ON-LINE PROCESS ANALYZERS

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PREFACE

This book is an outgrowth of my introduction to the world of industrial chemistry by being assigned to develop on-line process analyzers in a large industrial chemical plant. Analytical chemistry is the primary intrinsic characteristic of process analyzer development. However, electrical engineering, chemical engineering, process control engineering, and broad knowledge of practical manufacturing plant operations are also vital to the successful design, engineering, operation, and maintenance of process analyzers. Because of the cross-disciplinary nature of process analyzer work, I saw the need for a short, practical introduction to process analyzers for reference by workers in process analyzer manufacturing, engineering, installation, use, and maintenance.

Furthermore, I encourage the use of this text in the academic environment so that students entering industry might be better prepared for the work which awaits them. The text is also intended to be suitable for in-house or institutional continuing education courses for individuals who already have worked with process analyzers. The text is written at the college level so that individuals who have completed basic chemistry and physics and some intermediate chemistry will feel comfortable with the material.

The text is organized into four distinct parts: I, Fundamental Instrumental Methods; II, Derived Instrumental Methods; III, Sample Systems; and IV, Process Analyzer Project Management. Part I includes explanations of the six analytical methods that account for most process analyzer applications in the chemical and related manufacturing industries. Part II covers derived analytical methods that are likely to be encountered in many manufacturing industries. Part III describes process analyzer sample systems because, from a practical standpoint, most of the effort in process analyzer applications engineering

involves obtaining a sample suitable for the analyzer. Part IV is a discussion on project management for practical process analyzer design, engineering, and maintenance.

Each chapter in Part I includes a section on theory. However, this theory is only intended to explain the basic physical principles that apply to the method under discussion. The theory sections are not intended as descriptions of academic research; to have included academic research material would have detracted from the purpose of the book. Rather, the applications sections of the chapters reflect the intention of the book as an aid to process analyzer manufacturers and users.

Each chapter can be read independently of the others, depending upon the reader's background and objective. For example, an engineer or chemist who is faced with designing a gas chromatograph installation for air monitoring can read only the gas chromatography and air monitoring chapters and carefully scan the sample system chapter and the project management chapter for topics relevant only to the job at hand. On the other hand, an instrument/analyzer engineer may wish to read the entire text thoroughly in order to gain a broad understanding of the equipment available for the solution of chemical analysis problems. Process analyzer manufacturers should find the applications parts of each chapter helpful in understanding the market and the sample systems and project management chapters helpful in recognizing problems that process analyzer users face daily.

Some process analyzer designs have been excluded. Those that are not covered include X-ray fluorescence, color, Btu, and flash-point analyzers. This is not a reflection upon the manufacturers and users of these analyzers. Rather, it is a reflection of the limited uses of these analyzers and the need to put a practical limit on the scope of the book. On the other hand, process mass spectrometers were included because I feel that this is an underused process analytical method.

Lastly, I sincerely hope that this book will stimulate interest in and use of process analyzers as economical, money-saving process control instruments. I encourage readers to get in touch with me with comments, kudos, criticism, and questions.

GARY D. NICHOLS

Geismar, Louisiana
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CONTENTS

List of Symbols xv

List of Trademarks xviii

PART I PROCESS ANALYZER FUNDAMENTAL METHODS

Chapter 1 Photometric Analyzers 3

Introduction, 3
Infrared Photometry, 4
Ultraviolet and Visible Photometry, 6
Instrumentation, 9
Photometric Analyzer Geometries, 19
Applications, 23
References, 27
Bibliography, 27

Chapter 2 Gas Chromatography 28

Introduction, 28
Instrumentation, 30
Theory, 43
Capillary Columns, 49
Applications, 52
References, 58
Bibliography, 59

Chapter 3 Liquid Chromatography 60
Introduction, 60
Instrumentation, 61
Theory, 72
Types of HPLC, 79
Applications, 82
References, 88
Bibliography, 88

