

Principles and Practice of Analytical Chemistry

Fourth Edition

F. W. FIFIELD and D. KEALEY
Kingston University



BLACKIE ACADEMIC & PROFESSIONAL

An Imprint of Chapman & Hall

London · Glasgow · Weinheim · New York · Tokyo · Melbourne · Madras

Contents

Preface	ix
Acknowledgements	xi
CHAPTER 1 INTRODUCTION	1
The scope of analytical chemistry. The function of analytical chemistry. Analytical problems and their solution. The nature of analytical methods. Trends in analytical methods and procedures. Glossary of terms.	
CHAPTER 2 THE ASSESSMENT OF ANALYTICAL DATA	14
2.1	Definitions and basic concepts 14
2.2	The nature and origin of errors 16
2.3	The evaluation of results and methods 18
The reliability of measurements. The analysis of data. The application of statistical tests. Limits of detection. Quality control charts. Standardization of analytical methods. Chemometrics.	
CHAPTER 3 pH, COMPLEXATION AND SOLUBILITY EQUILIBRIA	37
3.1	Chemical reactions in solution 38
Equilibrium constants. Kinetic factors in equilibria.	
3.2	Solvents in analytical chemistry 42
Ionizing solvents. Non-ionizing solvents.	
3.3	Acid-base equilibria 43
Weak acid and weak base equilibria. Buffers and pH control. The pH of salt solutions.	
3.4	Complexation equilibria 50
The formation of complexes in solution. The chelate effect.	
3.5	Solubility equilibria 53
Solubility products.	
CHAPTER 4 SEPARATION TECHNIQUES	55
4.1	Solvent extraction 56
Efficiency of extraction. Selectivity of extraction. Extraction systems. Extraction of uncharged metal chelates. Methods of extraction. Applications of solvent extraction.	
4.2	Chromatography 75
4.2.1 Gas chromatography. 4.2.2 High performance liquid chromatography. 4.2.3 Supercritical fluid chromatography. 4.2.4 Thin-layer chromatography. 4.2.5 Ion-exchange chromatography. 4.2.6 Gel-permeation chromatography.	

4.3	Electrophoresis	164
	Factors affecting ionic migration. Effect of temperature, pH and ionic strength. Electroosmosis. Supporting medium. Detection of separated components. Applications of traditional zone electrophoresis. High performance capillary electrophoresis.	
	CHAPTER 5 TITRIMETRY AND GRAVIMETRY	184
5.1	Titrimetry	184
	Definitions. Titrimetric reactions. Acid-base titrations. Applications of acid-base titrations. Redox titrations. Applications of redox titrations. Complexometric titrations. EDTA. Applications of EDTA titrations. Titrations with complexing agents other than EDTA. Precipitation titrations.	
5.2	Gravimetry	211
	Precipitation reactions. Practical gravimetric procedures. Applications of gravimetry.	
	CHAPTER 6 ELECTROCHEMICAL TECHNIQUES	223
6.1	Potentiometry	227
	Electrode systems. Direct potentiometric measurements. Potentiometric titrations. Null-point potentiometry. Applications of potentiometry.	
6.2	Polarography, stripping voltammetry and amperometric techniques	243
	Diffusion currents. Half-wave potentials. Characteristics of the DME. Quantitative analysis. Modes of operation used in polarography. The dissolved oxygen electrode and biochemical enzyme sensors. Amperometric titrations. Applications of polarography and amperometric titrations.	
6.3	Electrogravimetry and coulometry	257
	Coulometry. Coulometry at constant potential. Coulometric titrations. Applications of coulometric titrations.	
6.4	Conductometric titrations	261
	Ionic conductances.	
	CHAPTER 7 AN INTRODUCTION TO ANALYTICAL SPECTROMETRY	267
	Electromagnetic radiation. Atomic and molecular energy. The absorption and emission of electromagnetic radiation. The complexity of spectra and the intensity of spectral lines. Analytical spectrometry. Instrumentation.	
	CHAPTER 8 ATOMIC SPECTROMETRY	282
8.1	Arc/spark atomic (optical) emission spectrometry	287
	Instrumentation. Sample preparation. Qualitative and quantitative analysis. Interferences and errors associated with the excitation process. Applications of arc/spark emission spectrometry.	
8.2	Glow discharge atomic emission spectrometry	294
	Instrumentation. Applications.	

