Physical Methods in Chemistry and Nano Science

Collection Editor:
Andrew R. Barron

Physical Methods in Chemistry and Nano Science

Collection Editor:

Andrew R. Barron

Authors:

John J. Allen
Andrew R. Barron
Simon Bott
Cara Bovet
Jarrod Boyd
Ariana Bratt
Pinn-Tsong Chiang
Brandon Cisneros
Charles Conn
Laurie Cullum
Paul Derry
Gabriela Escalera
Huilong Fei
Ezekial Fisher
Dennis J. Flood
Varun Shenoy Gangoli
Ayrat Gizzatov
Natalia Gonzalez Pech
Amanda M. Goodman
Sravani Gullapalli
Ty Hanna
Lauren Harrison
Mayra Hernandez Rivera
Kewei Huang
Chih-Chau Hwang
Nina Hwang
Meghan Jebb
Chengmin Jiang
Wilhelm Kienast
Sequoyah King
Inna Kurganskaya
Michelle LaComb
Justin Law
Jiebo Li
Lei Li
Xianyu Li
Wayne Lin
Yen-Hao Lin
Yen-Tien Lu
Andreas Luttge
Samuel Maguire-Boyle
Danielle Michaud
Shawdon Molavi
Gabriel Oaxaca
Brittany L. Oliva
Alvin Orbaek
Sehmus Ozden
Courtney Payne
Zhiwei Peng
Graham Piburn
Stacy Prukop
Tawana Robinson

Gedeng Ruan
Hannah Rutledge
Avishek Saha
Richa Sethi
Basil Shadfan
Carissa Smith
Nikolaos Soultanidis
Zhengzong Sun
Ryan Thaner
Juan Velazquez
Farrukh Vohidov
Xiewen Wen
Changsheng Xiang
Zheng Yan
Ruquan Ye
Zhun Zhao
Caoimhe de Fréin

Online:
< http://cnx.org/content/col10699/1.14/ >

C O N N E X I O N S

Rice University, Houston, Texas

This selection and arrangement of content as a collection is copyrighted by Andrew R. Barron. It is licensed under the Creative Commons Attribution 3.0 license (http://creativecommons.org/licenses/by/3.0/).
Collection structure revised: June 26, 2012
PDF generated: June 26, 2012
For copyright and attribution information for the modules contained in this collection, see p. 681.

Table of Contents

Introduction 1

1 Elemental Analysis

1.1 Introduction to Atomic Absorption Spectroscopy 3
1.2 ICP-AES Analysis of Nanoparticles 17
1.3 ICP-MS for Trace Metal Analysis 24
1.4 Introduction to Combustion Analysis 28
1.5 Ion Selective Electrode 43
1.6 A Practical Introduction to X-ray Absorption Spectroscopy 47
1.7 Fluorescence Spectroscopy 58
1.8 X-ray Photoelectron Spectroscopy 75
1.9 Auger Electron Spectroscopy 84
1.10 An Introduction to Energy Dispersive X-ray Spectroscopy 90
1.11 Rutherford Backscattering of Thin Films 98
1.12 An Accuracy Assessment of the Refinement of Crystallographic Positional Metal Disorder in Molecular Solid Solutions 106
1.13 Principles of Gamma-ray Spectroscopy and Applications in Nuclear Forensics 111
Solutions 117

2 Physical and Thermal Analysis

2.1 Melting Point Analysis 119
2.2 Solution Molecular Weight of Small Molecules 123
2.3 Molecular Weight of Polymers 129
2.4 Size Exclusion Chromatography and its Application in Polymer Science 144
2.5 Thermogravimetric Analysis 154
2.6 Differential Scanning Calorimetry (DSC) 180
2.7 BET Surface Area Analysis of Nanoparticles 185
2.8 Introduction to Cyclic Voltammetry Measurements 196
2.9 Determination of Relaxation Parameters of Contrast Agents 206
Solutions 211

