

X-RAY ABSORPTION and EMISSION in ANALYTICAL CHEMISTRY

Spectrochemical Analysis with X-rays

H. A. Liebhafsky

H. G. Pfeiffer

E. H. Winslow

P. D. Zemaný

General Electric Research Laboratory

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Preface

Like it or not, the chemistry is going out of analytical chemistry. For a long time indeed, Chaucer with his

The lyf so short, the craft so long to lerne,
Th' assay so hard, so sharp the conquering.

The Parlement of Foules

proved a better prophet than he knew. But, nowadays, physics and electronics are in part being fused with analytical chemistry to make the assay easier and the conquering less painful.

This fusion of disciplines, though desirable and inevitable, complicates the writing of books in fields where it occurs. Spectrochemical analysis by means of x-rays is definitely such a field. For whom shall a book on this subject be written? Our answer is clear. This book was written for the analytical chemist who wants to use these x-ray methods and to understand them. We have striven for correctness in physics, electronics, and statistics; but we have tried first of all to help the analytical chemist in his work.

Nomenclature is bound to flourish in a field that rests on several disciplines. We have pruned the growth, judiciously we hope, after considering all the various shoots, even the more exotic. To keep the book within bounds, equipment for description and literature for reference had to be selected. The choice was made with the analytical chemist in mind. In general, references later than August 1957 could not be included.

We planned this book to be useful even if read only in part. The first chapter is a summary of what is known about x-rays that is pertinent to spectrochemical analysis, and it should receive at least cursory attention from all readers. Those interested primarily in absorptiometry may then turn to Chapter 3 or 5; in film thickness, to Chapter 6; and in x-ray emission spectrography, to Chapters 7 and 8. The remaining five chapters are ancillary and deal with special topics.

Again with the analytical chemist in mind, we have not treated all topics equally. The electronics expert is likely to feel we have skimmed, especially in Chapter 2; Chapter 4 is oversimplified; statisticians will find much missing from Chapter 10; and other important developments could have been treated in Chapters 9 and 11.

Because this book rests on diverse disciplines, we have had to seek—and have received—help to an unusual degree. For their help, we gladly thank Dr. C. A. Bennett, Mr. J. E. Bigelow, Mr. H. C. Buchholtz, Mr. J. R. Churchill, Dr. R. L. Griffith, Dr. T. A. Hall, Mr. J. W. Kemp, Dr. H. P. Klug, Dr. W. F. Loranger, Dr. D. M. Miller, Dr. B. W. Roberts, Dr. J. Rouvina, and Mr. M. L. Salmon. We also thank the editors of *Analytical Chemistry*, who were kind enough to let us draw extensively upon the material we have published in that journal. And, finally, we shall be most happy to thank our readers for showing us mistakes and shortcomings that have escaped proofreading and revision!

H. A. LIEBHAFSKY
H. G. PFEIFFER
E. H. WINSLOW
P. D. ZEMANY

Schenectady, New York
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Chapter 1.

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Origin and Properties of X-rays

During World War II and thereafter, the methods of x-ray detection were improved until it is now a matter of simple routine to measure relative x-ray intensity easily and precisely. This improvement, which was accelerated by the rapid progress in nuclear physics, has promoted a rapidly growing appreciation of the great advantages that can attend the application of x-ray absorption and emission to chemical analysis. In their rush to make these applications, analytical chemists have occasionally made discoveries predictable from earlier work, usually by physicists, in the field of x-rays.

In this introductory chapter, we hope to describe the properties of x-rays most useful to the analytical chemist, to trace the discovery of these properties, and to foreshadow their importance in analytical chemistry.

It has often been said that the penetrating power of x-rays is their most remarkable property. As concerns analytical chemistry, however, the simplicity of their spectra deserves at least equal emphasis—after all, this simplicity makes for simple analytical methods, in which even the deviations are often predictable. Both the penetrating power (small chance of being absorbed) and the simplicity may be attributed to the high energy of x-rays. More precisely, these important properties are

Note. Section numbers in parentheses refer to other sections the reader may wish to consult.

traceable ultimately to the fundamental facts of atomic structure. In most atoms, for example, the electrons nearest the nucleus are few in number, well shielded from chemical influences, and subject to serious disturbance only by quanta of high energy, such as x-rays.

