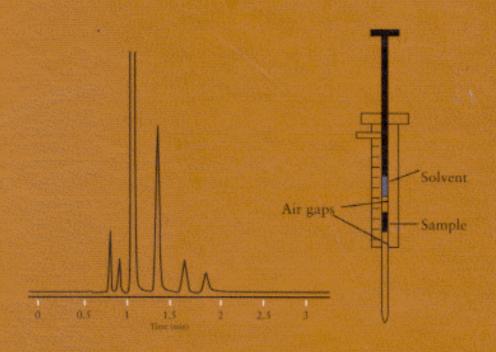
# Modern Practice of Gas Chromatography

## FOURTH EDITION



Edited by ROBERT L. GROB EUGENE F. BARRY

## **CONTENTS**

	Preface	xi
1.	Introduction Robert L. Grob	1
PA	RT I THEORY AND BASICS	
2.	Theory of Gas Chromatography Robert L. Grob	25
3.	Columns: Packed and Capillary; Column Selection in Gas Chromatography  Eugene F. Barry	65
4.	Optimization of Separations and Computer Assistance  John V. Hinshaw	193
5.	High-Speed Gas Chromatography Richard D. Sacks	229
PA	RT II TECHNIQUES AND INSTRUMENTATION	
6.	Detectors in Modern Gas Chromatography Luis A. Colón and Lisa J. Baird	277
7.	Techniques for Gas Chromatography/Mass Spectrometry  John A. Masucci and Gary W. Caldwell	339
8.	Qualitative and Quantitative Analysis by Gas Chromatography Robert L. Grob and Mary A. Kaiser	403
9.	Inlet Systems for Gas Chromatography Nicholas H. Snow	461
10	. Gas Management Systems for Gas Chromatography Reginald J. Bartram	491
		ix

**INDEX** 

P	A	RT	III A	٨	PPI	T	$C\Delta$	TI	ì	IC	

11.		Preparation Techniques for Gas Chromatography H. Snow and Gregory C. Slack	547			
12.		hemical Measurements by Gas Chromatography  Taiser and Cecil R. Dybowski	605			
13.	Petroleum and Petrochemical Analysis by Gas Chromatography  Edward F. Smith, Mark E. Craig, and Clifford C. Walters					
14.	4. Clinical and Pharmaceutical Applications of Gas Chromatography Juan G. Alvarez					
15.	5. Environmental Applications of Gas Chromatography  John L. Snyder  769					
16.	5. Forensic Science Applications of Gas Chromatography Thomas A. Brettell					
17.	7. Validation and QA/QC of Gas Chromatographic Methods Thomas A. Brettell and Richard E. Lester					
AP	PENDIXE	es ·				
Apj	pendix A.	Effect of Detector Attenuation Change and Chart Speed on Peak Height, Peak Width, and Peak Area Robert L. Grob and Eugene F. Barry	991			
Apj	pendix B.	Gas Chromatographic Acronyms and Symbols and Their Definitions  Robert L. Grob and Eugene F. Barry	995			
Арј	oendix C.	Useful Hints for Gas Chromatography Robert L. Grob and Eugene F. Barry	1007			

1011

#### CHAPTER ONE

## Introduction

#### ROBERT L. GROB

Professor Emeritus of Analytical Chemistry, Villanova University, Villanova, Pennsylvania

- 1.1 HISTORY AND DEVELOPMENT OF CHROMATOGRAPHY
- 1.2 DEFINITIONS AND NOMENCLATURE
- 1.3 SUGGESTED READING ON GAS CHROMATOGRAPHY
- 1.4 COMMERCIAL INSTRUMENTATION

## Theory of Gas Chromatography

#### ROBERT L. GROB

Professor Emeritus of Analytical Chemistry, Villanova University, Villanova, Pennsylvania

2.1	CHROMA	ATOGR A	PHIC	METHODS
Z.1	CHRONIA	UUUKA	FRIL.	かたし ロしかつき

- 2.1.1 Classification of Methods
- 2.1.2 General Aspects
- 2.1.3 Frontal Analysis
- 2.1.4 Displacement Development
- 2.1.5 Elution Development
- 2.1.6 Isotherms
- 2.1.7 Process Types in Chromatography
- 2.1.8 Linear Ideal Chromatography
- 2.1.9 Linear Nonideal Chromatography
- 2.1.10 Nonlinear Ideal Chromatography
- 2.1.11 Nonlinear Nonideal Chromatography

### 2.2 GENERAL ASPECTS OF GAS CHROMATOGRAPHY

- 2.2.1 Applications of Gas Chromatography
- 2.2.2 Types of Detection
- 2.2.3 Advantages and Limitations

#### 2.3 GAS CHROMATOGRAPHY

- 2.3.1 Plate Theory
  - 2.3.1.1 Discrete-Flow Model
  - 2.3.1.2 Continuous-Flow Model
- 2.3.2 Rate Theory
  - 2.3.2.1 Modifications of the van Deemter Equation
  - 2.3.2.2 Flow

## Columns: Packed and Capillary; Column Selection in Gas Chromatography

EUGENE F. BARRY

3.6

3.6.1 3.6.2

3.6.3

3.6.4

Chemistry Department, University of Massachusetts Lowell, Lowell, Massachusetts

3.1 CENTRAL ROLE PLAYED BY COLUMN

3.2 JUSTIFICATION FOR COLUMN SELECTION AND CARE
 3.3 LITERATURE ON GAS CHROMATOGRAPHIC COLUMNS
 3.4 GAS CHROMATOGRAPHIC RESOURCES ON THE INTERNET

3.5.2.3 Carbonaceous Materials

Requirements of a Stationary Phase

**Evaluation of Column Operation** 

3.6.4.4 Required Plate Number

3.6.4.1 Column Efficiency

3.6.4.3 Resolution

McReynolds Classification of Stationary Phases

3.6.4.2 Effective Number of Theoretical Plates

Kovats Retention Indices

STATIONARY PHASES

#### Part 1 Overview

		Part 2 Packed-Column Gas Chromatography
3.5	SOLID	SUPPORTS AND ADSORBENTS
	3.5.1	Supports for GLC: Diatomaceous Types, Halocarbons
		3.5.1.1 Diatomite Supports
		3.5.1.2 Teflon Supports
	3.5.2	Adsorbents for GSC: Porous Polymers, Molecular Sieves, Carbonaceous
		Materials
		3.5.2.1 Porous Polymers
		3.5.2.2 Molecular Sieves

