QUANTITATIVE X-RAY SPECTROMETRY

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Preface

X-ray fluorescence spectrometry is now well into its third decade of use, initially utilizing the wavelength-dispersive spectrometer and more recently being supplemented with the energy-dispersive systems. Like most other analytical methods, it has seen the birth pains of innovation and has struggled through a period of misunderstanding and overexploitation before finally reaching the stable plateau of a reliable and well-accepted analytical technique. There are probably in excess of 10,000 users of the x-ray fluorescence method in the world today, and these are found in a wide range of disciplines including process control, materials analysis, exploration, mining, metallurgy, and almost every other major branch of science.

Da Vinci is reported to have said "Experiment is the interpreter of science, experiment never deceives, it is only our judgement which sometimes deceives itself when it expects results which experiment refuses." The irony of this statement will certainly not be lost on any spectroscopist who in the early days attempted to solve a complex matrix problem and finished up with an unreasonable set of "alpha" coefficients. The impact of the minicomputer in the mid-1960s did much to replace art by science, and we are fast approaching the chemist's dream of elemental analysis without standards. Certainly in the case of the energy-dispersive spectrometer, it has become a necessary and integral part of the system, and most modern wavelength-dispersive spectrometers boast some degree of automation for hardware control and data manipulation.

All three of us devote a large fraction of our working lives teaching mature scientists and technicians details of the x-ray method from the basic principles to a detailed discussion of the subtleties and idiosyncrasies of the two types of instruments. We are thus well aware of the needs of the practicing spectroscopists and the requirement for a detailed discussion of the practical aspects of the application of quantitative methods. We hope that this book will fill a gap in the existing literature as well as supplement certain areas already covered. As an example, texts are available covering either energy-dispersive or wavelength-dispersive instruments, but none of these give detailed coverage of the similarities and contrasts of the two methods. We have chosen to discuss instrumentation in great detail specifically in the area of photon counting and its associated errors, for it is in this basic process where many systematic errors in quantitative work arise.

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Introduction

1.1 EARLY DEVELOPMENT OF X-RAY EMISSION ANALYSIS

The use of x-ray emission spectrometers for elemental analysis became widespread in the late 1950s and early 1960s. X-ray spectroscopy itself dates back to around 1910 when Barkla [1] obtained the first positive evidence of characteristic x-ray emission spectra. Three years later, Moseley [2-4] established the relationship between frequency and atomic number which laid the foundation of the technique for the identification of elements by x-ray emission analysis. Although the potential of the new technique was quickly appreciated, the practical difficulties in the use of the equipment available at that time severely limited the application of the method. A major difficulty stemmed from the use of electrons as the excitation source. In addition to the requirement for a high vacuum and a conducting specimen, most of the electron energy is converted to heat, causing problems of volatility following excessive heating of the specimen. In the mid-1920s, several workers [5-10] pointed out that the use of an x-ray source would obviate many of the practical problems encountered with the electron source, but unfortunately, the lower efficiency of photon excitation coupled with the rather primitive detection instrumentation made this approach of x-ray *fluorescence* analysis impracticable. Nevertheless, it was the fluorescence approach that was to be employed in the commercial instrumentation that became available in the early 1950s.

Until the late 1960s, nearly all spectrometers were the so-called wavelength-dispersive spectrometers in which wavelengths are separated by Bragg diffraction from a single crystal. More recently, *energy-dispersive spectrometers* have become available in which a lithium-drifted silicon or germanium detector is used to give a distribution to voltage pulse amplitudes proportional to the distribution of photon energies. Electronic separation of the pulse height distribution then gives a photon energy spectrum. Each of these x-ray photon separation techniques has its own advantages and disadvantages, and a detailed description of each method will be found in the succeeding chapters of this book.

1.2 BASIS OF QUALITATIVE X-RAY EMISSION ANALYSIS

There are always four stages in any scheme of x-ray emission analysis. The excitation of characteristic radiation from the specimen by bombardment with high-energy photons, electrons, protons, etc.; the selection of a characteristic emission line from the element in question by means of a wavelength or energy-dispersive spectrometer; the detection and integration of the characteristic photons to give a measure of characteristic emission line intensity; and finally, the conversion of the characteristic emission line intensity to elemental concentration by use of a suitable calibration procedure.

All elements will give one or more sets (series) of characteristic emission lines and the number of these lines measurable by a spectrometer will depend upon the range and separating ability (resolution) of the spectrometer. Most commercial spectrometers operate over the range 0.2 to 20 Å (60-0.6 keV) and as such are able to detect the majority of the K and L series lines, plus a few lines from the M series of the higher atomic number elements. In practical terms, this means the detection of characteristic lines from all elements above atomic number 8 (oxygen) with the number of lines per element varying from two or three for the low atomic numbers, to 20-30 for the high atomic numbers. One or two lines are normally sufficient for the positive identification of an element in qualitative terms. The Moseley law relates the frequency ν with the atomic number Z.

$$\nu = K(Z - \sigma)^2 \tag{1.1}$$

in which K and σ are both constants which vary with the spectral series. A simple relationship also exists between the wavelength λ and energy E of an x-ray photon

$$E = \frac{hc}{\lambda} \tag{1.2}$$

in this expression h is Planck's constant (6.626×10^{-27} erg·s) and c the velocity of light (3×10^{10} cm/s). When E is expressed in thousands of electron volts (keV) and λ in angstrom units ($1\ \text{Å} = 10^{-8}$ cm) the following approximate relationship is applicable:

$$E = \frac{12.398}{\lambda} \tag{1.3}$$

It is a common practice to use tables relating either wavelength or energy with atomic number for the qualitative identification of elements from their emission spectra. Most spectrometers lose sensitivity at longer wavelengths (lower energies) and their ability to detect the low-atomic-number elements generally falls off sharply around atomic number 12. This combined with the low penetration of long-wavelength x-rays and the fact that they arise from molecular rather than atomic orbital transitions (and are thus dependent upon chemical bonding) makes the x-ray emission method largely impracticable for elements below atomic number 9 (fluorine).