3 Chemical Speciation

3.1 Magnetism 213
3.2 Raman Spectroscopy 241
3.3 IR Spectroscopy 261
3.4 UV-Visible Spectroscopy 288
3.5 Photoluminescence and Fluorescence Spectroscopy 295
3.6 Mossbauer Spectroscopy 315
3.7 NMR Spectroscopy 321
3.8 EPR Spectroscopy 355
3.9 X-ray Photoelectron Spectroscopy 365
3.10 ESI-QTOF-MS Coupled to HPLC and its Application for Food Safety 380
3.11 Mass Spectrometry 388
Solutions 395

4 Reactions Kinetics and Pathways

4.1 Dynamic Headspace Gas Chromatography Analysis 397
4.2 Gas Chromatography Analysis of the Hydrodechlorination Reaction of Perchloroethylene 408
4.3 Temperature-Programmed Desorption Mass Spectroscopy Applied in Surface Chemistry 413

5 Dynamic Processes

5.1 NMR of Dynamic Systems: An Overview 425
5.2 Rolling Molecules on Surfaces Under STM Imaging 429

6 Molecular and Solid State Structure

6.1 Crystal Structure 441
6.2 Structures of Element and Compound Semiconductors 459
6.3 X-ray Crystallography 470
6.4 Neutron Diffraction 492
6.5 XAFS 502
6.6 Circular Dichroism Spectroscopy and its Application for Determination of Secondary Structure of Optically Active Species 509
6.7 Protein Analysis using Electrospray Ionization Mass Spectroscopy 518
6.8 The Analysis of Liquid Crystal Phases using Polarized Optical Microscopy 526

7 Structure at the Nano Scale

7.1 Microparticle Characterization via Confocal Microscopy 535
7.2 Transmission Electron Microscopy 542
7.3 Scanning Tunneling Microscopy 560
7.4 Spectroscopic Characterization of Nanoparticles 577
7.5 Measuring the Specific Surface Area of Nanoparticle Suspensions using NMR 608
7.6 Characterization of Graphene by Raman Spectroscopy 619

8 Surface Morphology and Structure

8.1 The Application of VSI (Vertical Scanning Interferometry) to the Study of Crystal Surface Processes 623
8.2 Atomic Force Microscopy 634
8.3 SEM and its Applications for Polymer Science 639
8.4 Catalyst Characterization Using Thermal Conductivity Detector 650

9 Device Performance

9.1 A Simple Test Apparatus to Verify the Photoresponse of Experimental Photovoltaic Materials and Prototype Solar Cells 661

Index 670
Attributions 681

Introduction[1]

Course Introduction

Chem 475 is a survey course of research techniques used in modern chemistry, materials science, and nano science. The topics are grouped, not be method *per se*, but with regard to the type of information that can be obtained. Thus, the topics are ordered as follows:

- Elemental composition.
- Physical and thermal analysis.
- Chemical speciation.
- Dynamic processes.
- Reaction kinetics and pathways.
- Molecular structure.
- Structure at the nano scale.
- Surface morphology and structure.
- Optical properties.
- Device performance.

As a consequence of this organization methods can be found in different chapters. For example, X-ray photoelectron spectroscopy is included under *elemental composition* with regard to its use for determining the chemical composition, while it is included under *chemical speciation* with regard to determining the identity of component chemical moieties.

The modules in this course (to date) have been developed by the students in the class and the topics are representative of their research interests. As the course develops, further modules will be added and consequently some may overlap in subject matter.

[1] This content is available online at <http://cnx.org/content/m23040/1.9/>.

Chapter 1

Elemental Analysis

1.1 Introduction to Atomic Absorption Spectroscopy[1]

1.1.1 Brief overview of atomic absorption spectroscopy

1.1.1.1 History of atomic absorption spectroscopy

The earliest spectroscopy was first described by Marcus Marci von Kronland in 1648 by analyzing sunlight as is passed through water droplets and thus creating a rainbow. Further analysis of sunlight by William Hyde Wollaston (Figure 1.1) led to the discovery of black lines in the spectrum, which in 1820 Sir David Brewster (Figure 1.2) explained as absorption of light in the sun's atmosphere.

