

Appendix A

X-ray fluorescence (XRF) spectrometry*

Introduction

X-ray fluorescence (XRF) spectrometry is an atomic spectrometric method based on the detection of emitted x-ray radiation excited atom (Figure45). This technique is a two-step process that begins with the removal of an inner shell electron of an atom. The resulting vacancy is filled by an outer shell electron. The second step is the transition from the outer shell electron orbital to an inner shell electron orbital. The transition is accompanied by an emission of an x-ray photon. The fluorescent photon is characteristic of the element and is equal to the difference in energy between the two electron energy levels. Because the energy difference is always the same for given energy levels, the element can be identified by measuring the energy of the emitted photon. In turn, the intensity of the emitted photons determines the concentration of the element. Therefore the measure of photon energy provides the identification of the element and the intensity of the photon emission provides a measure of the amount of the element.

This emission process is similar to other fluorescent measurement techniques, but it is restricted to the x-ray region of the electromagnetic spectrum that ranges from 0.1 to over 120 keV, or 11 to 0.1 nm. The typical x-ray analytical region is less than 50 keV. The photon energies detected are designated as K, L, or M x-rays, depending on the energy level being filled; for example, a K shell vacancy filled by an L level electron results in the emission of a K_{α} x-ray, as shown in Figure 44. There are as many possible x-ray lines as there as inner shell electrons. However, the most useful and most intense x-ray lines are the K shell electrons for elements from boron through

* Havrilla, G. J., 1997

cerium, whereas the L and some M lines are used for the remainder of the periodic table. Although the multitude of emitted x-ray lines could make for complex spectra, the relative low intensities of the lines below the L level allow for clear spectra with a minimum of interferences.

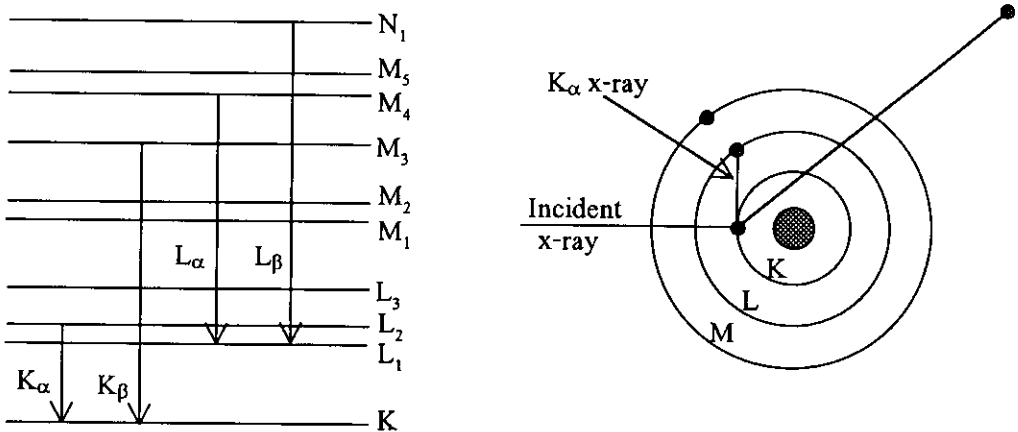


Figure 44 X-ray fluorescence process and energy level diagram. An incident x-ray photon removes an inner shell. The vacancy is filled by an outer shell electron, which gives up an x-ray photon in characteristic of the element. The energy or wavelength of the photon is determined by the energy gap between energy levels of the electron filling the inner shell vacancy (Havrilla, 1997).

Overall, the analytical capability of x-ray fluorescence has been used since 1922 to cover a wide dynamic range from trace levels of ng/mL to major composition as high as 100 wt%. The accuracy and precision of this method are unrivaled when standards are matrix matched to unknowns. This is evident in numerous industries where x-ray fluorescence is used to monitor product composition and ensure tight specification tolerances. The popularity of XRF is also a result of the limited sample

preparation that is usually required. This affords the analyst fast turnaround for composition analyses of large volumes of valuable product.

