

W. G. BERL

Physical  
Methods in  
Chemical Analysis

VOLUME I

# PHYSICAL METHODS IN CHEMICAL ANALYSIS

*Edited by*

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VOLUME I

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## PREFACE

What are the functions of the chemical analyst? Are they not to provide and apply the tools and techniques with which the individual components of unknown chemical aggregates can be identified qualitatively and quantitatively? The entire science of chemistry, be it structural organic chemistry, reaction kinetics, or the biochemistry of living cells, rests squarely on this ability to disentangle the numerous strands of a complex system and to isolate those parts that are of significance to the problem under investigation. And the analyst is charged with the task of providing the means and methods which permit this identification quickly and accurately in more and more complex situations.

In the past quarter of a century a change, or rather a widening of horizons, has taken place in the domain of chemical analysis. The change has been gradual at first but is proceeding at a vastly accelerated pace at the present time. The nineteenth century saw an unparalleled flowering of what are now the "classical" methods of chemical analysis, namely the development of gravimetric and volumetric methods. The objective in these methods is to operate on an unknown sample in such a way that a chemical reaction takes place, specific to the components that are to be determined. One would weigh precipitates and residues, measure evolved or consumed gases, titrate acid-base and oxidation-reduction systems. The main problem was to discover type-specific reactions that lent themselves to the making of quantitative deductions and to refine and simplify the measuring techniques. Marvels of ingenuity, reliability, and accuracy resulted. In all cases, however, it was necessary to change the substrate permanently. This fact alone was a weakness needing remedy. But what was the analyst to do when confronted by complex hydrocarbon or amino acid mixtures where the mere qualitative separation represented an almost impossible task? And how could he solve with his classical tools the subtler questions of alloy and polymer structure, problems dealing with arrangement and design rather than the purely quantitative determination of elemental composition. Nevertheless, these are problems assigned to the analyst for solution. The answer is, of course, that the analytical chemist has added to his tools a new series of methods and devices, often developed for quite other purposes—namely, the instruments and techniques that determine the physical constants of chemical substances. A fertile field was uncovered with

which to supplement the classical techniques. For in the sensitive and inventive hands of the analyst this supplementing of type-specific chemical reactions with the measurement of type-specific physical constants opens a wider field of usefulness than had been provided heretofore. Frequently, speed, accuracy, and specificity have been greatly enhanced. And of equal significance are the discoveries and utilization of powerful and improved methods of separation, indispensable in the investigation of complex systems where even the most refined of available methods are inadequate to distinguish and measure with sufficient precision.

In the following two volumes our aim has been to describe those physical methods that have either proved themselves of considerable value in quantitative analytical work or are destined to play an important role in the future. The reader will find a discussion of the various "Unit Operations," the techniques and instruments that can be used by the analyst in the identification, both qualitative and quantitative, of atomic, molecular, and ionic species, crystal phases and arrangements, surface structures and area, etc. Enough experimental and theoretical data have been assembled to minimize the need of consulting more specialized texts or the original literature, in the sense of enabling the reader to become familiar with the underlying principles of the methods and to analyze the applicability of the techniques to his specific problems.

The subject matter, wherever possible, is arranged in the following manner:

- 1) Survey and development of the theoretical base on which the "Unit Operation" rests, together with the derivation of the formulae and working equations necessary in the interpretation of the experimental results.
- 2) Discussion and description of the methods, types of apparatus, and equipment, general test procedures, preparation and selection of samples, evaluation of experimental data, and reference to alternate procedures.
- 3) Discussion of the various broad fields of application and prominent examples where the techniques have been successfully applied. Estimation of limitations, experimental error, and inherent accuracy. Probable future extensions and applications in other fields.
- 4) Literature references to specialized texts and to the journals where important segments of the experimental methods or applications are discussed.

In a field as extensive and as rapidly expanding as this one the practicing analyst is obliged to maintain close scrutiny over the current literature. He must, however, be sufficiently grounded in the basic principles

of the various physical methods in order to carry out his tasks in the most intelligent, efficient, and scientific manner. It is hoped that the contributions to these volumes will aid him in this understanding.