3.6.4.5	Separation	Factor
---------	------------	--------

- 3.6.4.6 Separation Number
- 3.6.4.7 Analysis Time
- 3.6.5 Optimization of Packed-Column Separations
  - 3.6.5.1 Eddy Diffusion
  - 3.6.5.2 Molecular Diffusion
  - 3.6.5.3 Mass Transfer Contribution

#### 3.7 COLUMN PREPARATION

- 3.7.1 Description of Coating Methods
- 3.7.2 Tubing Materials and Dimensions
- 3.7.3 Glass Wool Plugs and Column Fittings
- 3.7.4 Filling the Column
- 3.7.5 Conditioning the Column and Column Care

#### Part 3 Capillary Column Gas Chromatography

#### 3.8 INTRODUCTION

- 3.8.1 Significance and Impact of Capillary GC
- 3.8.2 Chronology of Achievements in Capillary GC
- 3.8.3 Comparison between Packed and Capillary Columns

#### 3.9 CAPILLARY COLUMN TECHNOLOGY

- 3.9.1 Capillary Column Materials
  - 3.9.1.1 Fused-Silica and Other Glasses
  - 3.9.1.2 Extrusion of a Fused-Silica Capillary Column
  - 3.9.1.3 Aluminum-Clad Fused-Silica Capillary Columns
  - 3.9.1.4 Fused-Silica-Lined Stainless-Steel Capillary Columns
- 3.9.2 Preparation of a Fused-Silica Capillary Column
  - 3.9.2.1 Silanol Deactivation
  - 3.9.2.2 Static Coating of Capillary Columns
  - 3.9.2.3 Capillary Cages
  - 3.9.2.4 Test Mixtures for Monitoring Column Performance

### 3.10 CHROMATOGRAPHIC PERFORMANCE OF CAPILLARY COLUMNS

- 3.10.1 Golay Equation versus van Deemter Expression
- 3.10.2 Choice of Carrier Gas
  - 3.10.2.1 Measurement of Linear Velocity
  - 3.10.2.2 Effect of Carrier-Gas Viscosity on Linear Velocity
- 3.10.3 Phase Ratio
- 3.10.4 Practical Considerations of Column Diameter, Film Thickness, and Column Length
  - 3.10.4.1 Column Diameter
  - 3.10.4.2 Film Thickness of Stationary Phase
  - 3.10.4.3 Column Length
  - 3.10.4.4 Capillary Columns of 0.53 mm i.d. (The Megabore Column)
- 3.10.5 Coating Efficiency

## 3.11 STATIONARY-PHASE SELECTION FOR CAPILLARY GAS

#### CHROMATOGRAPHY

- 3.11.1 Requirements and History
- 3.11.2 Cross-Reference of Columns from Manufacturers
- 3.11.3 Polysiloxanes
- 3.11.4 Polyethylene Glycol Phases

- 3.11.5 Crosslinked versus Chemically Bonded Phases
  - 3.11.5.1 Crosslinking of a Stationary Phase
  - 3.11.5.2 Chemical Bonding
  - 3.11.5.3 MS-Grade Phases versus Polysilarylene or Polysilphenylene Phases
  - 3.11.5.4 Solgel Stationary Phases
  - 3.11.5.5 Phenylpolycarborane-Siloxane Phases
- 3.11.6 Specialty Columns
  - 3.11.6.1 EPA Methods
  - 3.11.6.2 Chiral Stationary Phases
  - 3.11.6.3 Gas-Solid Adsorption Capillary Columns (PLOT Columns)
- 3.11.7 Capillary Column Care and First Aid
  - 3.11.7.1 Ferrule Materials and Fittings
  - 3.11.7.2 Column Installation
  - 3.11.7.3 Column Conditioning
  - 3,11,7.4 Column Bleed
  - 3.11.7.5 Retention Gap and Guard Columns
  - 3.11.7.6 Column Fatigue and Regeneration
- 3.11.8 Applications

#### Part 4 Column Oven Temperature Control

- 3.12 THERMAL PERFORMANCE VARIABLES AND ELECTRONIC CONSIDERATIONS
- 3.13 ADVANTAGES OF TEMPERATURE PROGRAMMING OVER ISOTHERMAL OPERATION
- 3.14 OVEN TEMPERATURE PROFILES FOR PROGRAMMED-TEMPERATURE GC
- 3.15 CAPILLARY CAGE DESIGN
- 3.16 SUBAMBIENT OVEN TEMPERATURE CONTROL

# Optimization of Separations and Computer Assistance

JOHN V. HINSHAW

Serveron Corporation, Hillsboro, Oregon

A	1	337TT37	OPTIM	117C
ш.		WHI	1 11 11 11 11 11 11 11 11 11 11 11 11 1	HZ.C.

- 4.2 BASIC CHOICES
  - 4.2.1 Packed versus Capillary Columns
  - THE INFLUENCE OF COLUMN VARIABLES
  - 4.3.1 Inner Diameter
  - 4.3.2 Length
- 4.4 THE INFLUENCE OF OPERATIONAL VARIABLES
  - 4.4.1 Carrier-Gas Linear Velocity
  - 4.4.2 The Influence of Column Temperature
    - 4.4.2.1 Isothermal Operation
    - 4.4.2.2 Temperature-Programmed Operation
- 4.5 THE ROLE OF COMPUTERS IN OPTIMIZATION
  - 4.5.1 System Models for Optimization
    - 4.5.1.1 Isothermal Elution
    - 4.5.1.2 Temperature-Programmed Elution
    - 4.5.2 Peak Shape Simulation
- 4.6 CONCLUSION

#### 230

#### HIGH-SPEED GAS CHROMATOGRAPHY

- 5.11.2 At-Column Heating
- 5.11.3 Effects of Heating Rate on Analysis Time and Peak Capacity