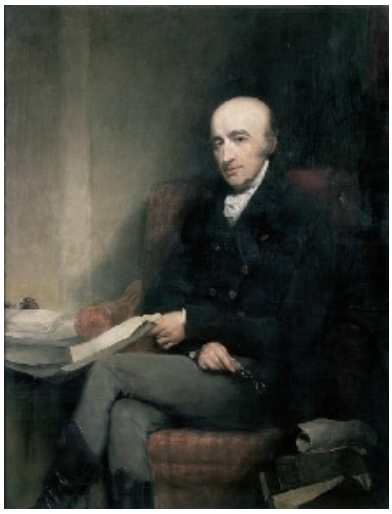

Figure 1.1: English chemist and physicist William Hyde Wollaston (1659 - 1724).

[1] This content is available online at <http://cnx.org/content/m38330/1.1/>.

Figure 1.2: Scottish physicist, mathematician, astronomer, inventor, writer and university principal Sir David Brewster (1781 - 1868).

Robert Bunsen (Figure 1.3) and Gustav Kirchhoff (Figure 1.4) studied the sodium spectrum and came to the conclusion that every element has its own unique spectrum that can be used to identify elements in the vapor phase. Kirchoff further explained the phenomenon by stating that if a material can emit radiation of a certain wavelength, that it may also absorb radiation of that wavelength. Although Bunsen and Kirchoff took a large step in defining the technique of atomic absorption spectroscopy (AAS), it was not widely utilized as an analytical technique except in the field of astronomy due to many practical difficulties.

Figure 1.3: German chemist Robert Bunsen (1811 - 1899).

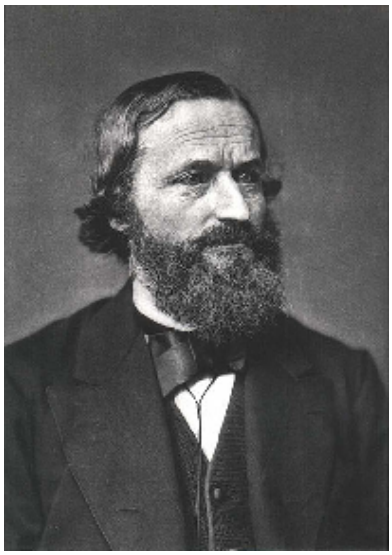

Figure 1.4: German physicist Gustav Robert Kirchhoff (1824 - 1887).

In 1953, Alan Walsh (Figure 1.5) drastically improved the AAS methods. He advocated AAS to many

instrument manufacturers, but to no avail. Although he had improved the methods, he hadn't shown how it could be useful in any applications. In 1957, he discovered uses for AAS that convinced manufactures market the first commercial AAS spectrometers. Since that time, AAS's popularity has fluctuated as other analytical techniques and improvements to the methods are made.

Figure 1.5: British physicist Sir Alan Walsh (1916 - 1988).

1.1.1.2 Theory of atomic absorption spectroscopy

In order to understand how atomic absorption spectroscopy works, some background information is necessary. Atomic theory began with John Dalton (Figure 1.6) in the 18^{th} century when he proposed the concept of atoms, that all atoms of an element are identical, and that atoms of different elements can combine to form molecules. In 1913, Niels Bohr (Figure 1.7) revolutionized atomic theory by proposing quantum numbers, a positively charged nucleus, and electrons orbiting around the nucleus in the what became known as the *Bohr model of the atom*. Soon afterward, Louis deBroglie (Figure 1.8) proposed quantized energy of electrons, which is an extremely important concept in AAS. Wolfgang Pauli (Figure 1.9) then elaborated on deBroglie's theory by stating that no two electrons can share the same four quantum numbers. These landmark discoveries in atomic theory are necessary in understanding the mechanism of AAS.

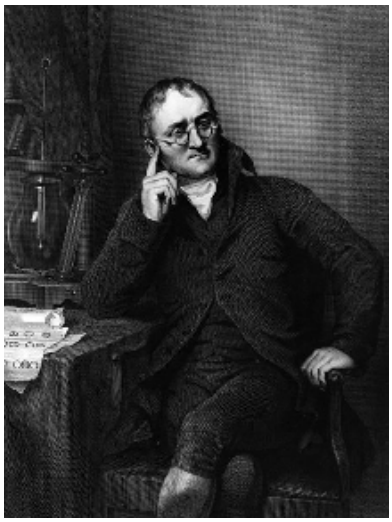

Figure 1.6: English chemist, physicist, and meteorologist John Dalton FRS (1766 - 1844).