The subject matter has been divided in such a way that all methods dealing with the interaction of radiation with matter (in addition to mass spectrometry) appear together in Volume I. Electrical, magnetic, and miscellaneous techniques and the methods of separation will appear in Volume II.

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# Absorption Phenomena of X-Rays and $\gamma$ -Rays

By

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## 1. INTRODUCTION

The unique penetration of x-rays through matter, varying with the type of matter, or conversely the variations in absorption of the rays, was the second observation made by Röntgen in his 1895 discovery, the first being the luminescence of a barium platinocyanide screen some feet away from a completely covered cathode ray tube. In his first communication "On a New Kind of Rays," presented in December, 1895, are the following sentences (translated from the German) (7):

It is seen, therefore, that some agent is capable of penetrating black cardboard which is quite opaque to ultraviolet light, sunlight, or arc-light. It is therefore of interest to investigate how far other bodies can be penetrated by the same agent. It is readily shown that all bodies possess this same transparency, but in very varying degrees. . . . A piece of sheet aluminum, 15 mm. thick, still allowed the x-rays (as I will call the rays for the sake of brevity) to pass, but greatly reduced the fluorescence (of a screen placed behind the specimen). Glass plates of similar thickness behave similarly; lead glass is, however, much more opaque than glass free from lead. . . . If the hand be held before the fluorescent screen, the shadow shows the bones darkly, with only faint outlines of the surrounding tissues. Water and several other fluids are very transparent. . . . Plates of copper, silver, lead, gold and platinum also allow the rays to pass, but only when the metal is thin. Platinum 0.2 mm. thick allows some rays to pass; silver and copper are more transparent. Lead 1.5 mm. thick is practically opaque. If a square rod of wood 20 mm. on a side be painted on one face with white lead it casts little shadow when it is so turned that the painted

face is parallel to the X-rays, but a strong shadow if the rays have to pass through the painted side. The salts of the metal, either solid or in solution, behave generally as the metals themselves. The preceding experiments lead to the conclusion that the density of the bodies is the property whose variation mainly affects their permeability.

Today, more than fifty years after the momentous discovery, it is easy to forget that Röntgen made these first observations on penetration and absorption of these rays and immediately instituted the first practical applications, which today are so well established in medical diagnosis, industrial radiography, microradiography, photometric analysis, gauging, absorption spectroscopy, photochemical reactions, biological effects, and medical therapy. For all but the last three, direct observations of differential absorption is involved; for the last three it is clear that absorption of rays must precede chemical and biological changes. Röntgen and his contemporaries had only the measurements of absorption for evaluation of quality (or wavelength distribution) until the discovery in 1912 of diffraction by crystals. With this discovery absorption phenomena as such were eclipsed and in part nearly forgotten, while "shadowgraphs" of bones and tissues were taken more or less for granted. Within the past few years with the advent of such useful instruments as r-meters, electron multiplier tubes, Geiger tubes, etc., there has been a reawakening to the practical usefulness in many directions of observing absorption of x- and  $\gamma$ -ray beams in all types of materials. The ease and speed with which measurements can be made in comparison with other techniques has brought to the fore the analytical possibilities in academic and industrial laboratories. New automatic apparatus is on the market and many new applications are being found. It is the purpose of this chapter to illustrate some of these applications of Röntgen's first experimental observations.