#### Part 4 Selectivity Enhancement Methods

- 5.12 COPING WITH REDUCED PEAK CAPACITY
- 5.13 ADJUSTMENT OF SELECTIVITY
  - 5.13.1 Mixed Stationary Phases
  - 5.13.2 Designer Stationary Phases
  - 5.13.3 Tunable/Programmable Selectivity with Tandem Capillary Columns
  - 5.13.4 Pulse Flow Modulation with Tandem Capillary Columns

#### Part 5 Portable and Miniaturized HSGC Systems

- 5.14 REQUIREMENTS FOR MINIATURIZED, AUTONOMOUS HSGC SYSTEMS
- 5.15 MICROELECTROMECHANICAL COMPONENTS FOR HSGC
  - 5.15.1 Microfabricated Columns
  - 5.15.2 Microfabricated Sensors and Preconcentrators
    - 5.15.3 Complete MEMS GC

**ACKNOWLEDGMENTS** 

# **Detectors in Modern Gas Chromatography**

#### LUIS A. COLÓN and LISA J. BAIRD

Department of Chemistry, The State University of New York at Buffalo, Buffalo, New York

6.1	INTRO	DDUCTION
6.2	GENE	RAL ASPECTS
	6.2.1	Noise Characteristics
	6.2.2	Sensitivity
	6.2.3	Limit of Detection
	6.2.4	Dynamic Range
	6.2.5	Response Factor
	6.2.6	Selectivity
	6.2.7	Other Practical Considerations
6.3	THER	MAL CONDUCTIVITY DETECTOR
	6.3.1	Introduction
	6.3.2	Operating Principles
	6.3.3	Detector Design
	6.3.4	Performance Characteristics
		6.3.4.1 Response
		6.3.4.2 Noise, Detection Limits, and Linearity
	6.3.5	Other Practical Considerations
6.4	FLAM	E IONIZATION DETECTOR
	6.4.1	Introduction
	6.4.2	Operating Principles
	6.4.3	Detector Design
	6.4.4	Performance Characteristics
		6.4.4.1 Response
		6.4.4.2 Noise, Detection Limits, and Linearity
	6.4.5	FID Modifications
	6.4.6	
6.5	<b>ELEC</b>	TRON-CAPTURE DETECTOR
	6.5.1	Introduction
	6.5.2	Operating Principles and Variables
		6.5.2.1 Cell Design and Radiation Source

		6.5.2.2 Flowrate
		6.5.2.3 Voltage
	6.5.3	Performance Characteristics
		6.5.3.1 Response
		6.5.3.2 Linear Range and Detection Limits
	6.5.4	
	6.5.5	Other Practical Considerations
6.6		MIONIC DETECTOR
	6.6.1	Introduction
	6.6.2	Operating Principles and Variables
		6.6.2.1 Mechanism
		6.6.2.2 Flowrate and Heating Current
	6.6.3	
	6.6.4	Other Considerations
6.7	PHOTO	DIONIZATION DETECTOR
	6.7.1	Introduction
	6.7.2	Operating Principles
	6.7.3	Detector Characteristics
6.8	HELIU	M IONIZATION DETECTORS
	6.8.1	Introduction
	6.8.2	- 1
		6.8.2.1 Helium Discharge Ionization Detector (HDID)
		6.8.2.2 Pulse Discharge Helium Ionization Detector (PDHID)
6.9		E PHOTOMETRIC DETECTOR
	<b>6.9</b> .1	Operating Principles
	6.9.2	Design
	6.9.3	Performance Characteristics
		6.9.3.1 Noise and Detection Limits
		6.9.3.2 Sensitivity and Dynamic Range
6.10	CHEM	ILUMINESCENCE DETECTORS
	6.10.1	Introduction
	6.10.2	Sulfur Chemiluminescence Detector
		Nitrogen Chemiluminescence Detector
6.11	ATOM	C EMISSION DETECTOR
6.12	OTHER	R DETECTORS
	6.12.1	Hall Electrolytic Conductivity Detector
	6.12.2	Ultrasonic Detector

## Techniques for Gas Chromatography/ Mass Spectrometry

#### JOHN A. MASUCCI and GARY W. CALDWELL

Johnson and Johnson Pharmaceutical Research and Development, L.L.C., Spring House, Pennsylvania

7.	ı T	NIT	DC	71/1	UCI	TIO.	N
1.		IN I	ĸu	יענ	UUI	II.	IN

- 7.1.1 Brief History of Gas Chromatography/Mass Spectrometry
- 7.1.2 Scope of Chapter
- 7.1.3 Overview of Gas Chromatography/Mass Spectrometry

# 7.2 GENERAL GAS CHROMATOGRAPHY/MASS SPECTROMETRY CONSIDERATIONS

- 7.2.1 Sample Preparation
- 7.2.2 Chemical Derivatization
- 7.2.3 Chromatography
- 7.2.4 Gas Chromatography/Mass Spectrometry Interfaces
- 7.2.5 Temperature Problems
- 7.2.6 Ion Sources
- 7.2.7 Mass Analyzers
- 7.2.8 Detectors
- 7.2.9 Scanning Techniques
- 7.2.10 Data Presentation
- 7.2.11 Background Artifacts

## 7.3 GAS CHROMATOGRAPHY/ELECTRON IONIZATION MASS

#### SPECTROMETRY

- 7.3.1 Electron Ionization
- 7.3.2 Oualitative Methods: Structure Elucidation
- 7.3.3 Quantitative Methods
- 7.3.4 Negative-Electron Ionization

# 7.4 GAS CHROMATOGRAPHY/POSITIVE-ION CHEMICAL IONIZATION MASS SPECTROMETRY

- 7.4.1 Advantages of Positive-Ion Chemical Ionization
- 7.4.2 Kinetic and Thermodynamic Considerations
- 7.4.3 Instrumentation
- 7.4.4 Chromatographic Carrier Gas Substituted as the Reagent Gas

#### 340 TECHNIQUES FOR GAS CHROMATOGRAPHY/ MASS SPECTROMETRY

7.4.5	Helium Chromatographic Carrier Gas and Different Reagent Gases
7.4.6	Hydrocarbon Positive-Ion Chemical Ionization Reagent Systems