X-ray fluorescence affords the analyst a wide variety of opportunities to answer the perennial question, “What is it?” The classic scenario is to determine the elemental composition of a complete unknown. This can be handled while the client waits, using energy-dispersive x-ray fluorescence (EDXRF). All elements from sodium through uranium can be detected simultaneously. Depending on the matrix and the element of interest, detection limits range from tens to hundreds of parts per million. The next step in this scenario is usually when the client asks, “About how much is present?” This again can be handle with EDXRF or, if the analyze is known, with wavelength-dispersive x-ray fluorescence (WDXRF). In this case, an assortment of equations and algorithms have been developed to determine element composition with out the use of standards. This is a rapid way to obtain semi-quantitative information on the sample composition. The final question in this process is “Exactly how much is present?” This is where WDXRF is most useful. Highly accurate and precise analyses are routinely achieved when calibration standards match the unknowns. This is why metal, cement, oil, and petrochemical industries rely so heavily on XRF for composition analyses of product batches.

Although XRF is regarded as a mature technique, new developments in instrumental capabilities are pushing the limits of conventional XRF technology to lighter elements and lower limits of detection. In addition, recent developments, including synchrotron RXF, total reflection XRF, and x-ray micro fluorescence, are changing the capabilities of XRF within analytical chemistry. These new developments are just part of XRF’s potential in solving today’s analytical problems.

Instrument description

The basic principle of XRF is emission and detection of x-rays. The energy or wavelength of the emitted x-ray determines the element and the intensity of the x-ray emission defines the concentration of that element, there are two differences that provide some intrinsic advantages and disadvantages. Figure 46 illustrates the schematics of each approach.

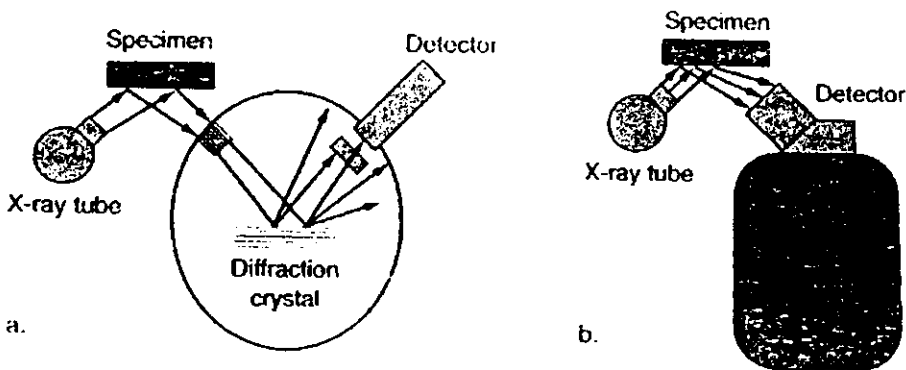


Figure 46 Schematic diagrams of wavelength and energy dispersive x-ray fluorescence instruments. (a) The wavelength dispersive instrument relies on diffraction crystals to separate the x-rays from the sample. (b) The energy dispersive system has a solid state SiLi detector that converts x-ray photons into pulses that are processed electronically (Havrilla, 1997).

In both cases, the process begins with excitation and a number of sources are used. The source of excitation also differentiates the various x-ray techniques. The most conventional and primary excitation sources are x-ray tubes. This distinguishes XRF from X-ray microanalysis in scanning electron microscopy (SEM), where electrons are used for excitation. The basic difference between the two methods is the depth of penetration of the excitation source and subsequent emission. The tube excitation source typically penetrates microns to millimeters within the sample,

whereas electron excitation is limited to less than a few microns of specimen depth. X-ray tube excitation results in essentially a bulk determination with XRF, versus surface or spatially restricted composition determination in SEM. Particle-induced x-ray emission (PIXE) uses protons or other heavy particles to induce x-ray emission. Radioisotopes are also used as excitation sources in XRF but their intensity is several orders of magnitude weaker than tube excitation. These sources are convenient for portable instrumentation and have limited sensitivity because of flux limitations. The last source type is synchrotron radiation (SR). The attractive features of SR include intensity, polarization, and collimation. The major drawback of SR is the limited access to the facility.