## 2. THE LAWS OF ABSORPTION

The absorption of x- and  $\gamma$ -rays follows the exponential equation

$$I_x = I_0 e^{-\mu x} \quad (1)$$

$$\text{or} \quad \log \frac{I_0}{I_x} = \mu x \quad (2)$$

where  $I_x$  is the intensity of radiation of initial intensity  $I_0$ , after passage through  $x$  centimeters of homogeneous matter,  $e$  is the natural base of logarithms, and  $\mu$  is the linear absorption coefficient. If the beam of radiation has a cross section of 1 cm.<sup>2</sup> then  $\mu$  represents the fraction of energy absorbed per cubic centimeter of the absorber traversed. Because of a more frequent interest in absorption per gram instead of per cubic centimeter a more useful form of eq. (1) is

$$I_x = I_0 e^{-\frac{\mu}{\rho} \rho x} \quad (3)$$

where  $\rho$  is the density of the absorbing layer and  $\mu/\rho$  is the mass absorption coefficient, which is a simple function of atomic number and independent of physical state and temperature. The value of  $\mu/\rho$  for a chemical compound is an additive function of the mass absorption coefficients of the constituent elements. Thus, in an example cited by Sproull (13), x-rays passing from the ceiling to the floor of a room containing hydrogen and oxygen may be 90% absorbed through the total height of gas, and on the floor there is 10% of the initial intensity. A spark is passed so as to cause combination to steam, without any change in absorption. When the steam is condensed to water, x-rays reaching the floor through the water or ice will also have 10% of initial intensity. For a given element  $\mu/\rho$  increases with an increase in wavelength of the radiation absorbed, discontinuities appearing at the characteristic K, L, M, N, etc. absorption wavelengths. The  $\mu/\rho$  values for many of the most important elements over a range of wavelengths are tabulated in the *Handbook of Chemistry and Physics*, 30th ed., Chemical Rubber Publishing Co., 1948, pp. 2005-2010.

The mechanism of the absorption process is shown by the fact that

$$\mu/\rho = \tau/\rho + \sigma/\rho \quad (4)$$

where  $\tau/\rho$  is the true or fluorescent mass coefficient and  $\sigma/\rho$  is the coefficient due to scattering;  $\mu/\rho$  is also a function of atomic number and of wavelength as shown by the equation

$$\mu/\rho = (CZ^4\lambda^3)N/A \quad (5)$$

where  $C$  is a constant over a range between characteristic absorption edges,  $Z$  the atomic number,  $\lambda$  the wavelength,  $N$  Avogadro's number, and  $A$  the atomic weight.

The laws of absorption apply to single wavelengths (or monochromatic beams) even though x-ray tubes generate a whole spectrum of rays. However, each such polychromatic beam has an "effective" wavelength, that is, the wavelength of a monochromatic beam absorbed to the same extent.

### 3. THICKNESS GAUGING

The exponential law indicates that absorption of a given x-ray beam of given intensity must vary with  $x$ , the thickness of the homogeneous material. This suggests the simplest application of an absorption technique, namely the evaluation of gauge and its constancy. Many

materials occur in such shapes that micrometer thickness measurements are difficult or impossible. With an x- or  $\gamma$ -ray beam such determinations can be made without in any way touching the sample. It is necessary only to measure the diminution in initial intensity  $I_0$  in passage through a layer. This may be done with a fluoroscopic screen or a photographic film, although only roughly since under the best conditions a difference in thickness of about 2% is required for visual differentiation of the blackening of the photographic emulsion. Still better is an ionization chamber or r-meter or Geiger counter, which can be made extremely sensitive so that a difference of the order of 0.1% is detectable. The logical practical equipment is a combination of phosphor and an electron-multiplier photoelectric tube first used for intensity measurement in 1942 by Morgan (10), for preliminary chemical analysis by Liebhafsky and Winslow (9) in 1945, and for rapid examination of fuses by Smith (12) in 1945. Operation with amplifiers and automatic continuous operation have followed.

During the war it became necessary to roll thin metal sheets of constant gauge, free from defects, for various types of precision equipment. At a constant voltage and current, x-rays could be passed through the sheet traveling at 800 feet per minute on the rolling mill. The unabsorbed radiation passes into an electron multiplier tube, the current in which is amplified to be read on an ammeter or otherwise arranged to signal when there is variation in gauge of the sheet. Variations in primary x-ray intensity are compensated by a null method since a beam from the opposite side of the target passes through a stationary sample of standard required gauge and then into another multiplier tube and the circuit linked with that registering absorption in the moving sheet. This technique of gauging is now established practice for a wide variety of rolled metal sheets. Plated strips or sheets and tubing may also be checked for uniformity of thickness. Continuous testing of deviations from concentricity of wire cores in insulation of high tension cables is now established practice.

