the EPA's 1992 Waste Testing & Quality Assurance Symposium Work Shop on oily waste. The following is Clifford Narquis's of BP Research, definition of oily waste (see Appendix VII):

Although it is nearly impossible to precisely define the term "oily waste", the following analysis can provide a basis for further discussion:

a) An oil is generally an immiscible or relatively insoluble liquid, varying in composition but consisting of organic constituents. Petroleum oil principally consist of hydrocarbons; vegetable and animal oils are glycerides, and fatty acids; and essential oils are terpenes, alkaloids, etc.

b) An oily waste is an industrial process waste or residual bearing oil in a visual and/or measurable proportions.

c) Oil in oily wastes can occur in any matrix, including: sorbed to dry solids; in sludges or slurries; multi-phasic liquids or sludges/slurries with multi-phasic liquids, if water is present. Proper treatment and disposal of all such matrices is a concern of the petroleum industry.

d) Oily wastes possess a wide variety of compositions and physical and toxicological properties.

6.2 Problems/Issues

Problems with the TC Model

- ! The model does not differentiate between oily and aqueous liquids.
- ! The model assumes a person drinks 2 liters a day of well water for 70 years. This assumption is not applicable for oily wastes.
- ! The disposal scenario depicted by EPA is not an accurate description of today's practices. For example, liquids are no longer accepted in municipal landfills.
- ! The model does not correct for absorption of oily waste on soils. Oil may also adhere to other landfill matrices instead of mixing with the aqueous phases.

The difficulty in analyzing oily wastes by TCLP may be categorized as modeling, analytical and regulatory problems.

The Leachability Subcommittee of the EPA Science Advisory Board's Environmental Engineering Committee has published its recommendations. A copy of this report is in Appendix VII of this document. This document outlines the properties of an optimum leach test.

Issues with Oily and Multi-phasic Waste and TCLP

- ! It is difficult to separate the phases.
- ! Volatiles may evaporate during handling.
- ! The tumbling action of the two liter extraction vessel can form emulsions which are difficult to separate.
- ! The oily material may obstruct the filter. When this happens with the ZHE, the test must be repeated.
- ! Oily materials often yield oil and aqueous leachate which must be analyzed separately. This increases costs and time of analysis.
- ! The method requires determination of dry weight percent solids. When the "solid" is actually oil or organic, drying can be hazardous and inappropriate. It may be impossible to achieve a constant weight when performing a percent solids determination.

- ! When multiple phases and multiple bottles are used in sampling, each container will show different amounts of each phase.
- ! It may be impossible to separate solids from oil. If volatiles are analyzed, additional sample manipulation to remove solids will result in loss of volatiles.

6.3 Suggestions

! Suggestions for performing TCLP extractions on oily wastes include the following:

- Planning
- Regulatory approval
- Separate phases for analysis
- Documentation of phase type and volumes

As previously indicated, these are suggestions. There are no consistently and absolutely appropriate methods when performing TCLP extractions on oily wastes.

! Planning is more critical when oily or multi-phasic samples are collected and analyzed. Discuss the sample matrix with the laboratory before collecting samples.

! Once an approach is formulated, regulatory approval may be needed. This approval is of greater importance if deviations from the TCLP extraction method are required due to the matrix.

! If two liquid phases are present, each phase should be separated and analyzed individually.

! The SW-846 Methods specify several procedures for analyzing oily waste. BNA methods include 3580B for preparation followed by 8270B. The pesticides method includes 3580B using hexane as the extraction solvent followed by 8080B. The VOAs are analyzed by 8240B. Metals can be prepared by method 3040B and analyzed by appropriate analytical methods.

! The number, appearance, and volume of each phase should be documented before collection of the sample. The phase volume can be estimated by measuring the height of the phase in the container and the diameter of the container. This information can be used to estimate the amounts of material available for testing.

! Phase volume should be estimated after sample collection and prior to analysis.

! In multi-phasic liquid samples, the relative density of each phase should be documented.