The dispersion of the emitted x-rays allows the different x-ray energies to be measured and the intensities of each x-ray photons determined. This is where the two different measurement systems arise: wavelength dispersive and energy dispersive. In WDXRF, the emitted x-rays are dispersed based on their wavelength using diffraction, as shown in Figure 46. The planes of a crystal are used to disperse the emitted x-ray photons from the specimen based on Bragg's law:

$$n\lambda = 2d \sin \theta$$

where n is an integer, λ is the wavelength of the photon, d is the lattice spacing, and θ is the angle of incidence of the radiation. The d values of the typical crystals used in WDXRF range from 0.14 to 8 nm. The smaller d values are for natural crystals such as lithium fluoride and germanium. The larger d values are obtained with synthetic crystals. These are typically used for light element analysis; larger d values are used of longer wavelengths. The WDXRF system is a sequential measurement, where the instrument must step through the 2θ values of the goniometer (Figure 46). This provides for higher spectral WDXRF is the simultaneous WDXRF instrument. This instrument has detectors at fixed 2θ values. This allows for rapid, sensitive analysis

and is most often found in critical process control systems such as steel and cement plants.

In contrast to the sequential nature of WDXRF, the energy dispersive system collects all the x-ray photons simultaneously onto the detector. Each photon generates an electrical pulse with amplitude that is proportional to the energy of the x-ray photon. Further electronic processing involves amplification and analysis by a multi-channel analyzer. The EDXRF system has the advantage of detecting all of the elements simultaneously, which means that analyses are rapid and unexpected elements are not missed. The major drawback, however, is that the overall resolution of the EDXRF system is not as good as the WDXRF. Consequently, these are tradeoffs in selecting which dispersive system is best for particular applications.

Three basic detectors are used in XRF instrumentation: gas ionization, scintillation, and solid- stated semiconductors. The first two detectors are found in WDXRF systems. Gas ionization detectors consist of two electrodes, a wire anode in the center of a metal cylinder cathode, and filler gas that is an argon (90 %) and methane (10 %) mixture (P10 gas). In this type of detector the x-ray photon enters through a window in the cylinder and ionizes the gas. The resulting ions and electrons are used for longer x-ray wavelengths of the lighter elements ($Z < 27$). There are both sealed and flow-proportional counters, with the flow-proportional counter used in most commercial instrumentation.

The scintillation detector consists of a thallium-doped sodium iodide crystal on the front of a photomultiplier tube, the x-ray from the specimen strike the sodium iodide crystal and generates photons that illuminate the photocathode of the photomultiplier. The photons generate photoelectrons that are amplified and detected. The number of photons produced is proportional to the energy of the x-rays. This detector is used for higher energy x-rays (short wavelength) for elements with $Z > 25$.

Typically, both the proportional counter and scintillation detectors are used for the midrange elements $25 < Z < 35$.