Chapter 4 Electrochemical Process Analyzers 89
Introduction, 89
Potentiometry, 90
Coulometry, 102
Amperometry, 104
Conductivity, 105
Automatic Titrators, 112
References, 115
Bibliography, 116

Chapter 5 Oxygen Analyzers 117
Introduction, 117
Paramagnetic Oxygen Analyzers, 117
Electrochemical Oxygen Analyzers, 123
Oxygen Analyzer Applications, 128
References, 135
Bibliography, 136

Chapter 6 Process Mass Spectrometry 137
Introduction, 137
Theory, 139
Instrumentation, 146
Applications, 158
References, 165
Bibliography, 166

PART II DERIVED PROCESS ANALYSIS METHODS

Chapter 7 Water Quality Monitoring 169
Introduction, 169
Chlorine, 171
Silica, 171
Boiler Feed Water and Steam Condensate, 173
Turbidity, 174

Total Organic Carbon, 178
Dissolved Oxygen, 179
Hardness, 181
Hydrocarbons, 182
References, 185

Chapter 8 Air Quality Analyzers 186
Introduction, 186
Photometric Analyzers, 187
Electrochemical Analyzers, 190
Chromatographic Analyzers, 193
References, 196

Chapter 9 Moisture Analysis 197
Introduction, 197
Aluminum Oxide Sensors, 198
Phosphorus Pentoxide Sensors, 199
Photometric Moisture Analysis, 200
Corrosion Monitors, 202
Oscillating Crystals, 205
Applications, 206
References, 210
Bibliography, 210

Chapter 10 Physical Properties 211
Introduction, 211
Density, 212
Index of Refraction, 214
Viscosity, 218
Dielectric Constant, 220
Thermal Conductivity, 223
Extrinsic Physical Properties, 224

PART III SAMPLE SYSTEMS

Chapter 11 Sample Systems 227
Introduction, 227
Sample System Components, 230
General Characteristics of Sample Systems, 252
Applications, 259
References, 263
Bibliography, 263

PART IV PROCESS ANALYZER PROJECT MANAGEMENT

Chapter 12 Project Engineering and Management 267

Analyzer Project Management, 267
Engineering Economics, 270
Process Control, 274
Materials of Construction, 274
Site Preparation and Utilities, 276
Process Analyzer Record-Keeping, 276
Process Analyzer Maintenance, 278
Vendor Relations, 281
Engineering Consultants, 282
Technological Advancements, 283
Reference 283

Appendix 284

Electrical and Fire Code, 284
Organizations with Significant Concern for Process Analyzers, 287
Bibliography, 288

Index 291

LIST OF SYMBOLS

Symbol	*Definition*	*Chapter*
a	Diffusion layer thickness	5
a	Area of heat transfer	11
A	Absorbance	1
A	Eddy diffusion term	2, 3
A	Cross-sectional area	4, 9
A	Interfacial area	10
A	Electrode area	10
b	Path length	1
B	Molecular diffusion term	2
B	Axial diffusion term	3
c	Concentration	1, 11
C	Mass transfer term	2
C	Concentration gradient	5
C	Capacitance	10
C_0	Capacitance in a vacuum	10
C_M	Mass transfer (radial)	3
C_S	Mass transfer (interface)	3
d	Pipe or tube diameter	11
d	Mass transfer coefficient	11
D	Diffusion coefficient	5
D_0	Reference diffusion coefficient	5
e	Electronic charge	6
e	Dielectric constant	10