- ! When multiple containers of multi-phasic waste are received, each container will have different amounts of each phase. If multiple sample containers are collected and each container is multi-phasic, the number, appearance, volume and relative density should be documented for each container.
- ! If regional and state regulators will allow, one container can be mixed and analyzed. By knowing the volumes in the other sample containers, the total composition can be mathematically calculated.
- ! If one phase is organic and contains < 0.5% solids, this may be directly characterized by the appropriate analytical method after filtration without TCLP extraction.
- ! Subsampling increases the possibility of sampling error.
- ! The percent solids should be determined in multi-phasic samples before filling the ZHE. This prevents overfilling the ZHE.
- ! The TCLP method requires drying the solids at $100^{\circ}\text{C} \pm 20^{\circ}\text{C}$ to determine percent dry solids. This may not be achievable for organic multi-phasic material because of safety considerations. If this cannot be done, the reason should be documented. The percent wet solids is used to calculate the weight of extraction fluid. If this occurs, the lab should discuss this with the client prior to using the percent wet solids as the solids content. This will greatly effect the final analyte concentrations.
- ! Particle size reduction is difficult on oily material because the solids congeal. This is especially true if the material cannot be dried.
- ! Extreme caution should be taken when adding acid to organic waste. Heating the organic waste in the presence of acid to 50°C should be done with great caution. This may be required in order to determine which extraction fluid is used.

6.4 Most Commonly Asked TCLP Question

I have an oily waste, which flows through a filter. My detection limits are higher than the regulatory action levels. What should I do?

You have four options:

1. Recycle or burn.
2. Classify by prior knowledge as non-hazardous.
3. Treat the waste as hazardous.
4. If the oil passes through the filter, analyze the TCLP leachate.

1. If the oily waste can be classified as used oil, it can be burned or recycled and a TCLP analysis is not needed (40 CFR 266.40; 261.6(a)).
2. The waste can be treated as hazardous if no information is available to allow classification by prior knowledge.
3. By knowledge of the generation of the oily waste, the generator may be able to certify that the waste could not contain any of the TC analytes at concentrations above the regulatory action levels. (40 CFR 262.11c(2)). The waste may be a regulated hazardous waste under other EPA waste code classifications.
4. The liquid which passes through the filter can be analyzed to determine whether it contains TC analytes. If the SW 846 methods are not appropriate for TC analytes, any method which is sensitive enough to meet regulatory limits and has documented QC may be used.

The following pages include correspondence on oily waste explaining EPA's strategy for classifying oily wastes as hazardous or non-hazardous.

6.5 Analytical Options

The methods discussed from SW 846 may not provide adequate identification and quantification of the waste. Inadequate method performance may be caused by matrix interferences. The following methods may assist in dealing with organic matrix problems. This list is not exhaustive. Method development may be required to accommodate specific interferences. If development is required, method validation should be performed and approvals may be required when SW 846 is required by the regulations.

- ! Isotopic dilution
- ! High resolution GC/MS

Isotopic Dilution

One option outlined by EPA in the memoranda is the use of isotopic dilution methods. The isotopic dilution methods use stable isotopically-labeled analogs of the compounds of interest. These labeled compounds are added prior to sample preparation and analysis. In the case of volatiles and semivolatile analyses by GC/MS, they are added prior to purging or extraction. Two methods are currently listed in 40 CFR Part 136 Appendix A which use the isotopic dilution technique. One is a purge and trap capillary GC/MS, method 1624, and the other is semivolatile extraction followed by capillary GC/MS, method 1625.

In both methods, the calibration is established by relative responses based on a ratio of the isotopically-labeled compound versus the unlabeled compound over five concentration ranges. The relative response of the labeled versus unlabeled compound in the sample is compared to the calibration curve or average response factor to quantitate the analyte in the sample.

An example of a labeled compound is toluene-d8, which is deuterated toluene (all hydrogens are replaced by deuterium). Carbon-13 labeled compounds may also be used.

The advantages of isotopic labeling are greater accuracy in quantitation and the ability to quantitate despite interferences. The disadvantages are the expense and difficulty in obtaining labeled analogs of the compounds of interest, and the time needed to develop the procedure. Laboratories which have experienced GC/MS staff who have done dioxin analyses or who have many years of GC/MS experience should be capable of providing these analyses.

High Resolution GC/MS

High resolution GC/MS could also be used to quantitate the compounds. There are no published methods for waste analysis by high resolution GC/MS. However, this technique should provide greater sensitivity, lower detection limits and the ability to deal with interferences. The disadvantages are the same as isotope detection. Regulatory approval should be obtained before utilizing expensive isotope dilution or high resolution GC/MS analyses.