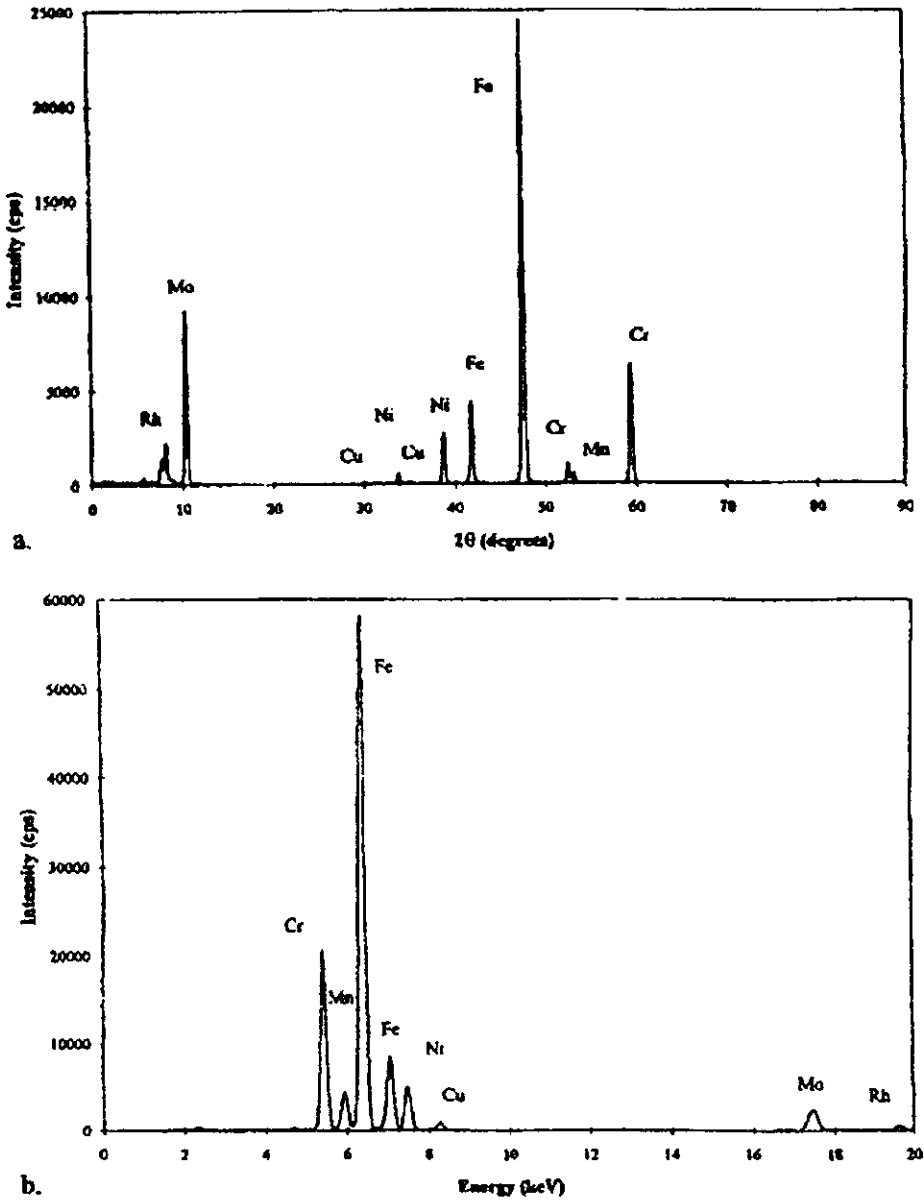


Figure 47 Analysis of 316-grade stainless steel. (a) Wavelength dispersive spectrum shows the major and minor component. Note the identification of the manganese peak at around $53^\circ 2\theta$. (b) Energy dispersive spectrum. The same elements are shown in this spectrum, but the manganese peak is buried beneath the chromium; the WDXRF spectrum spent only several seconds at each point of the spectrum.

The solid state detector is a lithium-drifted silicon Si(Li) wafer. The x-ray strikes the Si(Li) detector and generates a series of pulses that correspond to the x-ray energy. The pulse height is proportional to the x-ray energy. The concentration of the element is determined by counting the pulses. The detector and preamplifier are cooled with liquid nitrogen to minimize current noise. The issue of spectral resolution is illustrated in Figure 46, which compares the spectrum of a 316-grade stainless steel specimen obtained with WDXRF (Figure 47(a)) and EDXRF (Figure 47(b)) instruments. Although the WDXRF spectrum has better resolution, it took almost 30 min to acquire, whereas the EDXRF spectrum took only 5 min. In addition, the manganese peaks are overlapped by the chromium and iron peaks in the EDXRF spectrum, yet resolved in the WDXRF spectrum. This illustrates the need to determine the best approach, arriving at a compromise among resolution, sensitivity, speed, and cost.

General uses

- Qualitative identification and quantitative determination of element composition of a variety of samples for solids and liquids. Minimal sample preparation, wide dynamic range, and nondestructive methodology make x-ray fluorescence (XRF) the method of choice for many industrial analyses.
- Determination of sulfur in diesel fuel to meet environmental regulations.
- Control of tube oil additive concentrations with both off-line and on-line applications.

- Quality control and customer support for catalyst manufacture and plant use.
- Process control of steel and cement production.
- Support of mineralogical and geological exploration and waste site field evaluation.
- Sorting of metal alloys.
- Forensic applications in evaluating evidence.
- Coating thickness and composition process monitoring for paper and metals industries.

Samples

Any solid or liquid sample can be analyzed. Hazardous materials require special sample cells to prevent instrument contamination. Sample sizes range from micrograms to gram quantities depending on the methodology used.

Analysis time

A qualitative spectrum on an energy dispersive XRF (EDXRF) instrument can be obtained within 5 min to provide gross element composition. Quantitative programs for high accuracy and precision on a sequential wavelength dispersive XRF (WDXRF) instrument can take up to 30 min for 15 elements, whereas a simultaneous instrument can do the same measurement within 5 minutes. This is just instrument time and does not take into account the level of sample preparation that might be required.

