Instrumental Analysis

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Preface

This text covers the most important methods of instrumental analysis which are generally not discussed in courses in physics and physical chemistry. The book is intended for undergraduate and graduate students. The material can be covered in about forty to sixty lectures, but a much shorter course is also possible. In this respect, Chapters 2, 3, 4, 8, and 9—which deal with potentiometry, polarography, emission spectroscopy, and absorption spectrometry—are essential even in an abridged course.

Theoretical discussions are quite elementary, but, I hope, rational. Simple diagrams which can be readily drawn on the blackboard are used throughout the book. Basic electrical and optical diagrams are given, but block diagrams are utilized in the representation of electronic circuits. The functions that amplifiers and other electronic components must fulfill in a given instrument are discussed, but I see no point in bewildering students with involved diagrams which are often available in the literature supplied by manufacturers. The reader is referred to Section 1 for further comments on the mode of approach adopted in this text.

Most chapters contain problems dealing with the extension and application of theory and with literature surveys of limited scope. The first group of problems is primarily intended for advanced students, while the two other groups are for general use. The short literature surveys may help undergraduate students to acquire some experience in library work.

Special attention is given to laboratory work to achieve proper balance between experiment and theory. More than fifty experiments are described in twenty-three sections, and suggestions for about twenty additional experiments are given. Experiments deal with the verification of the essential features of the various methods, rather than the application to the analysis of industrial materials. The reasons for this approach are given in Section 15–1.

It is a pleasure to express my sincere thanks to Dean A. R. Choppin of the College of Chemistry and Physics, Louisiana State University, and to Professor H. B. Williams, Head of the Chemistry Department. They helped greatly in creating the proper conditions and atmosphere for the writing of this book.

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Finally, I should like to express my appreciation to Mr. C. J. Malre who had the arduous task of preparing the preliminary version of the text from my hand-written notes. He also typed the final text and collaborated in the verification of references.

April 3, 1956
Baton Rouge, Louisiana

PAUL DELAHAY

ATOMIC WEIGHTS*

Element	Symbol	Atomic Number	Atomic Weight
Actinium	Ac	89	227
Aluminum	Al	13	26.98
Americium	Am	95	(243)
Antimony	Sb	51	121.76
Argon	A	18	39.944
Arsenic	As	33	74.91
Astatine	At	85	(210)
Barium	Ba	56	137.36
Berkelium	Bk	97	(245)
Beryllium	Be	4	9.013
Bismuth	Bi	83	209.00
Boron	B	5	10.82
Bromine	Br	35	79.916
Cadmium	Cd	48	112.41
Calcium	Ca	20	40.08
Californium	Cf	98	(246)
Carbon	C	6	12.010
Cerium	Ce	58	140.13
Cesium	Cs	55	132.91
Chlorine	Cl	17	35.457
Chromium	Cr	24	52.01
Cobalt	Co	27	58.94
Copper	Cu	29	63.54
Curium	Cm	96	(243)
Dysprosium	Dy	66	162.46
Erbium	Er	68	167.2
Europium	Eu	63	152.0
Fluorine	F	9	19.00
Francium	Fr	87	(223)
Gadolinium	Gd	64	156.9
Gallium	Ga	31	69.72
Germanium	Ge	32	72.60
Gold	Au	79	197.2
Hafnium	Hf	72	178.6
Helium	He	2	4.003
Holmium	Ho	67	164.94
Hydrogen	H	1	1.0080
Indium	In	49	114.76
Iodine	I	53	126.91
Iridium	Ir	77	193.1
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.92
Lead	Pb	82	207.21
Lithium	Li	3	6.940
Lutetium	Lu	71	174.99
Magnesium	Mg	12	24.32
Manganese	Mn	25	54.93
Mercury	Hg	80	200.61
Molybdenum	Mo	42	95.95
Neodymium	Nd	60	144.27
Neptunium	Np	93	(237)
Neon	Ne	10	20.183
Nickel	Ni	28	58.69
Niobium (columbium)	Nb	41	92.91
Nitrogen	N	7	14.008
Osmium	Os	76	190.2
Oxygen	O	8	16.0000
Palladium	Pd	46	106.7
Phosphorus	P	15	30.975
Platinum	Pt	78	195.23
Plutonium	Pu	94	(242)
Polonium	Po	84	210
Potassium	K	19	39.100
Praseodymium	Pr	59	140.92
Promethium	Pm	61	(145)
Proactinium	Pa	91	231
Radium	Ra	88	226.05
Radon	Rn	86	222
Rhenium	Re	75	186.31
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.48
Ruthenium	Ru	44	101.7
Samarium	Sm	62	150.43
Scandium	Sc	21	44.96
Selenium	Se	34	78.96
Silicon	Si	14	28.09
Silver	Ag	47	107.880
Sodium	Na	11	22.997
Strontium	Sr	38	87.63
Sulfur	S	16	32.066
Tantalum	Ta	73	180.88
Technetium	Tc	43	(99)
Tellurium	Te	52	127.61
Terbium	Tb	65	159.2
Thallium	Tl	81	204.39
Thorium	Th	90	232.12
Thulium	Tm	69	169.4
Tin	Sn	50	118.70
Titanium	Ti	22	47.90
Tungsten (wolfram)	W	74	183.92
Uranium	U	92	238.07
Vanadium	V	23	50.95
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.92
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