DISCOVERY OF X-RAYS

“Ich komme deshalb zu dem Resultat, dass die X-Strahlen nicht identisch sind mit den Kathodenstrahlen, dass sie aber von den Kathodenstrahlen in der Glaswand des Entladungsapparates erzeugt werden.”¹

1.1. Roentgen's Discovery

Today we might describe the discovery of x-rays as follows. In 1895, Roentgen experimented with “highly evacuated” tubes the glass walls of which suffered pulsating electron bombardment. Even when such a tube was covered with black cardboard, he observed that a neighboring barium platinocyanide phosphor fluoresced visibly and synchronously with the discharge through the tube. The cause: x-rays had been generated in the glass by electron excitation and had penetrated glass and cardboard to be detected by the phosphor. For his work with x-rays, Roentgen in 1901 received the first Nobel Prize in physics, also the first of six to be awarded in the field of x-rays by 1927.²

But Roentgen's achievements transcended mere discovery. He studied the properties of the new rays so well that he laid the foundations not only for important methods of x-ray detection (fluorescence of a phosphor, darkening of a photographic plate, ionization of a gas) and for radiography, but for the application of x-ray absorption to analytical chemistry as well.

THE GENERATION OF X-RAYS

“The idea of using a hot cathode in a Roentgen tube was not new, but . . . the principle had never been

¹ W. C. Roentgen's three great papers have been reprinted in *Ann. Physik u. Chem.*, **64**, 1-37 (1898), where they are more accessible than in the journals of first publication, there cited. The quotation is from page 9.

² The other five Nobel Prizes of this group were awarded to M. T. F. von Laue (1914), W. H. Bragg and W. L. Bragg (1915), C. G. Barkla (1917), K. M. G. Siegbahn (1924), and A. H. Compton (1927).

successfully applied in a vacuum good enough so that positive ions did not play an essential role.”³

1.2. Gas (or Ion) Tubes

The “highly evacuated” electron tubes available to Roentgen were the precursors of today’s gas tubes—or ion tubes, a better name. In these (Figure 1-1), positive ions are produced in a gas at low pressure ($\sim 10^{-2}$ mm Hg) by applying a potential difference usually exceeding 10 kv between the electrodes. The positive ions bombard the cathode to release electrons, which strike the target to generate x-rays. The maximum energy of the rays increases with the effective potential difference, and this in turn increases with decreasing gas pressure. A constant and reproducible x-ray beam therefore requires careful stabilization of the gas pressure.

The gas tube has two advantages that may be of overriding importance in special cases. As Figure 1-1 shows, it is easy to vary the target metal so that an x-ray spectrum characteristic of a particular metal can often be generated as needed. Furthermore, spectral purity can be maintained because the risk of target contamination is small in a gas tube properly operated.

1.3. The Coolidge Tube

In the Coolidge tube (Figure 1-2), the vacuum is so good³ that gases or positive ions derived therefrom do not influence the x-ray beam. The tube is sealed, a great advantage. Electrons for excitation are produced by heating a tungsten filament, the heating circuit being separate from that which provides the accelerating potential. Consequently, the rate at which electrons strike the target (tube current) can be adjusted independently of their energy (tube voltage). This makes possible the independent variation of intensity and wavelength in the x-ray beam. The Coolidge tube is normally self-rectifying; some gas tubes are not.

The foregoing characteristics of the Coolidge tube make it a highly convenient and flexible x-ray source. On the other hand, the high temperature of the cathode brings with it some risk of target contamination during life. The principal contaminant is tungsten, and the loss of spectral purity is therefore most pronounced when the target is made of another metal. The absence of target interchangeability in the usual Coolidge tube is less serious now that such tubes can be bought with

³ W. D. Coolidge, *Phys. Rev.*, **2**, 412 (1913).