- 7.4.7 Amine Positive Ion Chemical Ionization Reagent Systems
  7.4.8 Applications—Structure Elucidations and Quantification
- GAS CHROMATOGRAPHY/NEGATIVE-ION CHEMICAL IONIZATION
- MASS SPECTROMETRY
  - 7.5.1 Advantages of Negative Ion Chemical Ionization
  - 7.5.2 Kinetic and Thermodynamic Considerations
  - 7.5.3 Instrumentation

7.5

- 7.5.4 Electron-Capture Techniques
- 7.5.5 Acidity and Hydrogen-Bonding Techniques
- 7.6 DEVELOPING TRENDS IN GAS CHROMATOGRAPHY/MASS SPECTROMETRY
  - 7.6.1 Multidimensional (Gas Chromatography)<sup>m</sup>/(Mass Spectrometry)<sup>n</sup>
    - 7.6.2 High-Speed Gas Chromatography/Mass Spectrometry
- 7.6.3 Novel Ionization Methods for Gas Chromatography/Mass Spectrometry REFERENCES

# Qualitative and Quantitative Analysis by Gas Chromatography

#### ROBERT L. GROB

Professor Emeritus of Analytical Chemistry, Villanova University, Villanova, Pennsylvania

#### MARY A. KAISER

8.3.3

8.4

8.5

Trapping of Peaks

LOGIC OF QUALITATIVE ANALYSIS

E. I. Dupont de Nemours & Company, Central Research & Development, Wilmington, Delaware

DISCUSSION OF CHROMATOGRAPHIC DATA

#### Part 1 Qualitative Analysis

O. I	DIOC	cosion of cincountrodantine bring				
8.2	IDEN'	TIFICATION FROM GAS CHROMATOGRAPHIC DATA ONLY				
	8.2.1	Retention Data				
	8.2.2	Plot of Log Retention Time versus Carbon Number				
	8.2.3	Kovats Index				
	8.2.4	Multiple Columns				
	8.2.5	Relative Detector Response				
		8.2.5.1 Selective Detectors				
		8.2.5.2 Molecular Weight Chromatography				
	8.2.6	Simple Pretreatment				
		8.2.6.1 Extractions				
		8.2.6.2 Beroza's p Value				
		8.2.6.3 Water-Air Equilibrium				
	8.2.7	Tandem Gas Chromatographic Operations				
		8.2.7.1 Two Columns in Series				
		8.2.7.2 Subtractive Precolumns				
		8.2.7.3 Carbon Skeleton				
		8.2.7.4 Controlled Pyrolysis				
8.3	IDEN	TIFICATION BY GAS CHROMATOGRAPHIC AND OTHER DATA				
	8.3.1	Elemental and Functional Group Analysis				
	8.3.2	Coupling Gas Chromatography and Other Instrumental Techniques				

QUALITATIVE ANALYSIS WITHOUT PEAK IDENTIFICATION

## Part 2 Quantitative Analysis

8.6	GENE	RAL DISCUSSION
8.7	PEAK	SIZE MEASUREMENT
	8.7.1	Peak Height
		Height and Width at Half-Height
		Triangulation
		Cut and Weigh
		Planimeter
	8.7.6	Disk Integrator
		Electronic Integrators and Computers
	8.7.8	
8.8	STAN	DARDIZATION
	8.8.1	General
	8.8.2	External Standardization
		8.8.2.1 Static Gas Standards
		8.8.2.2 Dynamic Gas Standards
		8.8.2.3 Liquid Standards
	8.8.3	Internal Normalization
	8.8.4	Internal Standardization
	8.8.5	Standardization Summary
8.9		VTITATIVE ERROR
	8.9.1	General Discussion
	8.9.2	Sampling Techniques
	8.9.3	
		8.9.3.1 Syringe Injection
		8.9.3.2 Gas-Sampling Valve
	8.9.4	
8.10	VALII	DATION OF GAS CHROMATOGRAPHIC SYSTEMS
REFE	RENCE	ES

#### **CHAPTER NINE**

## **Inlet Systems for Gas Chromatography**

#### NICHOLAS H. SNOW

Department of Chemistry and Biochemistry, Seton Hall University, South Orange, New Jersey

9.1		DDUCTION AND OVERVIEWS
		Fundamental Problems with Capillary Injection
	9.1.2	Overview of Capillary Inlets
		9.1.2.1 Split
		9.1.2.2 Splitless
		9.1.2.3 On-Column
		9.1.2.4 Programmed-Temperature Vaporization
	9.1.3	Overview of Method Development Issues
	9.1.4	General Considerations for Proper Injection
		9.1.4.1 Syringes
		9.1.4.2 Consumables
		9.1.4.3 Ferrules, Connectors, and Fittings
9.2	PACK	ED-COLUMN INLET
	9.2.1	Description and Instrumentation
	9.2.2	Method Development Considerations
	9.2.3	Advantages
	9.2.4	Disadvantages
9.3		INLET
	9.3.1	Overview of the Instrumentation
	9.3.2	Basic Operation
	9.3.3	
	9.3.4	Glass Liners
	9.3.5	Ferrules and Fittings
		Setting the Inlet Temperature
		Setting the Flows and Split Ratio
		Discrimination and Linearity of Splitting
9.4		LESS INLET
	9.4.1	Overview of the Instrumentation
	9.4.2	Band-Broadening and Band-Focusing Mechanisms
	9.4.3	Setting the Temperatures

Setting the Flows and Purge OFF Time Optimization Recommendations

#### 462 INLET SYSTEMS FOR GAS CHROMATOGRAPHY

- 9.5 COOL ON-COLUMN INLET
  - 9.5.1 Overview of the Instrumentation
  - Special Considerations
    - 9.5.3 Large-Volume Injection
- 9.6 PROGRAMMED-TEMPERATURE VAPORIZATION INLET
  - 9.6.1 Overview of the Instrumentation
  - 9.6.2 Modes of Operation 9.6.2.1 Hot Split and Splitless

    - 9.6.2.2 Cold Split and Splitless
  - 9.6.2.3 Cold Splitless Solvent Vent (Large-Volume Injection)
  - 9.6.3 Advantages and Disadvantages
- SUMMARY AND CONCLUSIONS