1.3 QUANTITATIVE ANALYSIS

For the quantitative analysis of a given element, it is sufficient to measure one selected emission line and to relate the intensity of this line to concentration. Such a relationship is linear only over a very limited concentration range and in most cases the intensity of the emitted line is dependent not only on the concentration of the excited element but also upon the influence of other elements making up the specimen. These so-called matrix effects are both predictable and correctable by careful calibration and computation, and the advent of the small digital computer has done much to simplify the otherwise unwieldy and time-consuming calculations. Since the penetration of characteristic x-ray lines is small (typically 1-1000 μm), it is vital that the specimen be homogeneous over the depth of specimen contributing to the measured signal. This in turn may require a specimen preparation procedure that varies from being minimal to relatively sophisticated. Finally, accurate results can only be obtained when the source, spectrometer, and counting equipment are themselves stable and free from systematic errors. Modern spectrometers have potential precisions of around one-tenth of a percent and analytical accuracies approaching this value are obtainable where correct methodology is employed.

1.4 TYPES OF X-RAY SPECTROMETERS

All spectrometers comprise an excitation source, a means of separating and isolating characteristic lines, plus a device for measuring characteristic line intensities. More sophisticated systems may include a dedicated computer or hardwired data processor for data manipulation and even the calculation of elemental composition.

There are many types of x-ray spectrometers but several broad categories exist. Single-channel instruments are spectrometers which are designed to measure one element at a time, or many elements sequentially. The majority of flat-crystal wavelength-dispersive scanning spectrometers fit into this category, which is probably the most commonly employed. They have the advantage of great flexibility and a multiplicity of selectable single crystals is generally provided to offer good dispersion over a wide range of wavelengths. Such spectrometers are usually provided with a high-power x-ray tube as the source, which may offer broad-range excitation up to 100 kV. Inexpensive single-channel instruments may also be constructed using a proportional detector with suitable bandpass filters, using a radioisotopic source emitting γ-rays or x-rays. Such systems are particularly useful for the determination of single elements. All single-channel sequential spectrometers suffer the disadvantage of being slow relative to their multichannel counterparts.

The multichannel x-ray spectrometer provides the means of measuring many elements simultaneously. A multichannel spectrometer might consist of a series (7-30) of single-channel wavelength-dispersive spectrometers grouped in a semicircle around the specimen. Since fixed optics are being employed, the crystals employed are often curved to constant radius or in a logarithmic spiral to give the optimum between resolution and line intensity. Such a spectrometer is very fast and able to provide a high specimen throughout where the analytical problem is well defined. It is, however, rather inflexible and expensive. All energy-dispersive spectrometers are by definition multichannel but retain more flexibility than fixed-channel wavelength-dispersive systems. This is because the energy-dispersive system always measures the whole spectrum and the required portions can be selected from the acquired spectrum. Energy-dispersive systems thus combine many of the advantages of the single-channel and multichannel systems since they are fast but still retain a high degree of flexibility. They are, however, count-rate limited and many commercial systems employ a low-power x-ray tube as the source to deliberately limit the radiation flux from the specimen. Pulsed x-ray tubes may also be employed to reduce the counting loss of the scaling system. More sophisticated energy-dispersive spectrometers can employ one or more secondary emitters and/or filters, which limits the number of elements being excited thus making the excitation process more specific.

1.5 USE OF THE X-RAY SPECTROMETER IN THE ROUTINE ANALYTICAL LABORATORY

There are currently many thousands of x-ray spectrometers being utilized for routine qualitative and quantitative analysis. Sensitivities available for most elements reach the low part-per-million range, and the method is equally as applicable at high or low concentration levels. Accuracies of the order of a few tenths of a percent are achievable with analysis times on the order of minutes for scanning spectrometers and even less for multichannel instruments.

The x-ray spectroscopic technique is essentially nondestructive, and measurable signals can be obtained from as little as 1 mg of specimen. Optimum specimen sizes range from 0.1 to 5 g of solid material, and the technique is equally applicable to solids, liquids, and even gases. A wide range of well-analyzed calibration standards has become available over the past few years and this, combined with the development of "fundamental"-type algorithms relating x-ray emission intensity and elemental composition, is allowing the use of the x-ray method in a wide variety of analytical disciplines.

X-rays themselves pose a particular health hazard, and although a significant number of accidents did occur with earlier spectrometers, there is now strict governmental control over equipment design and acceptable dose levels. When correctly employed, the modern spectrometer is probably less of a radiation health hazard than the average color television receiver. Nevertheless, equipment must be used with proper precautions and a separate chapter of this text is devoted to this area.

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