X-ray gauge methods are particularly useful on compressible materials such as leather, cellophane, cloth textiles, rubber blankets, plastic films, paper, etc. It follows that porosity, as well as gauge, can be accurately determined, for x-rays measure only the true thickness of solid matter through which they pass without reference to free spaces and pores whereas only the apparent thickness is measurable by mechanical means such as micrometers. The porosity of the negative metallic lead plates in storage batteries as a function of temperature of formation and charging down to very low temperatures is an important factor, the capacity of the plates being determined by the penetration of sulfuric acid into the

interior of the active mass. No possible mechanical measurement of the spongy mass could be made; but absorption of x-rays through sections of the plate of the same area and same mass of active material give the variations in thickness and porosity, the latter decreasing nonlinearly with temperature and also with capacity of the plate. Commercial equipment for such purposes, the Measuray, is produced by the Sheffield Corporation of Dayton, Ohio.

#### 4. CHEMICAL ANALYSIS FROM RELATIVE ABSORPTIONS

It is at once apparent that rapid chemical analysis can be made to depend upon differences in absorption of x-rays, for the concentration of one chemical element in the presence of others determines the difference in absorption between a sample and a reference. In 1929 Aborn and Brown (1) used x-ray apparatus with an ionization chamber to analyze gasoline for lead tetraethyl content, utilizing the large difference in mass absorption coefficients of carbon and hydrogen in gasoline and the lead. It was possible to achieve an accuracy of one part in 14,000.

In 1946 Sullivan and Friedman (14) successfully utilized a Geiger counter for x-ray absorption measurements for this same analysis of lead tetraethyl in gasoline. As shown in eq. (5) the mass absorption coefficient increases as the cube of the wavelength. In a single-component system it is logical to employ the longest wavelength transmitted by the sample, thus obtaining a maximum change in intensity for a given change in sample thickness. However, leaded gasoline is a two-component system in which the  $\mu/\rho$  values change at different rates as the wavelength is varied. Hence an optimum wavelength generated at 17 kv. is used with an absorption cell length of 15-25 cm. A counter tube filled with krypton is designed such that 80% of the x-ray beam so generated is absorbed; or 80 out of 100 quanta entering the counter produce counts. At comparable sensitivity of the photomultiplier tube, the counter registered over 1000 counts per second. Standard deviation was 0.05 ml. of lead tetraethyl per gallon of gasoline, or 1%. Similarly a precision of 1% was obtained with samples containing a maximum of 0.46 ml. per gallon, corresponding to the detection of 0.005 ml. lead tetraethyl per gallon or 0.0002% lead. The analysis can be made in one-tenth the time of any far less satisfactory chemical method.

In spite of the success of this analysis and the suggestion of many others applied to mixtures of gases, liquids, and solids no suitable equipment was placed on the market until late in 1946. The General Electric X-ray Photometer is now in routine and research use for a wide variety of analytical problems (11).

The general arrangement is illustrated in Fig. 1. A tungsten target x-ray tube with beryllium window is operated at 15 to 45 kv. and 1 to 20 milliamps. with an enclosed power unit. Above the x-ray unit is a synchronous motor-driven chopper which alternately interrupts one-half of the x-ray beam after the other. A variable-thickness aluminum attenuator is placed above the chopper in one beam. Duplicate sample tubes are placed in the two beams above the attenuator. Sample cells up to 25 inches long can be accommodated; those for liquids and gases are arranged for continuous flow of the sample. Both halves of the beam fall on a common fluorescent screen protected from visible light by a thin