Appendix I
TCLP Methods From
40 CFR 261 Appendix II

SW 846 Method 1311
(Method Without Typographical Errors)

July 1992

Appendix II
40 CFR 268 Subpart D Land Ban Treatment Standards

Appendix III
Associated Design and
Larry Jackson's
TCLP Bench Sheets
and Calculations

Appendix IV
USEPA Region 2
Organic, Inorganic and TCLP Data Validation
Methods

Appendix V
References for Multi-phasic and Oily Waste

Appendix VI
Office of Solid Waste Methods Section
Memoranda #35, #36

Appendix VII
Recommendations and Rationale for Analysis of
Contaminant Release by the Environmental Engineering
Committee
Science Advisory Board
October 1991

Appendix VIII
USEPA Region 2
Special Analytical Services Request

Appendix IX
Office of Solid Waste Methods Section
Required Uses of SW 846

Appendix X
Stabilization/Solidification: Is It Always Appropriate?
and
Stabilization/Solidification of Wastes Containing Volatile
Organic Compounds in Commercial Cementitious
Waste Forms

Printed with permission from *STP 1123 Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes, 2nd Volume*, copyright American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103

Appendix XI
Army Waste Classification Guidance for Building
Demolition Debris Containing Lead Based Paint

Appendix XII
1992 Workshop on Characterizing Heterogeneous
Materials

Appendix XIII
Improper Hazardous Waste Characterizations:
Financial and Compliance Implications

Appendix XIV
Region 2 State TCLP Guidances

Appendix XV
Risk Assessment for Disposal of Solidified/Stabilized
Waste and Contaminated Soil

Appendix XVI
Barbara Metzger's 1992 Speech on
Environmental Data Use -
Meeting the Customer's Need

Guidelines for the Conduct of the Toxicity Characteristic Leaching Procedure

These guidelines have been prepared by Associated Design and Manufacturing Company for the informational use of environmental professionals engaged in the conduct of the Toxicity Characteristic Leaching Procedure (TCLP). They are intended to focus attention on important data collection activities associated with the TCLP. They are for guidance only and are not intended to replace sound professional judgment or regulatory requirements.

The guidelines are presented in the form of laboratory worksheets that can be used to document some of the most important points of the procedure. Each worksheet is supported by a discussion and recommendations of the data that should be recorded to document of the TCLP. The discussion is keyed to the worksheet for easy reference.

The paragraph references (¶ x.x.x.x) given in this document refer to the version of the TCLP which appeared in the July 29, 1990, Federal Register, p. 26986.

TCLP Worksheet No. 1

Sample Description

<i>Laboratory Sample No.</i>					
<i>Field Sample No.</i>					
A. Sample Description					
<i>Number of phases</i>					
<i>1. solid</i>					
<i>2. liquid</i>					
<i>a. lighter than water</i>					
<i>b. water</i>					
<i>c. heavier than water</i>					
B. Percent Solid Phase					
<i>1. weight of filter</i>					
<i>2. weight of subsample</i>					
<i>3. weight of filtrate</i>					
<i>4. weight percent solids (wet)¹</i>					
<i>5. weight percent solids (dry)²</i>					
<i>6. volume of initial aqueous filtrate</i>					
<i>7. volume of initial organic filtrate</i>					

1. The weight percent wet solids is given by the equation:

$$\frac{\text{weight of subsample} - \text{weight of filtrate}}{\text{weight of subsample}} \times 100$$

2. The weight percent dry solids is given by the equation:

$$\frac{\text{weight of dry waste} + \text{filter} - \text{weight of filter}}{\text{weight of subsample}} \times 100$$

Discussion and Recommendations

TCLP Worksheet No. 1

Sample Description

This worksheet documents important information regarding the general description of the sample and the number of phases observed in the sample as received from the field. This information is used to determine the amount of leaching fluid used to leach solid materials and the weighting factors used when calculating final analyte concentrations from multi-phasic samples.

A. Sample Description

Number of phases -- The number of phases present in the sample determine how the TCLP is conducted. Solid materials having no visible liquid phase are extracted as received from the field and the analyte concentration found in the leachate is the reported value. Liquid materials having no measurable solids content (< 0.5 wt. % dry solids) are defined as the TCLP extract (§ 2.1) and are filtered and analyzed directly.