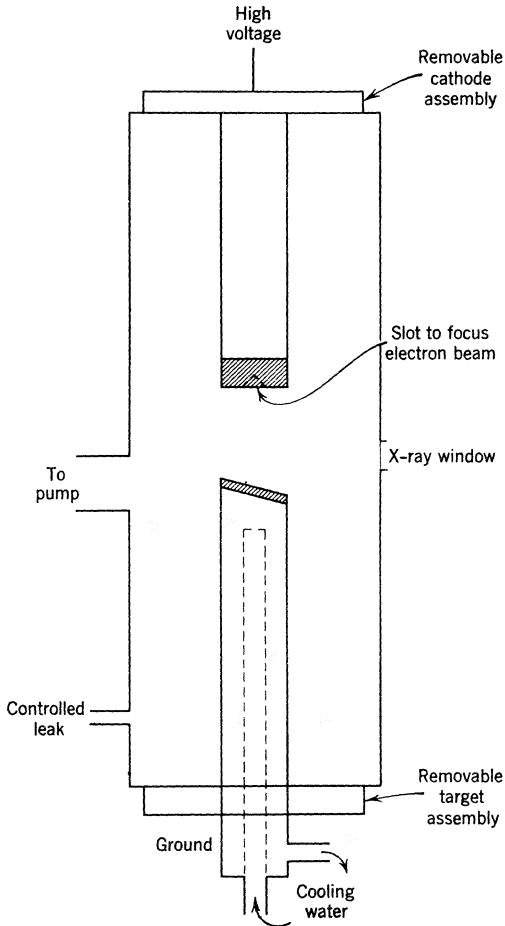


Fig. 1-1. Schematic diagram of demountable gas x-ray tube. The tube current and voltage are regulated by continuous pumping against a controlled leak to maintain stable operating conditions. The whole target assembly and the target metal button are easily changed. The cathode button, usually slotted for focusing, is easily removable for cleaning and reslotting. As Coolidge tubes have approached the spectral purity of gas tubes, the popularity of the latter has waned because of greater difficulty of operation and control.

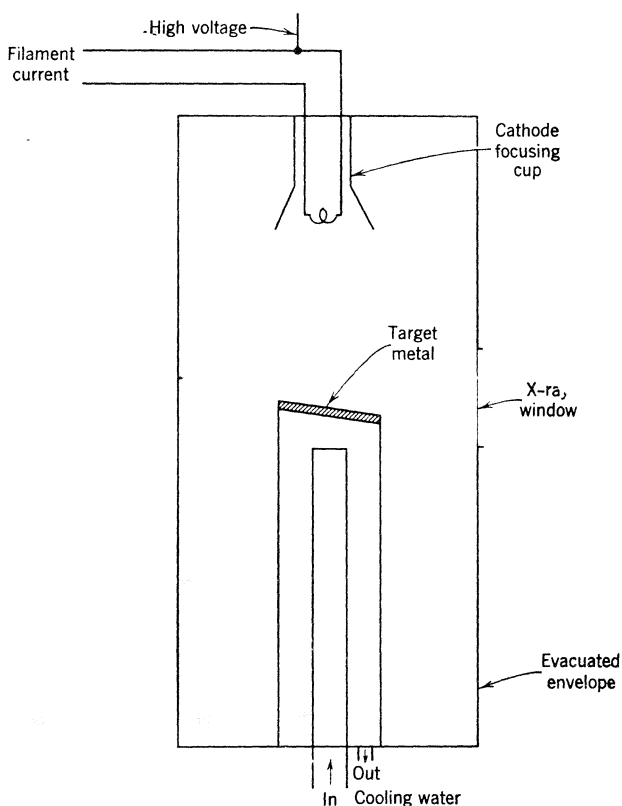


Fig. 1-2. Schematic diagram of the Coolidge (high-vacuum) x-ray tube. Coolidge tubes are widely used because they are stable and long-lived and permit tube current and voltage to be controlled independently.

targets of tungsten, molybdenum, chromium, copper, silver, nickel, cobalt, and iron. Tubes containing still other targets have been used for unusual applications and are available on special order.