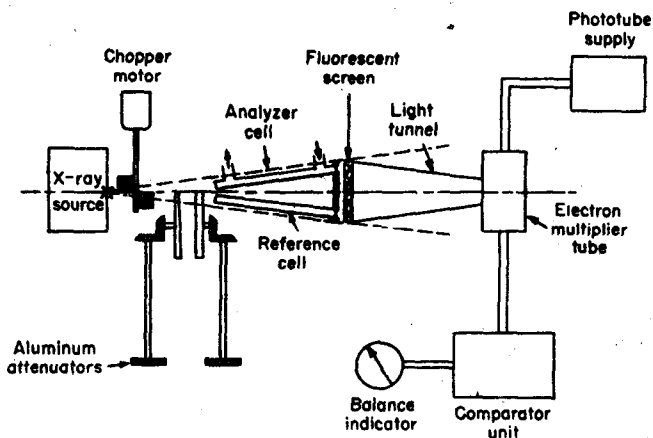


FIG. 1. X-ray photometer.

metallic filter. An electron-multiplier phototube with associated power supply and amplifier determines when the beams are of equal intensity.

In operation a reference sample is placed in the cell above the attenuator and the unknown in the other sample tube. The attenuator is adjusted until the balance indicator shows that the two beams are of equal intensity; this position indicates a certain thickness of aluminum, which is equal in absorption to the difference between the reference sample and the unknown. Prior calibration enables an immediate determination in terms of the amount of impurity or solute in the unknown. The instrument may operate automatically to indicate or record this result directly. The exploratory work leading to the development of this successful commercial equipment was done by Liebhaufsky and associates (8) for solids, liquids, and gases under simplest conditions. The relation between x-ray absorption and two masses ( $m_1$  and  $m_2$ ) of sample is:

$$\log [I_1/I_2] = \log [i_1/i_2] = k(m_2 - m_1) \quad (6)$$

where  $I_1$  and  $I_2$  are intensities of x-ray beams transmitted,  $i_1$  and  $i_2$  are corresponding average output currents (from the phototube) and  $k$  is a proportionality factor. With a monochromatic beam

$$\log I_0/I = \log i_0/i = km \quad (7)$$

where  $I_0$  and  $i_0$  refer to the empty cell. With the commonly used polychromatic beam from a tungsten target tube,  $k$  varies inversely with  $m$ . It is defined by

$$\mu/\rho = 2.303ak \quad (8)$$

where  $a$  is the cross-sectional area of a cell containing  $m$  grams of sample; as already indicated  $\mu/\rho$  varies with  $\lambda^3$ , and the value of  $\lambda_{\text{effective}}$  changes by absorption of the longer wavelengths. For quantitative analysis the effective wavelength must be determined for various thicknesses in order to determine  $\mu/\rho$  in turn.

The analysis of gases is particularly interesting and significant. The equation used is

$$2.303 \log i_0/i = \mu_m \rho l \quad (9)$$

where  $\mu_m$  is the mass absorption coefficient,  $\rho$  is the gas density, and  $l$  is the cell length in centimeters. Long wavelengths make possible a ratio of 6000 to 1 between output for hydrogen and chlorine.

The following examples of actual analyses for which the photometer is employed are typical of an almost endless list of possibilities.

1. Characterization of plastics (8) (for use in cell windows, all lying between beryllium and aluminum).
2. Sulfur content of oil.
3. Lead tetraethyl content of gasoline (1) (14).
4. Additives in heavy duty lubricating oils.
5. Ash content and quality of coal (11).
6. Heavy metal content of glass.
7. Chlorine or fluorine content of polymers and plastics. Here values of  $\mu/\rho$  are H = 0.435 (independent of wavelength), C = 0.567, Cl = 12.0.
8. Bromine content in gaseous brominated derivatives.
9. Determination of formula of organic compound. Typical results are as follows:

	$\mu/\rho$ Meas.	$\mu/\rho$ Calcd.	Formula exp.	Formula true
Methyl alcohol.....	0.869	0.867	$\text{CH}_2\text{O}_{1.01}\text{H}$	$\text{CH}_2\text{OH}$
Acetone.....	0.734	0.728	$(\text{CH}_2)_2\text{CO}_{0.96}$	$(\text{CH}_2)_2\text{CO}$
Sucrose (solution).....	0.869	0.884	$\text{C}_{12}\text{H}_{22}\text{O}_{10.5}$	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$

10. Concentration of fillers and impregnants in wood, cloth and rubber.
11. Mineral content and efficiency of softening of water.
12. Soil composition (qualitatively on account of complexity).
13. Adsorbed contents of charcoals and silica gels.