Limitations

General

- Elemental range is limited to boron and up. Detection of light element ($Z < 11$) limited to solids and essentially surface composition.
- Matrix interferences can prevent or limit detection of some elements.
- Standards for Quantitative analysis do not always match unknown matrix.

Accuracy

Depends on sample preparation and how well standards match the unknown matrix. In many situations, accuracy of less than 1 % error can be achieved with proper care and attention to details.

Sensitivity and detection limits

This varies with element and sample matrix. In general, parts-per-million detection limits can be achieved for nominal matrices such as catalysts, steels, soils, petroleum products, and geological materials for transition row elements and above. The lighter elements ($Z < 19$) have detection limits that are typically higher, ranging from high tens of ppm to high hundreds of ppm for Mg and Na. Synchrotron radiation, total reflection XRF, and new methodologies for microsampling are pushing detection limits well below the parts-per-million level.

Appendix B

Calculation of data from WDXRF

The amount of elements remained in the residue sample was determined from the elements concentration in the mixture pellets (Table 18) by using the mixture pellet weight and the sample weight, (Table 17).

Example: calculation of the Fe content in Am5 sample

From WDXRF data, Am5 sample has Fe content in mixture 11328.58 ppm, it means:

$$\begin{aligned}
 &\text{The mixture } 1,000,000 \text{ g has Fe content } 11328.58 \text{ g} \\
 &\text{The mixture } 6.0139 \text{ g has Fe content } \frac{11328.58}{1,000,000} \times 6.0139 \\
 &\hspace{15em} = 0.0681 \text{ g} \\
 \therefore &\text{Am5 sample } 1.0003 \text{ g has Fe content } 0.0681 \text{ g} \\
 &\text{Am5 sample } 100 \text{ g has Fe content } \frac{0.0681}{1.0003} \times 100 \\
 &\hspace{15em} = 6.8109 \text{ g}
 \end{aligned}$$

So, the Am5 sample has 6.81 % Fe content

or use equation (3)

$$\boxed{\% \text{ element} = \frac{AxB}{10000C}} \quad (3)$$

Where:

A was the concentration of element in mixture pellet

B was the mixture weight

C was the sample weight

Table 17 The weight of sample, starch used, and mixture.

Sample	Sample weight (g)	Starch weight (g)	Mixture weight (g)
ilmenite	0.9936	5.0158	6.0094
Am5	1.0003	5.0136	6.0139
Am10	1.0036	5.0168	6.0204
Am15	1.0061	5.0108	6.0169
B1Na5	0.9953	5.0586	6.0539
B1Na15	1.0029	5.0121	6.015
B2	1.008	5.0352	6.0432
Ci1	1.0002	5.0612	6.0614
Ci24	1.0055	5.027	6.0325
D1	0.9804	5.0189	5.9993
D2	1.0095	5.0091	6.0186
AA	1.0001	5.0096	6.0097
CA	1.005	4.9988	6.0038
Fs120	1.0111	5.0125	6.0236

Table 18 Concentration of elements in the sample.

Sample	Concentration (%)						
	Fe	Mn	Nb	W	Sn	Y (ppm)	Zr
ilmenite	5.97	0.84	0.03	0.22	0.55	<2.29	0.02
Am5	1.13	0.31	0.16	0.51	2.15	32.08	0.05
Am10	1.02	0.19	0.09	0.46	1.39	<2.29	0.05
Am15	1.41	0.26	0.13	0.56	1.85	<2.29	0.05
B1Na5	1.03	0.19	0.09	0.51	1.39	<2.29	0.04
B1Na15	0.95	0.19	0.09	0.50	1.22	<2.29	0.04
B2	0.67	0.18	0.18	0.52	3.00	46.43	0.08
Ci1	0.97	0.14	0.14	0.50	2.02	13.79	0.06
Ci24	0.48	0.07	0.13	0.54	1.70	<2.29	0.05
D1	1.77	0.22	0.13	0.66	1.73	4.70	0.05
D2	0.26	0.03	0.12	0.68	1.73	<2.29	0.06
AA	0.32	0.12	0.17	0.69	3.00	38.27	0.09
CA	0.15	0.11	0.11	0.55	1.52	<2.29	0.04
Fs120	0.24	0.29	0.16	0.42	2.84	42.14	0.08