Figure 1.7: Danish physicist Niels Henrik David Bohr (1885 - 1962).

Figure 1.8: French physicist and a Nobel laureate Louis de Broglie (1892 - 1987). Copyright: American Institute of Physics.

Figure 1.9: Austrian physicist Wolfgang Pauli (1900 - 1958).

Atoms have valence electrons, which are the outermost electrons of the atom. Atoms can be excited when irradiated, which creates an absorption spectrum. When an atom is excited, the valence electron moves up an energy level. The energies of the various stationary states, or restricted orbits, can then be determined

by these emission lines. The resonance line is then defined as the specific radiation absorbed to reach the excited state.

The Maxwell-Boltzmann equation gives the number of electrons in any given orbital. It relates the distribution to the thermal temperature of the system (as opposed to electronic temperature, vibrational temperature, or rotational temperature). Plank proposed radiation emitted energy in discrete packets (quanta) (1.1), which can be related to Einstein's equation, (1.2).

$$E = h\upsilon \tag{1.1}$$

$$E = mc^2 \tag{1.2}$$

Both atomic emission and atomic absorption spectroscopy can be used to analyze samples. Atomic emission spectroscopy measures the intensity of light emitted by the excited atoms, while atomic absorption spectroscopy measures the light absorbed by atomic absorption. This light is typically in the visible or ultraviolet region of the electromagnetic spectrum. The percentage is then compared to a calibration curve to determine the amount of material in the sample. The energy of the system can be used to find the frequency of the radiation, and thus the wavelength through the combination of equations (1.2) and (1.3).

$$\nu = c/\lambda \tag{1.3}$$

Because the energy levels are quantized, only certain wavelengths are allowed and each atom has a unique spectrum. There are many variables that can affect the system. For example, if the sample is changed in a way that increases the population of atoms, there will be an increase in both emission and absorption and *vice versa*. There are also variables that affect the ratio of excited to unexcited atoms such as an increase in temperature of the vapor.

1.1.2 Applications of atomic absorption spectroscopy

There are many applications of atomic absorption spectroscopy (AAS) due to its specificity. These can be divided into the broad categories of biological analysis, environmental and marine analysis, and geological analysis.

1.1.2.1 Biological analysis

Biological samples can include both human tissue samples and food samples. In human tissue samples, AAS can be used to determine the amount of various levels of metals and other electrolytes, within tissue samples. These tissue samples can be many things including but not limited to blood, bone marrow, urine, hair, and nails. Sample preparation is dependent upon the sample. This is extremely important in that many elements are toxic in certain concentrations in the body, and AAS can analyze what concentrations they are present in. Some examples of trace elements that samples are analyzed for are arsenic, mercury, and lead.

An example of an application of AAS to human tissue is the measurement of the electrolytes sodium and potassium in plasma. This measurement is important because the values can be indicative of various diseases when outside of the normal range. The typical method used for this analysis is atomization of a 1:50 dilution in strontium chloride ($SrCl_2$) using an air-hydrogen flame. The sodium is detected at its secondary line (330.2 nm) because detection at the first line would require further dilution of the sample due to signal intensity. The reason that strontium chloride is used is because it reduces ionization of the potassium and sodium ions, while eliminating phosphate's and calcium's interference.

In the food industry, AAS provides analysis of vegetables, animal products, and animal feeds. These kinds of analyses are some of the oldest application of AAS. An important consideration that needs to be taken into account in food analysis is sampling. The sample should be an accurate representation of what is being analyzed. Because of this, it must be homogenous, and many it is often needed that several samples are run. Food samples are most often run in order to determine mineral and trace element amounts so that

Thank You for previewing this eBook

You can read the full version of this eBook in different formats:

- HTML (Free /Available to everyone)
- PDF / TXT (Available to V.I.P. members. Free Standard members can access up to 5 PDF/TXT eBooks per month each month)
- Epub & Mobipocket (Exclusive to V.I.P. members)

To download this full book, simply select the format you desire below