8.3	Plasma emission spectrometry	296
	Instrumentation. Sample introduction for plasma sources. Analytical measurements. Applications of plasma emission spectrometry.	
8.4	Inductively coupled plasma–mass spectrometry (ICP–MS)	304
	Principles. Instrumentation. Applications.	
8.5	Flame emission spectrometry	308
	Instrumentation. Flame characteristics. Flame processes. Emission spectra. Quantitative measurements and interferences. Applications of flame photometry and flame atomic emission spectrometry.	
8.6	Atomic absorption spectrometry	317
	Absorption of characteristic radiation. Instrumentation. Sample vaporization. Quantitative measurements and interferences. Atomic fluorescence spectrometry.	
8.7	X-ray emission spectrometry	331
	X-ray processes. Instrumentation. Applications of X-ray emission spectrometry.	
	CHAPTER 9 MOLECULAR SPECTROMETRY	351
9.1	Visible and ultraviolet spectrometry	361
	Polyatomic organic molecules. Metal complexes. Qualitative analysis – the identification of structural features. Quantitative analysis – absorptiometry. Choice of colorimetric and spectrophotometric procedures. Fluorimetry. Applications of UV/visible spectrometry and fluorimetry.	
9.2	Infrared spectrometry	377
	Diatomic molecules. Polyatomic molecules. Characteristic vibration frequencies. Factors affecting group frequencies. Qualitative analysis – the identification of structural features. Quantitative analysis. Sampling procedures. Applications of infrared spectrometry.	
9.3	Nuclear magnetic resonance spectrometry (nmr)	393
	Instrumentation. The nmr process. Chemical shift. Spin–spin coupling. Carbon-13 nmr. Pulsed Fourier transform nmr (ft-nmr). Quantitative analysis – the identification of structural features. Quantitative analysis. Applications of nmr spectrometry.	
9.4	Mass spectrometry	425
	Instrumentation. Principle of mass spectrometry. Characteristics and interpretation of molecular mass spectra. Applications of mass spectrometry.	
9.5	Spectrometric identification of organic compounds	436
	CHAPTER 10 RADIOCHEMICAL METHODS IN ANALYSIS	447
10.1	Nuclear structure and nuclear reactions	448
	Decay reactions. The kinetics of decay reactions. Bombardment reactions and the growth of radioactivity.	
10.2	Instrumentation and measurement of radioactivity	455
	Radiation detectors. Some important electronic circuits. The statistics of radioactive measurements.	

10.3	Analytical uses of radionucleides	465
	Chemical pathway studies. Radioisotope dilution methods. Radio-immunoassay. Radioactivation analysis. Environmental monitoring.	
CHAPTER 11 THERMAL TECHNIQUES		475
11.1	Thermogravimetry	477
	Instrumentation. Applications of TG.	
11.2	Differential thermal analysis (DTA)	482
	Instrumentation. Applications of DTA	
11.3	Differential scanning calorimetry (DSC)	489
	Instrumentation. Applications of DSC. DTA and DSC.	
11.4	Thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA)	493
	Instrumentation. Applications of TMA. Dynamic mechanical analysis.	
11.5	Pyrolysis – gas chromatography	497
	Instrumentation.	
CHAPTER 12 OVERALL ANALYTICAL PROCEDURES AND THEIR AUTOMATION		504
12.1	Sampling and sample pretreatment	504
	Representative samples and sample storage. Sample concentration and clean-up: solid phase extraction.	
12.2	Examples of analytical problems and procedures	509
	1: Evaluation of methods for the determination of fluoride in water samples. 2: Analysis of a competitive product. 3: The assessment of the heavy metal pollution in a river estuary. 4: The analysis of hydrocarbon products in a catalytic reforming study.	
12.3	The automation of analytical procedures.	519
	The automation of repetitive analysis. Constant monitoring and on line analysis. Laboratory robotics.	
CHAPTER 13 THE ROLE OF COMPUTERS AND MICRO-PROCESSORS IN ANALYTICAL CHEMISTRY		528
13.1	Introduction	528
	Instrument optimization. Data recording and storage. Data processing and data analysis (chemometrics). Laboratory management. Expert systems.	
13.2	Computers and microprocessors	534
	Mini- and microcomputers. Microprocessors.	
13.3	Instrument-computer interfaces	537
13.4	The scope of microprocessor control and computers in analytical laboratories	542
	1. A microprocessor-controlled potentiometric titrator. 2. An infrared spectrometer interfaced to a dedicated microcomputer. 3. A computing integrator for chromatographic analysis. 4. A microprocessor-based X-ray or γ -ray spectrometer.	
	Index	551