Multi-phase samples must be separated (§ 7.1.1.2) and each phase treated individually. Aqueous phases may be combined with the leachate from solid phase materials before analysis if the two aqueous materials are compatible (§ 7.2.13.2). If the two aqueous materials are not compatible, then each liquid must be analyzed by the appropriate methods and the results combined numerically to determine the final reported value (§ 7.2.14).

- A.1. Solid -- record the visible presence of a solid material heavier than water. If the sample contains more than one solid phase (example, wood chips and sediment mixed with water) record the information in the laboratory notebook.
 - A.2. Liquid -- record the number of liquid phases observed in the sample according to their apparent density. It may be impossible to distinguish apparent density if only one liquid phase is observed and there is no indication on the accompanying chain-of-custody form (COC). If this is the case, record it as aqueous material and let the subsequent analytical record show if the liquid is organic after the container is opened at the appropriate time.
- B. Percent of Solid / Liquid Phase(s) -- paragraphs 7.1.1 through 7.1.2.3 of the method describe the procedure to follow for the determination of the percent solids of the samples. It is also convenient to measure the percent of any non-miscible liquid phases at this point because the information is required in § 7.2.14.

Laboratory subsampling of the material delivered to the laboratory must be thoroughly documented. The total contents of the sample container should be considered as "the sample" and care must be taken to ensure the representativeness of any subsample. Heterogeneous and multi-phasic materials can be difficult to subsample properly and frequently require significant judgment on the part of the analyst.

Discussion -- At this point , it is important to review the COC and confirm the number of containers of each sample provided to the laboratory and the types of analyses requested. If the analysis of volatile components is requested, the determination of percent solids in multi-phasic samples must be completed before proceeding to the leaching of the solid material in the zero headspace extractor (ZHE) to prevent overfilling the ZHE. It is best if a separate sample has been provided for this purpose (§ 6.2). The laboratory should establish an SOP to address how to proceed if only one container is available.

It is common that when more than one container of multi-phasic materials is received from the field, each container will show different amounts of each phase. This provides a challenge to the laboratory which must report the data based on percent phase composition of the sample. A practical solution is to record the depth (measured from outside the container) of the layers in the each container after the contents have been allowed to settle and determine the combined volume of each phase in all the containers. Then measure the phase composition on a single container (after thorough mixing to obtain a representative subsample). Combine these two sets of values to determine the correct volume/mass adjustments on the TCLP results.

The laboratory should also establish an SOP on how to proceed when only a limited amount of sample is available and the analyses requested exceed the amount of sample provided.

- B.1. Weight of filter -- This value must be measured before loading the filter into the filter holder because the mass of the filter is used in performing the calculation for percent dry solids.
- B.2. Weight of sample aliquote -- a representative 100 gram sample (§ 7.1.1.5) is withdrawn from the sample container for filtration. If liquid material is decanted from the sample before subsampling, its volume/weight must be recorded and factored into the calculations of percent solids.

Discussion -- Many multi-phasic samples are difficult to filter. This is especially true of oily wastes and sludges. The method directs that any material retained by the filter after following the instructions is defined as solid waste (§ 7.1.18). Experience has shown that the reproducibility of the percent solids determination with these types of samples is highly variable. Subsequent steps in the extraction procedure (§ 7.2.5 and 7.3.4.2) use the % solids value to estimate the mass of the original waste used to obtain an appropriate sized subsample of the solid for extraction.

The method directs that the material retained by the filter be dried at 100 ± 20 °C (§ 7.1.2.2) to determine the percent dry solids. This may not be achievable for organic multi-phasic materials because of safety considerations and the fact that many organic liquids boil considerably higher than water and it may be impossible to achieve a constant weight for successive weighings ($\pm 1\%$).

The laboratory should establish a standard operating procedure (SOP) addressing these types of samples. Basically, the laboratory has three choices of how to proceed. It may

- ! attempt to dry all samples as directed by the method;

- ! *dry samples containing only water as the liquid phase; and/or*
- ! *define the retained material as a dry solid for the purpose of further testing.*

This decision may have significant impact on the amount of material selected for leach testing and on the reported analyte values. The laboratory should consider discussing this issue with their clients and any regulatory groups to whom the data will be submitted.

- B. 4 Weight percent solids(wet) equals:

$$\frac{\text{weight of subsample} - \text{weight of filtrate}}{\text{weight of subsample}} \times 100$$

The procedure defines the material retained by the filter as the solid phase of the waste (§ 7.1.1.8). This value is used to calculate the volume of the original multi-phasic material which must be filtered to yield the proper amount of solid waste for the extraction procedure.