# **Gas Management Systems for Gas Chromatography**

#### REGINALD J. BARTRAM

10.4.1.2 Purging

Aliteci	h Associate	es, Inc., State College, Pennsylvania
10.1	INTROD	UCTION
10.2		AND EFFECTS OF MOBILE-PHASES SELECTION
	10.2.1	Factors Governing Choice of Carrier Gas
	10.2.2	<u> </u>
	10.2.3	Viscosity Effects Causing Possible Problems during Temperature
		Programming
	10.2.4	Consideration of Flow Devices—Positive Attributes of Modern
		Electronic Pressure Control Devices
	10.2.5	Mass Flow Controllers for Packed Columns
	10.2.6	Pressure Control for Capillary Problems
	10.2.7	Proper Measurement of Flowrates with Packed Columns and
		Appropriate Devices
	10.2.8	Measurement of Linear Velocity with Capillary Columns
10.3	CARRIE	R-GAS PURITY, CONNECTIONS, TUBING, AND RELATED ISSUE
	10.3.1	Basic Installation Concerns
		10.3.1.1 Power Requirements
		10.3.1.2 Gas Choices
		10.3.1.3 Cylinders or Generators?
		10.3.1.4 Gas Purity
		10.3.1.5 Regulators and Associated Connectors
	10.3.2	Tubing and Plumbing
		10.3.2.1 Tubing Choices
		10.3.2.2 Cleaning
		10.3.2.3 Cutting, Reaming, and Bending
		10.3.2.4 Valves and Fittings
		10.3.2.5 Making Connections
10.4		M INSTALLATION AND ASSEMBLY
	10.4.1	System Assembly
		11) A. I. I. Binding and Hilmingting I Agre

	10.4.1.3	Purifier Connections
10.4.2	Installatio	on
	10.4.2.1	Single-Gas Chromatograph
	10.4.2.2	Two- to Four-Gas Chromatographs
	10.4.2.3	5-20-Gas Chromatographs
RADEMARK	S	<u> </u>

#### CHAPTER ELEVEN

# Sample Preparation Techniques for Gas Chromatography

NICHOLAS H. SNOW

Department of Chemistry and Biochemistry, Seton Hall University, South Orange, New Jersey

GREGORY C. SLACK

Wyeth Pharmaceuticals, Rouses Point, New York

11	1.1	INT	'ROI	DU	CTI	on

- 11.1.1 Types of Samples for Gas Chromatography
- 11.1.2 Fundamentals of Extraction Theory
  - 11.1.2.1 Theory of Liquid-Liquid Extraction
  - 11.1.2.2 Extraction Efficiency
  - 11.1.2.3 Efficiency of Multiple Extractions

## 11.2 PRACTICE OF LIQUID-LIQUID EXTRACTION

- 11.2.1 Macroscale Liquid-Liquid Extraction
  11.2.1.1 Soxhlet Extraction
- 11.2.2 Microscale Liquid-Liquid Extraction
- 11.2.3 Single-Drop Microextraction
- 11.3 SOLID-PHASE EXTRACTION
- 11.3.1 Basic Principles of Solid-Phase Extraction
  - 11.3.2 Comparison between Solid-Phase Extraction (SPE) and Liquid-Liquid Extraction (LLE)
  - 11.3.3 Procedures and Equipment
  - 11.3.4 Applications of SPE

#### 11.4 HEADSPACE EXTRACTION

- 11.4.1 Basic Principles
- 11.4.2 Static Headspace Extraction (SHE)
  - 11.4.2.1 Instrumentation and Equipment for SHE
  - 11.4.2.2 Sample Preparation for SHE
  - 11.4.2.3 Optimizing SHE Efficiency and Quantitation for Liquid Samples
- 11.4.3 Quantitative Techniques in Static Headspace Gas Chromatography
  11.4.3.1 External Standard Calibration
  - 11.4.3.2 Internal Standard Calibration

11.5

11.6

	11.4.3.3 Standard Addition Calibration
11.4.4	
11.4.5	
SORBE	ENT-BASED MICROEXTRACTIONS
11.5.1	Solid-Phase Microextraction (SPME)
11.5.2	SPME Method Development
	11.5.2.1 Choosing Extraction Fibers and Chemistry
	11.5.2.2 Extraction Mode and Agitation Method
	11.5.2.3 Optimization of Desorption Conditions
	11.5.2.4 Optimization of Extraction Volume
	SPME Applications
11.5.4	Stirbar Sorptive Extraction (SBSE)
11.5.5	Flowthrough Techniques
	R SAMPLE PREPARATION METHODS
11.6.1	Supercritical-Fluid Extraction
	11.6.1.1 Fundamentals of Supercritical Fluids
	11.6.1.2 Instrumentation for SFE
	11.6.1.3 Dynamic versus Static SFE
11.6.2	Accelerated Solvent Extraction (ASE)
11.6.3	Microwave-Assisted Extraction (MAE)
11.6.4	Membrane-Based Extractions
	Pyrolysis
11.6.6	Automation
11.6.7	Derivatization
11.6.8	Thermal Desorption
	LUSIONS

REFERENCES

11.7

# **Physicochemical Measurements** by Gas Chromatography

	_			
MARY	Д	KA	ISHE	ł

E. I. DuPont de Nemours & Company, Central Research & Development, Wilmington, Delaware

#### CECIL R. DYBOWSKI

Chemistry Department, University of Delaware, Newark, Delaware

12.1	GAS-SOLID CHROMATOGRAPHY, ADSORPTION, AND SPECIFIC
	SURFACE AREA
	12.1.1. Adsorbent Properties

- 12.1.2 Adsorption of Gases at Solid Surface
- 12.1.3 Specific Surface Area
- 12.1.4 Gas Chromatographic Surface Area Determination
- SURFACE THERMODYNAMICS 12.2
- SOLUTION THERMODYNAMICS 12.3
- 12.4 VAPOR PRESSURE AND HENRY'S LAW
- 12.5 COMPLEXATION CONSTANTS
- 12.6 VIRIAL COEFFICIENTS
  - 12.6.1 Second Virial Coefficients
  - 12.6.2 Gas-Solid Virial Coefficients
- KINETICS 12.7
- 12.8 PYROLYSIS. THEMOLYSIS, AND COMBUSTION
- OTHER APPLICATIONS OF GC TO PHYSICOCHEMICAL 12.9

