

Advances in Field-Portable XRF

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Field-portable x-ray fluorescence (XRF) allows us to take the laboratory to the sample. The latest generation of such handheld x-ray spectrometers is presented here. This article provides a look at the science and technology of this instrumentation, along with analytical capabilities.

X-ray fluorescence (XRF) spectrometry is a mature technology for elemental chemical analysis, dating from the early 1900s. Field-portable XRF is a more recent development, a little more than 30 years old (1). As technology advances, analytical instrumentation becomes smaller, allowing us to take the laboratory to the sample. In this article, we look at the science and technology of the latest generation of hand-held x-ray spectrometers and their analytical capabilities in alloy analysis. These spectrometers include several new radioisotope-based instruments and one featuring miniature x-ray tube excitation.

Basic X-ray Fluorescence

X-rays interact with atoms in essentially two ways: scattering and the photoelectric effect. The emission of x-rays characteristic of the atom is due to the photoelectric effect. An x-ray source has a fixed probability of ejecting an electron from the inner shells of an atom of the sample. That is,

- 1) A source emits x-ray radiation;
- 2) The radiation strikes the sample;
- 3) The radiation interacts with atoms of the sample;
- 4) There is a given probability that an electron will be ejected from the inner shells.

An outer shell electron will fill the void created in the inner shell, and there is a certain probability that an x-ray characteristic of that

atom will be emitted. This process is called *fluorescence*. (Note: A certain probability exists that the atom in its excited state will eject a higher shell electron, which is called *the Auger effect*.)

All elements emit x-rays at their own characteristic energies. These x-rays are called *K lines* if they result from an electron filling the innermost — or K — shell, and *L lines* if they result from filling the next electron shell out, the L shell. Figure 1 shows an energy level diagram for titanium and the resulting K x-ray when a K-shell electron is ejected.

The energy of the x-rays identify the elements present in the sample and, in general, the intensities of the x-ray lines are proportional to the concentration of the elements in the sample, allowing quantitative chemical analysis. An x-ray energy spectrum is shown in Figure 2. A block diagram of an energy dispersive x-ray spectrometer is shown in Figure 3.

Excitation Source

Traditionally, all hand-held XRF spectrometers used radioisotope excitation. Now, however, recent advances in x-ray tube technology allow the use of these devices as an alternative means of excitation.

The new isotope-based spectrometers are designated models XLi — the “i” is for isotope. Analytical data are presented here for two radioisotope configurations: a 40-mCi ^{109}Cd isotope excitation source, and a 30-mCi ^{241}Am isotope. (Note: The curie [Ci] is the unit of nuclear activity and equals 3.7×10^{10} disintegrations per second.)

The ^{109}Cd source emits x-rays with energies of 22 and 25 keV when it decays to ^{109}Ag in the two-step nuclear process of electron capture and internal conversion. In addition, a small portion (3.8%) of its photon output is emitted at 88 keV. The 22- and 25-keV emissions of this isotope may be used for the K-shell excitation of atomic numbers 22 (Ti) through 44 (Ru) and L-shell excitation of atomic numbers 67 (Ho) through 94 (Pu). Additionally, an 88-keV

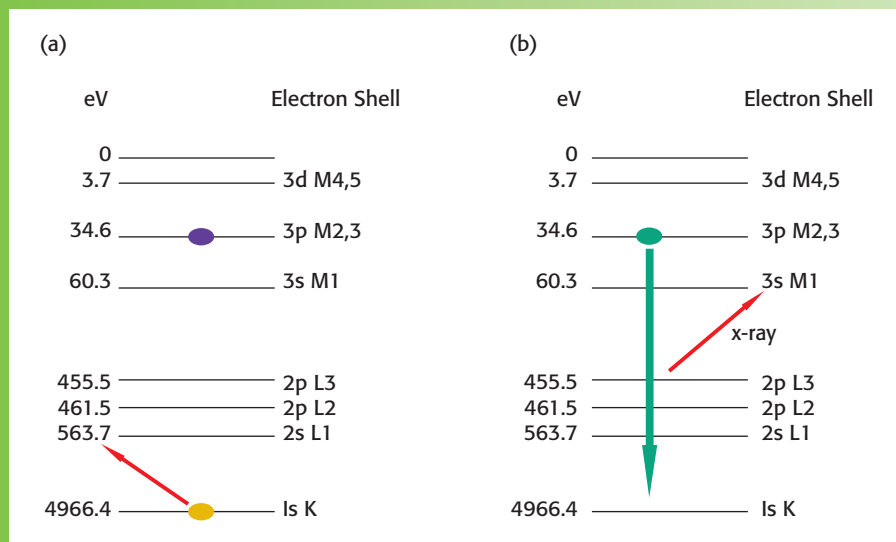


Figure 1. (a) Energy level diagram and (b) the emission of an x-ray.