- B.5 Weight percent solids (dry) -- the total mass of the filtered solids and the filter are removed from the filtration apparatus and dried at 100 ± 20 °C until a constant weight is achieved (§ 7.1.2.2). This value is used to calculate the dry solids content of the waste. *Use caution when drying samples that may contain flammable material.* It is important to factor in the tare weight of the filter for samples that have low solids values.

The weight percent solids (dry) is calculated by the equation:

$$\frac{(\text{weight of dry waste} + \text{filter}) - \text{weight of filter}}{\text{weight of subsample}} \times 100$$

If the weight percent dry solids is > 0.5%, the total waste is defined as a solid waste and steps must be taken to collect the appropriate weight of solid material for extraction (§ 7.1.2.4).

- B.6 Volume of initial aqueous filtrate -- this value is used in § 7.2.14 and 7.3.14 in the final calculation of analyte concentration.
- B.7 Volume of initial organic filtrate -- this value is used in § 7.2.14 and 7.3.14 in the final calculation of analyte concentration.

TCLP Worksheet No. 2

Selection of Extraction Fluid

<i>Laboratory Sample No.</i>					
<i>Field Sample No.</i>					
C. Extraction Fluid Determination -- does not apply to determination of volatile organic components					
1. particle size reduction? yes/no					
2. sample weight, ✓ if 5.0 ± 0.1 grams					
3. volume of water, ✓ if 96.5 ± 1.0 mL added					
4. initial pH (after 5 min. mixing time)					
5. if pH > 5.0, ✓ if 3.5 mL 1N HCl added					
6. ✓ if heated and held at 50 °C for ten minutes					
7. secondary pH (at room temp.)					
D. Selection of Extraction Fluid					
1. ✓ if pH from C.4 or C.7 is < 5.0, use extraction fluid No. 1.					
2. ✓ if pH from C.7 is > 5.0, use extraction fluid No. 2					

Discussion and Recommendations

TCLP Worksheet No. 2

Selection of Extraction Fluid for Metals, Semi-volatile Organic Components, and Pesticides/Herbicides

This worksheet documents the important steps which should be followed to correctly determine the appropriate extraction fluid for leaching solid wastes for the analysis of metals, semi-volatile organic components, and pesticides/herbicides. This procedure does not apply to the determination of volatiles using the zero headspace extractor (ZHE).

Discussion -- the Environmental Protection Agency's "worst case" waste disposal model assumes mismanaged wastes will be co-disposed with municipal solid waste in a 5:95 ratio. These wastes will be exposed to leaching by the acidic fluids formed in municipal landfills. The EPA's model further assumes the acid/base characteristics of the waste will be dominated by the landfill fluids. The TCLP laboratory procedure directs that alkaline wastes be extracted with a stronger acidic leach fluid than acid or neutral wastes so that the alkaline nature of the waste will not control the leaching chemistry of the TCLP test. This is in keeping with the waste disposal model's assumption that the acid fluids in the landfill will dominate leaching chemistry over time.

The procedure described in ¶ 7.1.4 of the method addresses the determination of the appropriate extraction fluid. It is a short term test whose results can have a significant impact on the final analytical results if the wrong extraction fluid is selected. This is especially true for metals determinations because of their sensitivity to the pH of the leach medium. The following discussion examines each step of the procedure and points out some sensitive technical points and how they can affect the results.

¶ 7.1.4.1 Particle size of test material -- The requirement to use 1mm particle size material in the test recognizes the fact that in a short term reaction between a liquid and a solid, high surface area is the most important characteristic of the solid. The rate of the reaction is controlled by the rate of diffusion of the liquid into the pores of the solid so a high surface area is necessary if the results of a short term test are to be reliable. Therefore, failure to take a representative subsample of the solid material and perform the necessary particle size reduction can result in significant bias. This is especially true if the waste contains a wide range of particle sizes and only the fines are selected for testing.

¶ 7.1.4.3 Heating of the reaction mixture -- The method specifies that the waste/acid slurry is to be held at 50°C for ten (10) minutes. Care should be taken to heat the sample to 50 °C as rapidly as possible without overheating. When the sample has completed the ten minute period at temperature, it should be allowed to cool and the pH determined as soon as possible. The longer the reaction between the acid solution and the solid waste is allowed to continue, the more likely that a falsely high pH reading will result. This will result in improper selection of the more acidic extraction fluid. Failure to reach and hold the required temperature can result in an artificially low pH reading for the test solution, leading the incorrect selection of the less acidic extraction fluid.