### MEASUREMENTS

- 12.9.1 Catalysis
- 12.9.2 Photochemistry
- 12.9.3 Inverse Gas Chromatography
- 12.9.4 Simulated Distillation
- 12.9.5 Solubility
- 12.10 OUALITY ASSURANCE, ACCURACY, PRECISION, AND CALIBRATION REFERENCES

#### CHAPTER THIRTEEN

# Petroleum and Petrochemical Analysis by Gas Chromatography

FDW/A	CM	ITH

ExxonMobil Chemical Company, Baytown, Texas

#### MARK E. CRAIG

ExxonMobil Chemical Company, Baytown, Texas

#### CLIFFORD C. WALTERS

ExxonMobil Research & Engineering Company, Clinton, New Jersey

1	12	1	1	T	J٦	ΓΊ	Ŕ	r	ľ	ח	H	$\mathbb{C}^r$	ГТ	വ	N	l

- 13.1.1 Historical Perspective
- 13.1.2 Standardization of Analyses
- 13.2 EXPLORATION AND PRODUCTION
  - 13.2.1 Geochemical Studies
  - 13.2.2 Synthetic Crude Oil

#### 13.3 REFINING

- 13.3.1 Refinery Gases
- 13.3.2 Simulated Distillation
- 13.3.3 Hydrocarbon Type Analysis13.3.4 Sulfur and Nitrogen Compounds
- 13.3.5 Gasoline Additives

#### 13.4 PETROCHEMICALS

- 13.4.1 Olefins
  - 13.4.1.1 Ethylene
  - 13.4.1.2 Propylene
  - 13.4.1.3 Butadiene
  - 13.4.2 Aromatics

#### 13.5 PROCESS CHROMATOGRAPHY

- 13.5.1 Process Chromatographs
  - 13.5.1.1 Sample System
  - 13.5.1.2 Analyzer
  - 13.5.1.3 Programmer

## PETROLEUM AND PETROCHEMICAL ANALYSIS BY GAS CHROMATOGRAPHY

13.5.2 Typical Applications

**ACKNOWLEDGMENTS** 

# Clinical and Pharmaceutical Applications of Gas Chromatography

JUAN G. ALVAREZ, MD, PhD

Department of Obstetrics & Gynecology, Beth Israel Hospital, Harvard Medical School, Boston, Massachusetts

Centro de Infertilidad Masculina Androgen, Hospital San Rafael, La Coruña, Spain

14.1 INTRODUCTION	IN	<b>JTR</b> (	DDU	JCTI	4O
-------------------	----	--------------	-----	------	----

#### 14.2 AMPHETAMINES

- 14.2.1 Pharmacological Considerations
  - 14.2.1.1 Chemistry and Structure
  - 14.2.1.2 Pharmacological Effects
  - 14.2.1.3 Mechanism of Action
  - 14.2.1.4 Absorption and Elimination
- 14.2.2 Gas Chromatographic Analysis
  - 14.2.2.1 Sample Preparation
  - 14.2.2.2 Analytical Procedure
  - 14.2.2.3 Quantification of Amphetamines

#### 14.3 INHALATIONAL ANESTHETICS

- 14.3.1 Pharmacological Considerations
  - 14.3.1.1 Chemistry and Structure
  - 14.3.1.2 Pharmacological Effects
  - 14.3.1.3 Mechanism of Action
  - 14.3.1.4 Absorption and Elimination
- 14.3.2 Gas Chromatographic Analysis
  - 14.3.2.1 Sample Preparation
  - 14.3.2.2 Analytical Procedure
  - 14.3.2.3 Quantification of Inhalational Anesthetics

#### 14.4 TRICYCLIC ANTIDEPRESSANTS

- 14.4.1 Pharmacological Considerations
  - 14.4.1.1 Chemistry and Structure
  - 14.4.1.2 Pharmacological Effects

			Mechanism of Action
		14.4.1.4	Absorption and Elimination
	14.4.2	Gas Chro	omatographic Analysis
		14.4.2.1	Sample Preparation
		14.4.2.2	
		14.4.2.3	Quantification of Tricyclic Antidepressants
14.5		PILEPTIC	DRUGS
	14.5.1		ological Considerations
		14.5.1.1	Chemistry and Structure
		14.5.1.2	Pharmacological Effects
			Mechanism of Action
			Absorption and Elimination
	14.5.2		matographic Analysis
			Sample Preparation
		14.5,2.2	Analytical Procedure
		14.5.2.3	Quantification of Antiepileptic Drugs
14.6		ALCOH	
	14.6.1	Pharmaco	ological Considerations
		14.6.1.1	Pharmacological Effects
			Mechanism of Action
			Absorption and Elimination
	14.6.2		matographic Analysis
		14.6.2.1	Sample Preparation
			Analytical Procedure
	DDIIG		Quantification of Volatile Organics
14.7		OF ABU	<del></del>
	14./.1	Pharmaco	logical Considerations
		14.7.1.1	Pharmacological Effects
	1470		Mechanism of Action
	14.7.2	Gas Chro	matographic Analysis
		14.7.2.1	Sample Preparation
		14.7.2.2	Analytical Procedure
140	DD OCT	14.7.2.3	
		AGLANDI	
	14.6.1		logical Considerations
			Chemistry and Structure
		14.8.1.2	Pharmacological Effects
		14.8.1.3 14.8.1.4	Mechanism of Action
	14.8.2		Absorption and Elimination
	17.0.2	14.8.2.1	natographic Analysis
		14.8.2.1	Sample Preparation
		14.8.2.2	Analytical Procedure
		14.0.2.3	Quantification of Prostaglandins