***Data between parentheses are mass numbers for most stable isotopes.**

Instrumental Analysis

Contents

Chapter 4. POLAROGRAPHY AND VOLTAMMETRY

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Chapter 5. AMPEROMETRIC AND VOLTAMMETRIC TITRATIONS

电[illegible]

Chapter 6. ELECTROGRAVIMETRY, ELECTROLYTIC SPEARATIONS, AND COULOMETRIC METHODS

coulomb [illegible]

电导 [illegible]

Chapter 7. CONDUCTOMETRY AND HIGH-FREQUENCY METHODS

Chapter 8. EMISSION SPECTROSCOPY

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✓ *Chapter 9.* ABSORPTION SPECTROMETRY AND FILTER PHOTOMETRY

[illegible] — 比浊测定法.

Chapter 10. FLUOROMETRY, TURBIDIMETRY, AND NEPHELOMETRY

喇光谱测定法

Chapter 11. RAMAN SPECTROSCOPY

Chapter 12. X-RAY METHODS

Chapter 13. MASS SPECTROMETRY

核一

Chapter 14. NUCLEAR RADIATION METHODS

[illegible]

Chapter 15. LABORATORY EXPERIMENTS

1

Scope of Instrumental Analysis

1-1. INTRODUCTION

Instrumental analysis deals with the application of methods of physics and physical chemistry to chemical analysis. These methods find an ever increasing number of applications for two reasons: (1) they greatly reduce the duration of many analyses which are quite tedious by noninstrumental methods; (2) they can be applied to the determination of substances under conditions in which classical methods fail.

There is no fundamental difference between instrumental and noninstrumental methods. Even such a classical method as gravimetry involves the use of an instrument, the balance, and the discussion of noninstrumental methods involves physical chemistry. It is true that equipment in instrumental analysis is often more complicated than the balance, but this is only a matter of degree, not a fundamental difference. "Instrumental analysis" is merely a convenient expression for grouping a variety of methods.

The opinion is sometimes advanced that instrumental analysis should be reserved for graduate studies. Yet, it should be recognized that many students find it most helpful to have some knowledge of instrumental analysis, and therefore an undergraduate course in this field fulfills a useful function. Some background in physics and physical chemistry is required, but this background can be acquired with little repetition of the material presented in other courses. A rather deep insight of most instrumental methods can be gained by a relatively simple and yet rational presentation.