C. Extraction Fluid Determination (§ 7.1.4)

C.1. Indicate if particle size reduction is required for the sample.

Discussion -- the laboratory should consider establishing an SOP to address the particle size reduction requirements for the TCLP procedure. Most solid samples will not be received from the field with a particle size of 1mm as required for this step of the procedure (§ 7.1.4.1). Many multi-phasic samples will not be amenable to size reduction because of the nature of the sample. Samples containing pebbles, rocks, or debris may be difficult to size reduce if the larger particles are hard. Proper subsampling of the waste may be difficult if the waste is heterogeneous.

C.2. Sample weight -- check the box if 5.0g of sample is used in the test. Record the actual weight if a different sized sample is used.

C.3. Volume of water -- the volume of water used in the test is dependant on the weight of sample being tested. If the sample weight (above) is 5g and 96.5 mL of water is added, check the box. If the weight is not 5g, record the volume of water added. (# of grams X 19.3mL).

C.4. Initial pH -- record the pH of the slurry after a five minute mixing period. Use narrow range pH indicator paper if organic material is observed floating on the top of the slurry to avoid damage to pH electrodes.

C.5. Procedure for alkaline wastes -- if the initial pH of the slurry is > 5.0, add 3.5 mL of 1N HCl to determine if the alkalinity of the waste is sufficient to require the use of the stronger acid extraction fluid.

C.6. Neutralization reaction conditions -- the slurry should be heated to 50 °C and held for ten minutes. The laboratory should consider validating their procedure to confirm these conditions are met. A bench procedure specifying the hot plate setting (or other source of heat), the time required to reach the desired temperature, the ten minute time at temperature, and the time required to return to room temperature should be established. This will assure the maximum degree of reproducibility in the determination of the alkaline potential of the wastes tested.

C.7. Secondary pH -- record the pH of the slurry after it has completed the cooling cycle.

D. Selection of Extraction Fluid

D.1. If either the initial pH or the secondary pH is < 5.0, select Extraction Fluid #1 as the leaching medium.

D.2. If the secondary pH is >5.0, select Extraction Fluid #2 as the leaching medium.

TCLP Worksheet No. 3

Determination of Extraction Fluid Volume for Metals, Semi-Volatile Organic Components and Pesticides/Herbicides

Laboratory Sample No.					
Field Sample No.					
E. Determination of Sample Size for Leach Testing -- the method requires a minimum 100 gram sample size for extraction (§ 7.2.5).					
1. particle size reduction? yes/no					
2. amount of dry solids (100g min.)					
3. amount of multi-phasic sample ¹					
a. weight of material					
b. weight of filtrate					
c. weight of solid material					
F. Determination of Amount of Extraction Fluid -- the selection of the correct extraction fluid is found in Section D, Worksheet No. 2.					
1. for dry solids (20X sample wt.)					
2. for multi-phasic samples ²					
G. Record of Extraction Test -- the extraction period is specified as 18 ± 2 hours.					
1. extraction start time					
2. extraction stop time					
3. filtration complete time					
4. pH of filtrate					
5. volume of filtrate					

Amount of multi-phasic material = (10⁴)(wt. percent wet solids)

1. The theoretical amount of multi-phasic waste

necessary to yield a 100g sample is given by:

2. The amount of extraction fluid needed to extract the solid material from a filtered multi-phasic waste is given by:

Amount of extraction fluid = 20 (weight of material filtered - weight of filtrate)

Discussion and Recommendations

TCLP Worksheet No. 3

TCLP Extraction Procedure for

Metals, Semi-volatile Organic Components, and Pesticides/Herbicides

This worksheet documents the performance of the TCLP extraction procedure for metals, semi-volatile organic compounds and pesticides/herbicides.

E. Determination of Sample Size for Leaching -- the specified size of sample for the leaching test is a minimum of 100g (§ 7.2.5). The regulatory control limit for defining if the waste is hazardous is based on the levels of analytes reported in the leachate based on this size sample and a twenty to one (20:1) liquid to solid ratio. If the amount of waste subjected to extraction is not 100g, than the volume of extraction fluid must be adjusted to preserve the liquid to solid ratio.