### 14.9 STEROIDS

14.9.1 Pharmacological Considerations

14.9.1.1 Chemistry and Structure

14.9.1.2 Mechanism of Action

14.9.1.3 Absorption and Elimination

REFERENCES

14.9.2 Gas Chromatographic Analysis 14.9.2.1 Sample Preparation

14.9.2.2 Analytical Procedure

14.9.2.3 Quantification of Steroids

#### CHAPTER FIFTEEN

# **Environmental Applications** of Gas Chromatography

IOHNI	CNIVITED

15.1

Lancaster Laboratories, Inc., Lancaster, Pennsylvania

INTRODUCTION

		Historical Perspective
	15.1.2	Role of Gas Chromatography in Environmental Analysis
15.2	GOVER	NMENT REGULATION IN ENVIRONMENTAL ANALYSIS
	15.2.1	Major Federal Legislation
		Government Agencies
	15.2.3	Role of the States
15.3	<b>ENVIR</b>	ONMENTAL SAMPLES
		Collection of Samples
		Handling and Storage of Samples
15.4	CLASS	ES OF COMPOUNDS DETERMINED BY GAS
	CHRON	MATOGRAPHY
		Volatile Organic Compounds
	15.4.2	Semivolatile Organic Compounds
	15.4.3	Pesticides and Polychlorinated Biphenyls (PCBs)
	15.4.4	
15.5		SPACE SAMPLING OF VOLATILE ORGANIC COMPOUNDS IN
	ENVIR	ONMENTAL ANALYSIS
	15.5.1	1 1
		Dynamic Headspace Sampling
15.6		ACTION TECHNIQUES FOR SEMIVOLATILE ORGANIC
		DUNDS IN AQUEOUS SAMPLES
		Liquid-Liquid Extraction
		Solid-Phase Extraction
		Solid-Phase Microextraction
15.7		ACTION TECHNIQUES FOR SEMIVOLATILE ORGANIC
		OUNDS IN SOIL AND SOLID SAMPLES
		Soxhlet Extraction
		Ultrasonic Extraction
	15.7.3	Pressurized Fluid Extraction

	15.7.4	Supercritical Fluid Extraction						
	15.7.5	Miscellaneous Extraction Methods						
15.8	CONCE	ENTRATION STEP FOR SEMIVOLATILE ORGANIC COMPOUNDS						
	15.8.1	Evaporative Techniques						
	15.8.2							
15.9	CLEAN	CLEANUP OF SAMPLE EXTRACTS						
	15.9.1	Gel Permeation Chromatography						
	15.9.2	· · · · — · · · · · · · · · · · · · · ·						
	15.9.3	Liquid-Solid Chromatographic Cleanups						
	15.9.4	Miscellaneous Cleanups						
15.10	DERIVA	ATIZATION TECHNIQUES						
15.11	GAS CHROMATOGRAPHIC METHODS FOR THE DETERMINATION							
-	VOLAT:	ILE ORGANIC COMPOUNDS IN ENVIRONMENTAL SAMPLES						
	15.11.1	Analysis of Volatile Organic Compounds by GCMS						
	15.11.2	Determination of Aromatic and Halogenated Volatile Organic						
		Compounds Using Photoionization and Electrolytic Conductivity						
		Detectors						
	15.11.3	Methods for Determining Gasoline-Range Organics						
	15.11.4	Alternative Methods for Determining Volatile Compounds						
15.12	12 GAS CHROMATOGRAPHIC METHODS FOR THE DETERMINAT							
		DLATILE ORGANIC COMPOUNDS						
	15.12.1	The Determination of Semivolatile Organic Compounds by Gas						
		Chromatography and Mass Spectrometry						
	15.12.2	Semivolatile Organic Compounds Determined Using Alternative						
		Detectors						
		15.12.2.1 Polynuclear Aromatic Hydrocarbons						
		15.12.2.2 Haloethers and Chlorinated Hydrocarbons						
		15.12.2.3 Phthalate Esters						
		15.12.2.4 Nitrosamines, Nitroaromatics, and Cyclic Ketones						
	15 10 0	15.12.2.5 Phenols						
	15.12.3	Petroleum Fingerprinting of Contaminated Soils and Water Using						
	15 10 1	GCFID						
	15.12.4	and a second sec						
15 12	DETERN	Polychlorinated Dibenzofurans						
15.13		MINATION OF PESTICIDES AND POLYCHLORINATED						
	BIPHEN	<del></del>						
	15.13.1	Organochlorine Pesticides and PCBs Using the Electron-Capture Detector						
	15.13.2							
	13.13.2	Gas Chromatographic Methods to Determine Organophosphorus						
		Pesticides Using the Nitrogen Phosphorus Detector and the Flame Photometric Detector						
	15.13.3							
	10.10.0	High-Resolution Separation of PCB Congeners with Electron-Capture Detection						
	15 13 4	Alternate Methods for the Determination of Pesticides and PCBs						
15.14	GAS CH	ROMATOGRAPHIC METHODS USING DERIVATIZATION TO						
10.1T	DETERM	MINE NONVOLATILE COMPOUNDS AND CHLORINATED ACID						
	~~ = 4 = 1141	TOTA OF THE COMPOUNDS AND CHECKINATED ACID						

**HERBICIDES** 

15.14.1 Chlorinated Acid Herbicides

15.14.2 Haloacetic Acids

15.15	GAS CH	ROMATOC	RAPHIC METHODS FOR THE DETERMINATION OF		
	ORGAN	OMETALL!	IC COMPOUNDS		
15.16	ANALY:	SIS OF AIR	BORNE POLLUTANTS		
	15.16.1	The Deterr	nination of Volatile Organic Compounds in Air Using		
		Adsorbents	and Gas Chromatography		
	15.16.2	The Determ	nination of Volatile Organic Compounds in Air Using		
		SUMMA (	Canisters and GCMS with Cryogenic Trapping		
	15.16.3		nination of Semivolatile Organic Compounds in Air		
15.17	HANDL	ANDLING OF GAS CHROMATOGRAPHIC DATA IN ENVIRONM			
	ANALY	SIS			
	15.17.1	Quantificat	ion		
	15.17.2	Qualificati	on		
	15.17.3	Quality As	surance and Control		
		15.17.3.1	Initial Demonstration of Proficiency (IDPF)		
		15.17.3.2	Surrogate Standards (SSs)		
		15.17.3.3	Method Blanks (MBs)		
		15.17.3.4	Laboratory Control Samples (LCSs)		
		15.17.3.5	Matrix Spike Samples and Duplicates (MSs and MSDs)		
		15.17.3.6	Quality Control Charts		
		15.17.3.7	Performance Evaluation Standards (PESs)		