1.4. Excitation by Electrons

When the target of an x-ray tube is struck by electrons, these are retarded by the atoms of the target. The energy the electrons lose is radiated in a spectrum that ranges from the x-ray region into the infrared; we say this spectrum has been produced by electron excitation.

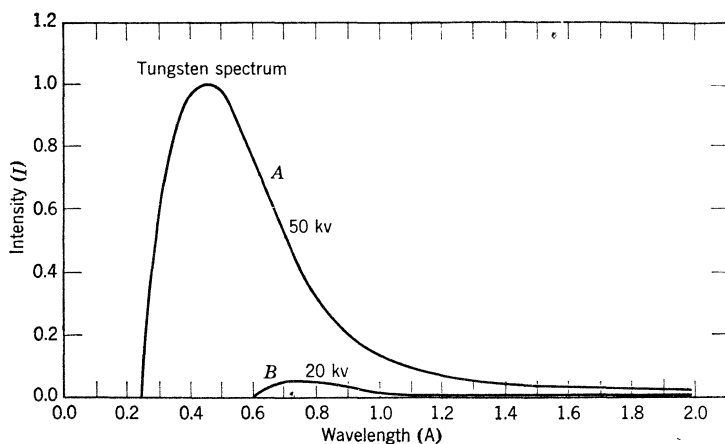


Fig. 1-3. The continuous x-ray spectrum. Note that the short-wavelength limit (Eq. 1-2) is 0.248 A for 50 kv and 0.620 A for 20 kv. A spectrum from a rectified a-c tube would have the peak displaced to the right and for a given input energy would have less x-ray output. (After Ulrey, *Phys. Rev.* [2], 11, 401.)

The elementary processes involved in this energy transfer can take place also in a sample being analyzed by x-ray methods.

In most analyses by these methods, the x-ray source is likely to be a Coolidge tube. For this reason, we shall examine the spectra that have been observed when an "infinitely thick" tungsten target in such a tube is bombarded by electrons of various energies. In Figure 1-3, intensities (arbitrary units)⁴ are plotted against wavelength in angstrom units⁵ for these spectra. Three items are noteworthy:

⁴ Several terms are in common use for the energy of an x-ray beam and for related quantities. *Intensity* is the most common of these. In this book, intensity will always be used as a relative measure, which means that the interpretation of experimental results will always involve intensity ratios; for example, I/I_0 could be the ratio of the intensity I of an attenuated beam to I_0 , the intensity of the source. Whenever confusion as to wavelength range could occur, but only then, I_λ will designate the intensity at wavelength λ while I designates the integrated intensity for the entire wavelength region; that is, $I = \int_{\lambda_1}^{\lambda_2} I_\lambda d\lambda$. In discussions of theory, the I 's are independent of optics or of detecting systems. Where space, time, and energy must be considered, the following terms are proper.

Radiant energy	The energy in the spectral region considered.
Radiant flux or power	Total rate at which energy flows.
Radiant intensity	Radiant flux per unit solid angle in a given direction. (Different from I defined above.)
Radiance	Radiant intensity per unit area of source.
Irradiance	Radiant flux per unit area incident on a surface.

1. All spectra begin abruptly at a short-wavelength limit that shifts systematically to shorter wavelengths as the electron energy increases.

2. Each spectrum is a continuum that extends over a wide range of wavelengths. The curves are left unfinished to call attention to the difficulty of working with long-wavelength x-rays.

3. The spectra in Figure 1-3 are observed spectra, obtained by an experimental method described later. The spectra as generated at the target differ from these in several important respects (see below).

1.5. The Continuous Spectrum

The continuous spectrum is thus characterized by a short-wavelength limit and an intensity distribution. Experiments on other target materials have shown that these characteristics are independent of the target material although the *integrated* intensity increases with atomic number. (See Equation 1-3.) The continuous spectrum, therefore, results generally from the interaction of electrons with matter. Attempts (none completely successful) have been made to treat this interaction theoretically by both classical and quantum mechanics.