E.1. Amount of dry solids -- record the weight of dry solids.

E.2. Amount of multi-phasic sample -- the amount of multi-phasic waste material necessary to produce a 100g sample after filtration can be estimated by the equation:

$$\text{Amount of multi-phasic material} = (10^4)(\text{wt. percent wet solids})$$

F. Determination of the Amount of Leaching Fluid

F.1. Dry solids -- for dry solids containing no filtrable fluids, the calculation of the correct volume of leaching fluid is straightforward. The amount is equal to twenty (20) times the mass of solid being leached. Note that the method specifies a 20:1 ratio based on the weight of extraction fluid required (§ 7.2.1.1). If the laboratory elects to use extraction fluid volume, rigorous adherence to the method requires a one time specific gravity correction to convert the required weight into the appropriate volume.

F.2. Multi-phasic samples -- the method says (§ 7.2.11) the percent wet solids can be used to calculate the weight of extraction fluid used to extract the solid waste resulting from the filtration of a known weight of multi-phasic waste. The equation for this calculation is:

$$\text{Amount of extraction fluid} = 0.2 (\text{percent wet solids}) (\text{weight of waste filtered})$$

This assumes there is no subsampling error between the original determination of the weight percent solid phase (wet) and the subsequent selection of a weight of the multi-phasic waste for filtration and extraction. This is frequently not so. The nature of many multi-phasic wastes and/or the necessity to use more than one sample container for the two determinations means that subsampling error can be significant. This error can be eliminated if the actual weight of filtered solids is determined at the time the material is separated for extraction. The equation for this calculation is:

Amount of extraction fluid = 20 (weight of material filtered – weight of filtrate)

The actual filtration procedure is detailed in ¶'s 7.2.2 through 7.2.8. Requirements for sample particle size reduction are given in ¶ 7.1.3 and 7.2.10. These should be followed as closely as the nature of the samples will allow and all departures from the instructions should be described in the laboratory notebook.

- G. Record of the TCLP Extraction Test -- the period of the extraction test is given as 18 ± 2 hours (¶ 7.2.12). Extraction should be started so the resulting slurry can be filtered as soon as possible after the 18 hours has past. The filtration effectively stops the extraction process. If the extraction fluid is left in contact with the waste for longer than the specified period (overnight or over the weekend), the extraction process continues and may lead to elevated levels of contaminants.
- G.1. Extraction start time -- record the time and date the extraction begins.
- G.2. Extraction stop time -- record the time and date the extraction is completed.
- G.3. Filtration completion time -- record the time and date the filtration is complete.
- G.4. pH of filtrate -- while not required by the method, this is a good indicator of test performance when performing duplicate laboratory analysis or analyzing field replicates. It can be a reliable measure of sample heterogeneity.
- G.5. Volume of filtrate -- record the total volume of filtrate collected from the sample. This value is required to make the appropriate volume corrections when reporting the results from multi-phasic wastes.

TCLP Worksheet No. 4

Zero Headspace Extraction (ZHE)

Laboratory Sample No.					
Field Sample No.					
H. Determination of Sample Size for Leach Testing -- maximum 25 grams					
1. amount of dry solids					
2. amount of multi-phasic sample ¹					
I. Determination of Amount of Extraction Fluid No. 1					
1. for dry solids (20X sample wt.)					
2. for multi-phasic samples ²					
a. weight of material					
b. weight of filtrate					
c. weight of solid material					
J. Record of ZHE Extraction Test -- the extraction period is as 18 ± 2 hours (§ 7.3.12.3).					
1. extraction start time					
2. starting pressure					
3. extraction stop time					
4. ✓ if positive pressure					
5. filtration completion time					
6. pH of filtrate					
7. volume of filtrate					

1. Determination of amount of multi-phasic sample for extraction:
 - a. if weight percent dry solids is < 5% (from Worksheet No. 1, B. 5), the waste is filtered and the filtrate is defined as the TCLP leachate (§ 7.3.4).
 - b. if weight percent dry solids is > 5% (from Worksheet No. 1, B. 5), the amount of multi-phasic material which should be filtered to yield a 25 gram sample is given by:

$$\text{Amount of multi-phasic material} = (2.5 \times 10^3)(\text{wt. percent dry solids})$$

2. The amount of extraction fluid #1 needed to extract the solid material from the filtered multi-phasic waste (H.2) is given by:

$$\text{Amount of extraction fluid} = 20 (\text{weight of material filtered} - \text{weight of filtrate})$$

Discussion and Recommendations

TCLP Worksheet No. 4

Zero Headspace Extraction for Determination of Volatile Organic Compounds

This worksheet describes the important information regarding the conduct of the zero headspace extraction (ZHE) of solid waste materials for volatile organic compounds.