Instruments are often composed of rather complicated electronic, optical, and mechanical parts, and a thorough knowledge of instrumentation engineering is essential in instrument design. This is not the case in the discussion of fundamentals of instrumental analysis. Instrumentation, which is encountered in all physical sciences, is a subject different from instrumental analysis.[1] We shall discuss the functions which instruments must fulfill often without going into the detail of instrumentation. For example, block diagrams will be used systematically in the representation of electronic components of instruments. However, fundamental electrical circuits (not electronic ones) and basic optical diagrams will be discussed because they are essential to the understanding of instrumental methods. Commercial instruments will be mentioned, but these will not be discussed in detail since they embody the ideas developed in the text. The student has opportunities to use commercial instruments in the laboratory, and he may find it fruitful to study the literature provided by manufacturers.[2]

Instrumental methods can be classified in various ways according to the criterion which is adopted: quantity being measured, type of methods, etc. We shall divide instrumental methods into the following three broad groups: (1) methods derived from electrochemistry; (2) methods based on the emission or absorption of radiation by matter; (3) miscellaneous methods which do not belong to the first two groups.

1-2. CLASSIFICATION OF ELECTROCHEMICAL METHODS

Instrumental methods derived from electrochemistry, i.e., methods of *electroanalytical chemistry*, will be discussed first because they involve simpler elements of instrumentation than most other methods.

A classification of electrochemical methods can be made by considering the operation of an electrochemical cell. Such a cell is composed of two metallic electrodes immersed in an electrolyte and connected to some device exchanging energy with the cell. A storage battery is an example of an electrochemical cell which supplies energy during discharge and consumes energy during the charging process. The electrochemical behavior of such a cell can be characterized by measuring different electrical quantities: quantity of electricity, voltage, current, resistance, and dielectric constant. The corresponding methods of analysis can be classified accordingly.

Analytical methods based on the measurement of a quantity of electricity are designated by the generic term of *coulometry*. The term is derived from "coulomb," which is one of the units for a quantity of electricity.

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[1] I. M. Kolthoff, *Chem. Eng. News*, **28**, 2882 (1950).

[2] It is suggested that a file of material on the most important commercial instruments—even those which are not used in the course—be kept in the laboratory and made available to students.

Coulometric methods are based on the proportionality relationship that exists between the quantity of electricity and the quantity of substance transformed during electrolysis.

Potentiometry groups a variety of electrochemical methods in which the result of the analysis is deduced from the voltage across an electrochemical cell. The term *potentiometry* is derived from the word "potential," which is used to designate the voltage across an electrochemical cell under conditions discussed in Chapter 2. The result of the analysis can be computed directly from the voltage across the cell, or the equivalence point of a titration can be determined from the variations of this voltage during titration (*potentiometric titrations*).

Amperometry designates methods involving current measurements. Amperometric methods are generally applied to the detection of the equivalence point of titrations (*amperometric titrations*).

The interpretation of current-voltage characteristics of electrochemical cells leads to several useful methods which are grouped under the general term of *voltammetry*. Various types of electrodes can be utilized in voltammetry, but one of them, the dropping mercury electrode, is particularly useful, and the corresponding voltammetric method is referred to as *polarography*.

The measurement of the resistance of an electrochemical cell can sometimes be useful in chemical analysis. The resistance is the ratio of the voltage applied to the cell to the current through the cell (Ohm's law). As we shall see in Chapter 7, the conductance, which is the reciprocal of the resistance, is generally used in electrochemistry. Methods based on conductance measurements are grouped under the term of *conductometry*. The result of an analysis can sometimes be computed directly from conductance measurements, but conductometry is more frequently applied to the determination of the equivalence point of titrations (*conductometric titrations*).

For reasons discussed in Chapter 7, conductances are generally measured by using alternating current at relatively low frequencies, for example, 1000 cycles per second. The possibility and usefulness of using much higher frequencies (several megacycles per second) were recognized rather recently, and several *high-frequency methods* have been devised. These methods can sometimes be applied to the measurement of dielectric constants.

Separations can be made by electrochemical methods. For example, copper can be removed from a solution of one of its salts by electrodeposition on a platinum electrode. This method, which is called *electrogravimetry*, is somewhat similar to conventional gravimetry inasmuch as electricity can be regarded as the reagent used in the precipitation of the element to be analyzed. A similar procedure can also be applied to the separation of an undesired constituent from a mixture (*electrolytic separation*).