The short-wavelength limit of the continuous spectrum is clearly a quantum phenomenon. X-ray generation by electron bombardment in principle resembles cathodoluminescence, and both processes are inverse photoelectric effects. The short-wavelength limit, λ_0 , discovered by Duane and Hunt⁶ obeys the relationship

$$\frac{hc}{\lambda_0} = h\nu_0 = \frac{mv_{\max}^2}{2} = Ve \quad (1-1)$$

in which the first two terms give the value of the largest x-ray quantum (minimum wavelength λ_0 , maximum frequency ν_0) in the continuous spectrum, and the third and fourth terms give the maximum energy⁷ of

This nomenclature is based upon optical practice as given by M. G. Mellon, *Analytical Absorption Spectroscopy*, John Wiley and Sons, New York, 1950.

⁵ A slightly different unit of length that is also used is the X unit (X.U.), proposed by Siegbahn. 1000 X.U. = 1 kX.U. = 1.00202 Å (angstroms). For further information on the origin of the X unit consult H. P. Klug and L. E. Alexander, *X-ray Diffraction Procedures*, John Wiley and Sons, New York, 1954, page 90; W. T. Sproull, *X-rays in Practice*, McGraw-Hill Book Co., New York, 1946, page 337.

⁶ W. Duane and F. L. Hunt, *Phys. Rev.*, **6**, 166 (1915).

⁷ A definite spectrum of the types shown in Figure 1-3 is produced for a given value of the d-c voltage applied. When rectified a.c. is applied, the spectrum at each instant of the a-c wave is that produced by the voltage at that instant. Thus the spectrum of the x-ray tube under these conditions is the sum of the spectra produced by all voltages from zero to the peak value of the a-c voltage. The short-wavelength limit will be given by the peak voltage. "Filtering" rectified a.c. brings the x-ray spectrum closer to that from a d-c power supply.

the bombarding electrons expressed as kinetic and as electrical energy. The symbols in Equation 1-1 have their usual meanings, and the equation is the basis for one of the best methods of determining Planck's constant, h .

Einstein⁸ was the first to realize that the quantum theory is necessary to explain the energy transfers observed in the photoelectric effect and in cathodoluminescence. One of the most remarkable sentences in the scientific literature⁹ ("Erzeugt ein Elementarvorgang einen andern, so ist die Energie des letzteren nicht grösser als die des ersteren.") serves admirably to describe the short-wavelength limit, which Einstein may therefore be said to have predicted.

A useful relation can be obtained from the first and fourth terms of Equation 1-1 by use of numerical values for e , h , and for c , the velocity of light,

$$\lambda_0 = 12.393/V \quad (1-2)$$

V being the (maximum) potential difference across the tube, in kilovolts.

The wavelength of maximum intensity (see Figure 1-3) in the continuous spectrum is often about $3\lambda_0/2$. This rough empirical rule¹⁰ is useful in estimating the *effective wavelength* of a *polychromatic* x-ray beam, this being the best wavelength that can be selected to describe how the polychromatic beam behaves in absorption measurements.

The total power, or integrated intensity,⁴ of the x-ray beam, in watts, is the product of the (empirical) efficiency¹¹ of x-ray production and cathode-ray power iV ; or

$$I_{\text{int}} = 1.4(10^{-9})iZV^2 \quad (1-3)$$

where i is the electron current, in amperes; Z the atomic number, and V the potential difference⁷ across the tube, in volts. This estimate of the beam energy becomes less reliable as V decreases, but it emphasizes the inefficiency of x-ray production by electron bombardment. In typical cases, less than 1% of the electron energy appears in the x-ray beam. Almost all the rest is degraded to heat, and special provisions for cooling the target are often necessary.

When electrons strike an "infinitely thick" target, they are quickly slowed as they interact with the atoms of the target. Consequently, they do not penetrate at all deeply.¹² Furthermore, different electrons

⁸ A. Einstein, *Ann. Physik*, **17**, 145 (1905).

⁹ A. Einstein, *Physik. Z.*, **10**, 191 (1909).

¹⁰ H. Kulenkampff, *Ann. Physik*, **69**, 594 (1922).

¹¹ W. T. Sproull, *X-rays in Practice*, page 14.

¹² In order to study as effectively as possible the mechanism of generation of the continuous spectrum, researches have been conducted with the use of extremely