Samples containing < 5.0 % dry solids are NOT subjected to ZHE leaching procedure. They are filtered in the ZHE device and the resulting filtrate is defined as the TCLP leachate and analyzed directly (§ 7.3.4).

H. Determination of Sample Size for Leach Testing -- the maximum sample size for this test is limited by the volume of the ZHE to approximately 25g (§ 7.3).

H.1. Amount of dry solids -- record the weight of dry solids charged to the ZHE but do not exceed 25g.

H.2. Amount of multi-phasic sample -- the amount of multi-phasic waste material necessary to produce a 25g sample after filtration can be estimated by the equation:

$$\text{Amount of multi-phasic material} = (2.5 \times 10^3)(\text{wt. percent wet solids})$$

I. Determination of the Amount of Leaching Fluid #1

I.1. Dry solids -- for dry solids containing no filterable fluids, the calculation of the correct volume of leaching fluid is straightforward. The amount is equal to twenty (20) times the mass of solid being leached. Note that the method specifies a 20:1 ratio based on the weight of extraction fluid required (§ 7.3.11). If the laboratory elects to use extraction fluid volume, rigorous adherence to the method requires a one time specific gravity correction to convert the required weight into the appropriate volume.

I.2. Multi-phasic samples -- the method indicates (§ 7.3.11) that the percent wet solids can be used to calculate the weight of extraction fluid used to extract the solid waste resulting from the filtration of a known weight of multi-phasic waste. The equation for this calculation is:

$$\text{Amount of extraction fluid} = \frac{20 \text{ (percent wet solids) (weight of waste filtered)}}{100}$$

This assumes there is no subsampling error between the original determination of the weight percent solid phase (wet) and the subsequent selection of a weight of the multi-phasic waste for filtration and extraction. This is frequently not the case. The nature of many multi-phasic wastes and/or the necessity to use more than one sample container for the two determinations means that subsampling error can be significant. This error can be eliminated if the actual weight of filtered solids is determined at the time the material is separated for extraction. The equation for this calculation is:

$$\text{Amount of extraction fluid} = 20 \text{ (weight of material filtered - weight of filtrate)}$$

The actual filtration procedure is detailed in ¶'s 7.3.7 through 7.3.9. Requirements for sample particle size reduction are given in ¶ 7.3.5 and 7.3.6. These should be followed as closely as the nature of the samples will allow and all departures from the instructions should be described in the laboratory notebook.

The addition of extraction fluid #1 to the ZHE is described in detail in ¶ 7.3.12.

- J. Record of the ZHE Extraction Test -- the period of the extraction test is given as 18 ± 2 hours (¶ 7.3.12.3). Extraction should be started so the resulting slurry can be filtered as soon as possible after the 18 hours has past. The filtration effectively stops the extraction process. If the extraction fluid is left in contact with the waste for longer than the specified extraction period (overnight or over the weekend), the extraction process continues and may lead to elevated levels of contaminants.
- J.1. Extraction start time -- record the time and date the extraction begins.
- J.2. Starting pressure -- the method requires the ZHE be pressurized to approximately 10 psi at the beginning of the test.
- J.3. Extraction stop time -- record the time and date the extraction is completed.

- J.4. Positive final pressure -- the method requires that the ZHE retain positive pressure at the conclusion of the extraction period or the test must be repeated (§ 7.3.13). Loss of pressure is an indication the ZHE leaked during the test resulting in a loss of volatile components.
- J.5. Filtration completion time -- record the time and date the filtration is complete.
- J.6. pH of filtrate -- while not required by the method, this is a good indicator of test performance when performing duplicate laboratory analysis or analyzing field replicates. It can be a reliable measure of sample heterogeneity.
- J.7. Volume of filtrate -- record the total volume of filtrate collected from the sample. This value is required to make the appropriate volume corrections when reporting the results from multi-phasic wastes. The filtration of oily wastes may be especially difficult.