15.17.4 Method Detection Limits and the Limit of Quantitation
15.18 THE FUTURE OF GAS CHROMATOGRAPHY IN ENVIRONMENTAL

ANALYSIS ACKNOWLEDGMENTS

# Forensic Science Applications of Gas Chromatography

#### THOMAS A. BRETTELL

INTRODUCTION

16.1

16.6

16.7

New Jersey State Police Forensic Science Laboratory, Hamilton, New Jersey

#### Part 1 Introduction

	16.1.1	Definition and Scope of Forensic Science			
	16.1.2	Functions of the Forensic Scientist			
16.2	PHYSIC	CAL EVIDENCE			
	16.2.1	Types of Evidence			
	16.2.2	Identification versus Comparison			
	16.2.3	Class versus Individual Characteristics			
		Part 2 Drug Analysis by Gas Chromatography			
16.3	CONSI	DERATIONS IN FORENSIC DRUG ANALYSIS WITH GAS			
	CHRON	MATOGRAPHY			
	16.3.1	Introduction to the Analysis of Drugs of Abuse			
	Controlled Dangerous Substance (CDS)				
		Laws and Schedules			
	16.3.3	Types of Physical Evidence: Sample Preparation			
16.4	QUALI	TATIVE ANALYSIS OF DRUGS OF ABUSE			
	16.4.1	Narcotics			
	16.4.2	Stimulants			
	16.4.3	Cocaine			
	16.4.4	Barbiturates			
	16.4.5	Benzodiazepines			
	16.4.6	Cannabinoids			
	16.4.7	Hallucinogens			
	16.4.8	Anabolic Steroids			
16.5	QUAN'	TITATIVE ANALYSIS OF DRUGS OF ABUSE			

SOURCE DISCRIMINATION AND IDENTIFICATION

CLANDESTINE LABORATORY ANALYSIS

### Part 3 Gas Chromatography in Forensic Toxicology

16.8	APPLICATIONS OF GAS CHROMATOGRAPHY IN FORENSIC
	TOXICOLOGY

16.8.1 Drug Analysis in Biological Fluids and Tissues

16.8.1.1 Sample Preparation

16.8.1.2 Screening for Drugs of Abuse

16.8.1.3 Analysis of Unconventional Samples

16.8.2 Analysis of Ethanol and Other Volatiles

16.8.2.1 Determination of Ethanol in Biological

**Fluids** 

16.8.2.2 Direct-Injection Technique

16.8.2.3 Static Headspace Procedure

16.8.2.4 Solid-Phase Microextraction

16.8.2.5 Miscellaneous

### Part 4 Applications of Gas Chromatographic Analysis of Trace Evidence

# 16.9 DETECTION OF IGNITABLE LIQUID RESIDUES FROM FIRE DEBRIS WITH GAS CHROMATOGRAPHY

16.9.1 Introduction

16.9.2 Collection and Packaging of Evidence

16.9.3 Chromatographic Characterization of Ignitable Liquid Residues

16.9.4 Sample Preparation

16.9.4.1 Distillation

16.9.4.2 Solvent Extraction

16.9.4.3 Static Headspace

16.9.4.4 Passive Headspace

16.9.4.5 Dynamic Headspace

16.9.4.6 Detection

16.9.5 Comparison of Gasoline Samples

### 16.10 EXPLOSIVES ANALYSIS WITH GAS CHROMATOGRAPHY

16.10.1 Introduction

16.10.2 Electron-Capture Detection of Explosives

16.10.3 Thermal Energy Analyzers

16.10.4 Gas Chromatography/Mass Spectrometry

# 16.11 FORENSIC SCIENCE APPLICATIONS OF PYROLYSIS GAS CHROMATOGRAPHY

16.11.1 Introduction

16.11.2 Pyrolysis Gas Chromatographic Methods

16.11.2.1 Curie Point Pyrolysis (Inductive Heating)

16.11.2.2 Filament and Ribbon Pyrolysis (Resistive Heating)

#### 16.11.3 Applications

16.11.3.1 Paint

16.11.3.2 Fibers

16.11.3.3 Other Polymers

16.11.3.4 Miscellaneous Applications of Pyrolysis Gas Chromatography

INTRODUCTION

CHROMATOGRAPHY

# Validation and QA/QC of Gas Chromatographic Methods

TH	10	М	$\Delta S$	Δ	RR	FI	ΤE	1
	ı	w	~~	_	1313	_		ᆫ

New Jersey State Police Forensic Science Laboratory, Hamilton, New Jersey

#### RICHARD E. LESTER

Federal Bureau of Investigation (FBI) Academy, Quantico, Virginia

17.1	INTRO	DUCTION					
17.2	<b>PROCU</b>	REMENT					
	17.2.1	<b>Facilities</b>					
	17.2.2	Installation	n and Setup				
	17.2.3	Installation	n Qualification (IQ)				
	17.2.4	Operations	al Qualification (OQ)				
17.3	PERFO	RMANCE	QUALIFICATION (PQ)				
	17.3.1	Service ar	nd Maintenance of a Gas Chromatograph				
		17.3.1.1	Original Quality Replacement Parts				
		17.3.1.2	Verification after Service				
17.4	PERSO	NNEL AN	D TRAINING				
17.5	STAND	STANDARD OPERATING PROCEDURES (SOPs)					
	17.5.1	Preparatio	n, Modification, and Revision of SOPs				
	17.5.2	Validation	of Gas Chromatographic Methods				
		17.5.2.1	Minimum Criteria				
			Selectivity				
		17.5.2.3	Initial Calibration				
		17.5.2.4	Calibration Linearity				
			Accuracy				
			Precision				
		17.5.2.7	Range of Method				
		17.5.2.8	Limit of Detection				
		17.5.2.9	Limit of Quantification				
			Ruggedness of Method				
		17.5.2.11	Robustness of Method				

17.5.2.12 Software Validation
17.5.3 Sample Tracking and Chain of Custody

### 970 VALIDATION AND QA/QC OF GAS CHROMATOGRAPHIC METHODS

- 17.5.4 Statistical Process Control 17.5.4.1 Duplicate Analysis 17.6 DOCUMENTATION
  - 17.6.1 Written Instructions
  - 17.6.2 Logbooks
  - 17.6.2 Logook 17.6.3 Reports
  - 17.6.4 Archiving, Storage, and Retrieval of Documents