The following order will be adopted in the study of the above methods:

Potentiometry
Voltammetry and Polarography
Amperometric Titrations
Electrogravimetry and Electrolytic Separations
Coulometry
Conductometry and High-Frequency Methods

The understanding of electrode potentials is essential in electroanalytical chemistry, and potentiometry therefore will be treated first. Amperometry is discussed after voltammetry and polarography because the latter two methods have a more general scope than the former one. Electrogravimetry is the simplest and the oldest of electrochemical methods, but it will be discussed after potentiometry and voltammetry because some of the ideas introduced in the treatment of these two methods are essential to the rational understanding of electrogravimetry. The same reason holds for coulometry. Conductometry and high-frequency methods will be treated lastly because they are very different from the other electroanalytical methods.

1-3. CLASSIFICATION OF METHODS INVOLVING EMISSION OR ABSORPTION OF RADIATION

Methods based on the study of absorption and emission of radiation are among the most useful and versatile of chemical analysis. Colorimetry is a familiar example of a simple method based on absorption of light. Methods involving visible and ultraviolet light were first applied to analytical chemistry, but the newer methods cover a much wider range of wave lengths. The following order will be adopted:

Emission Spectroscopy
Absorption Spectrometry in the Visible, Ultraviolet, and Infrared Ranges
Fluorometry
Turbidimetry and Nephelometry
Raman Spectroscopy
X-ray Methods

The characteristic spectrum produced by excitation of elements is applied to qualitative and quantitative analysis in *emission spectroscopy*. Several methods of excitation are employed: arc, spark, and flame. The latter method is used in an emission spectroscopy method referred to as *flame photometry*.

Absorption spectrometry is based on the measurement of the absorption of electromagnetic radiation by matter. The absorption varies with the wave length of the incident radiation, and measurements can be made at a single wave length or over a wide range of wave lengths. Filters are often utilized to obtain a narrow bandwidth radiation, and the corresponding analytical method is known as *filter photometry*. Absorption measurements are also made with a source of monochromatic radiation of variable wave length (*spectrophotometry* or *absorption spectrometry*).

The absorption of light by certain substances is accompanied by reemission of light in the familiar phenomenon of fluorescence. The measurement of the intensity of fluorescence serves useful analytical purposes, especially in the determination of traces (*fluorometry*).

Analytical determinations can sometimes be made by measuring the opacity of a suspension of small particles (*turbidimetry*), but the application of this method often leads to uncertain results. *Nephelometry*, which involves the measurement of the intensity of light scattered by a suspension of small particles, is somewhat more useful than turbidimetry. Light is scattered mainly without change of wave length (Rayleigh effect), but also with change of wave length (*Raman effect*). Application of the Raman effect to analytical chemistry has proved valuable.

Two other optical methods, namely, *refractometry* and *polarimetry*, find applications in the analytical laboratory. Refractometry, which deals with the measurement of indexes of refraction, is often used in the identification of organic compounds. Quantitative applications are also possible. Polarimetry is applied to the determination of optically active substances, such as dextrose. Refractometry and polarimetry will not be discussed here because these methods are generally covered in courses in organic and physical chemistry.

The optical methods mentioned so far involve measurements over a wide range of wave lengths, which in practice vary from 40 μ (1 micron = 10^{-4} cm) in the infrared to 2000 A (1 angstrom = 10^{-8} cm) in the ultraviolet. Measurements below 2000 A are difficult until the wave length is lowered in the X-ray range (1 A). The applications of X-rays to analysis include *absorption*, *diffraction*, and *emission* (*X-ray fluorescence*) methods.

1-4. MISCELLANEOUS METHODS WHICH DO NOT BELONG TO THE PREVIOUS TWO GROUPS

We shall reserve for the end of our discussion the following methods: (1) *mass spectroscopy* and various methods of gas analysis, and (2) *nuclear radiation methods*.

This does not conclude the list of possible applications of physics and physical chemistry to chemical analysis. For instance, useful analytical determinations can be based on the measurement of the following quanti-