It is self evident that this method has the general advantage of being completely nondestructive to any specimen, besides being rapid, accurate to within 1%, and continuous in all cases where it may be applied.

#### 5. ANALYSIS BY CHARACTERISTIC ABSORPTION

Just as emission and absorption spectroscopic analyses in the optical ranges of the electromagnetic spectrum are such important instrumental techniques, so may characteristic x-ray emission lines and absorption edges be utilized by the chemist. It has long been known that each chemical element has one characteristic K absorption wavelength, 3L, 5M, 7N, etc., the relationship to atomic number being governed by Moseley's law. Thus when an absorbing screen is placed in the path of an x-ray beam, and the transmitted beam is analyzed with the crystal spectrometer, sharp discontinuities or edges in the continuous spectrum may be found corresponding to the characteristic absorption wavelengths in the various series for each element present, these being independent of physical state or chemical combination. Not a great deal of use has been made of this particular technique over the years, probably because the emission spectra are somewhat more sensitive. The height of this edge or discontinuity is a quantitative measure of the amount of element in the unknown. This is governed by the equation

$$\frac{I_2}{I_1} = e^{-cp} \quad (10)$$

where  $I_2$  is the intensity of the radiation leaving the absorption screen on the short wavelength side of the discontinuity, and  $I_1$  the intensity of the long-wave side;  $c$  is the coefficient which must be experimentally determined and  $p$  is the amount of element present. In Table I are probably the best data available for values of  $c$  and  $m$ , the weight in



milligrams per square centimeter for the production of an absorption edge with a 5% intensity difference in the two sides.

TABLE I

At. number	Element	c K edge	c L edge	m K edge	m L edge
42	Mo	69		0.7	
47	Ag	45		1.1	
50	Sn	34		1.5	
51	Sb	31		1.6	
56	Ba	24		2.1	
58	Ce	22.5		2.2	
74	W	8		6.0	
82	Pb	5.7		16.0	
90	Th		50		1.0
92	U		45		1.1

The method has been used successfully for analysis of barium in glass, antimony, barium and lanthanum, bismuth in alloys, and many others (2). It has not been used successfully for elements below the atomic number of molybdenum. However, with the advent of Geiger spectrometers, and new x-ray tubes delivering extremely intense beams up to 5,500,000 roentgen per minute, many of the former difficulties are eliminated. It is easily possible to make analyses for elements as low in atomic number as potassium with such improved equipment.

Absorption spectroscopic analysis has been perfected to the stage of a microspectrographic procedure, permitting the chemical elementary analysis of single mammalian cells. Absorption of monochromatic x-radiation is measured by ionization chambers, Geiger counters, or photographically followed by microphotometry, for a series of wavelengths (isolated from primary or secondary fluorescent characteristic rays) lying on each side of a long wave absorption edge of the sought-for element (6). Thus it is possible to determine phosphorus and calcium in a  $10\mu$ -thick microtome section of a bony tissue within an area of  $10 \times 10\mu$ ; nitrogen and oxygen within an area of  $50\text{--}100\mu^2$  of a section  $2\mu$  thick. The actual weights are of the order of  $10^{-9}\text{--}10^{-12}$  g. Since such small localized areas may be examined the analysis may be directly correlated with the cytological picture. For these analyses the formula used is:

$$X = \frac{\ln(i_2/I_2) \cdot (\lambda_1/\lambda_2)^P - \ln(i_1/I_1)}{(\mu_1/\rho) - (\mu_2/\rho)(\lambda_1/\lambda_2)^P} \quad (11)$$

where  $X$  is the amount of the sought-for element in grams; the index 1