Symbol	*Definition*	*Chapter*
E	Cell potential	4
E	Potential	5
E	Diffusion activation energy	5
E_h	Half-cell potential	4
E_j	Junction potential	4
E_m	Measuring electrode potential	4
E_0	Standard electrode potential	4
E_r	Reference electrode potential	4
E_{tot}	Circuit potential	4
F	Faraday constant	4, 5
F	Force	10
F	Electrical force	10
g	Gravitational acceleration	11
h	Height	11
h	Heat transfer coefficient	11
H	See HETP	3
H	Magnetic field strength	6
HETP	Height equivalent to a theoretical plate	2
i	Current	4, 5, 9
i	Angle of incidence	10
i_c	Critical angle	10
j	Transported mass	11
k	Thermal conductivity	11
K	Instrument constant	9
l	Electrode gap	4, 10
l	Conducting path length	9
l	Separation of fluid layers	10
L	Column length	2
L	Conductance	4
m	Mass	6
M	Mass number	6
n	Number of electrons	4, 5
n	Index of refraction	10
N	Number of theoretical plates	2
N	Number of coulombs of charge	4
p	Pressure	11
p_{gauge}	Gauge pressure	11
P_r	Partial pressure (reference)	5
P_s	Partial pressure (sample)	5
q	Electrical charge	10
q	Heat	11
Q	Cell equilibrium constant	4
r	Radius of curvature	6

Symbol	*Definition*	*Chapter*
r	Angle of refraction	10
r	Distance of separation	10
R	Resolution	2, 6
R	Electrical resistance	4, 9
R	Universal gas constant	5
R	Corrosion rate	9
R_S	Resolution	3
Re	Reynolds number	11
s	Distance of travel	6
t	Time	4
t	Time of travel	6
t	Temperature	11, 11
t_D	Peak separation	3
t_M	Mobile hold-up time	3
t_R	Retention time	2, 3
t'_R	Adjusted retention time	3
T	Transmittance	1
T	Absolute temperature	5
u	Linear flow rate	2
u'	Average linear flow rate	3
v	Velocity	6
v	Fluid velocity	10
V	Volume of sample	4
V	Accelerating potential	6
w	Peak width	2
w	Separation of adjacent masses	6
w_h	Peak width at half height	3
x	Thickness of medium	11
y	Relative height	11
y	Mass transfer distance	11
Δ	Difference	
ε	Molar absorptivity	1
κ	Specific conductance	4
μ	Kinematic viscosity	11
ρ	Specific resistance	4
ρ	Electrical resistivity	9
ρ	Fluid density	11
σ	Stefan–Boltzmann constant	11

LIST OF TRADEMARKS

Teflon: E. I. DuPont
Monel: International Nickel Co.
Hastelloy: Cabot Corp.
Nichrome: Driver-Harris Co.
Irtran: Eastman Kodak Co.
Swagelok: Crawford Fitting Co.
Gyrolok: Hoke, Inc.
Carbopak: Supelco, Inc.
Supelcoport: Supelco, Inc.
Carbowax: Union Carbide, Inc.
Dowfax: Dow Chemical Co.
Porapak: Waters Associates, Inc.
Chromosorb: Manville Corp.
RP-2: Lycrosorb Co. and Lycrosphere Co.
Warfarin: Wisconsin Alumni Research Foundation
Kynar: Pennwalt Corp.
Nafion: E. I. DuPont

PART I

PROCESS ANALYZER FUNDAMENTAL METHODS

1

PHOTOMETRIC ANALYZERS

INTRODUCTION

Photometry is the quantitative measurement of the concentration of a substance based upon the property of the substance for absorbing electromagnetic radiation and the existence of a method for measuring the quantity of radiation absorbed. This broad definition of photometry could benefit from elaboration and clarification, but the definition is sufficient for explaining the use of photometry in process analysis. The "substance" to which the definition refers is the chemical process stream, including the stream component of particular interest in the process analysis and the chemical medium, whether desirable or undesirable, in which the component of interest is carried. This definition includes, but is not restricted to, visible light. The range of the electromagnetic spectrum of primary concern in this chapter begins with the far infrared region of the spectrum at about 25 wavenumbers (400 μm) and extends into the ultraviolet region at about 200 nm (0.2 μm).

Photometric analysis is possible because those substances that absorb electromagnetic radiation do so in proportion to the number of absorbing chemical species present. This phenomenon is commonly expressed mathematically as the Beer–Lambert law:

$$A = \varepsilon bc \tag{1}$$

where A is the absorbance, ε is the molar absorptivity, b is the thickness of the light-absorbing medium, and c is the concentration of the absorbing species in the medium.