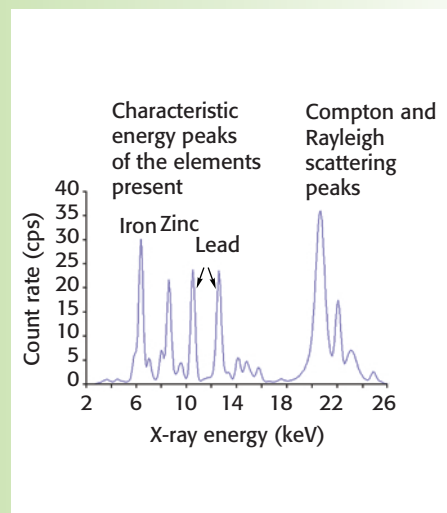


Figure 2. X-ray energy spectrum of a soil sample.

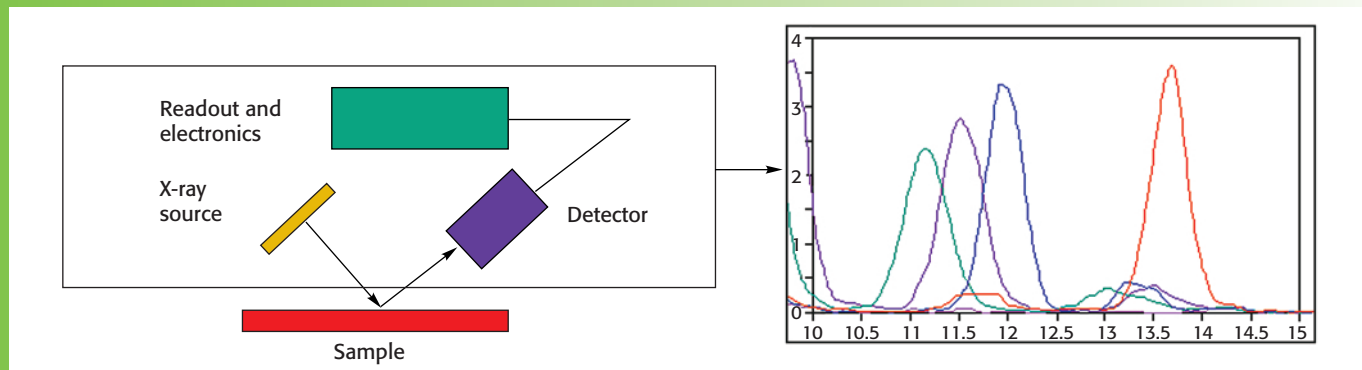


Figure 3. Block diagram of an x-ray spectrometer.

output will excite K-shells up to lead. The isotope has a half-life of 1.24 years, meaning that after this time the source activity is half its original value.

The ²⁴¹Am is a source of 59.5 keV x-rays allowing for the excitation of higher atomic number elements. This isotope has generally been used for the K-shell excitation of atomic numbers 45 (Rh) through 66 (Dy). However, ²⁴¹Am is also a source of lower excitations at approximately 13.95 and 17.7 keV (the neptunium L-lines). Normally, these radiations are blocked in the source holder. However, taking advantage of these emissions, rather than blocking them, allows for efficient excitation of the lower atomic number elements. This permits all elements from about atomic number 22 (Ti) through 94 (Pu) to be analyzed effectively with only one radioisotope source. This is significant because previous hand-held XRF analyzers required two separate ra-

dioisotope sources to cover this element range — that is, both ¹⁰⁹Cd and ²⁴¹Am. Furthermore, the americium isotope has a half-life of 432 years and therefore never requires replacement. Because of this, the XLi model using this isotope alone to cover the elements of interest has been dubbed the Infiniton.

Miniature x-ray tubes have only recently become a reality (see, for example, reference 2), allowing their incorporation into portable XRF spectrometers. Higher x-ray flux provides faster results and better precision than radioisotope sources. The low-power, hot-filament cathode x-ray tube used in generating data presented here had a silver transmission anode and was operated at 35 kV and 5 A. The new x-ray tube-based spectrometers are designated models XLt (“t” is for tube).

Radiation exposure, when properly operating the spectrometer, is < 0.1 mrem/h. As a point of reference, con-

sider that the average annual dose in the United States is ~ 360 mrem and that the typical chest x-ray involves a dose of ~ 6 mrem.

The Detector

The detector is a semiconductor diode called a silicon positive intrinsic negative (Si PIN). The large, central intrinsic region is a charge-depleted silicon slab sandwiched between the P (positive-anode) and N (negative-cathode) semiconducting layers of the diode. The incoming x-rays interact with the silicon atoms such that one electron-hole pair is produced for every 3.6 eV. A schematic of the Si PIN detector is shown in Figure 4. The incorporated field effect transistor (FET) in the TO-8 package provides the first stage amplification for the very weak detector signal.

A voltage is applied across the diode so that when an incoming x-ray produces ionization in the silicon region,

Table I. Precision results on stellite 25

Alloy	XLi 40-mCi ¹⁰⁹ Cd			XLi Infiniton 30 mCi ²⁴¹ Am			Certified values
	Average	Standard Deviation	% RSD	Average	Standard Deviation	% RSD	
Stellite 25							
Cr	20.14	0.196	0.97	19.95	0.252	1.27	20.0
W	15.68	0.245	1.56	15.14	0.195	1.29	15.1
Ni	9.65	0.185	1.92	10.29	0.238	2.31	9.78
Co	51.51	0.346	0.67	50.9	0.478	0.94	51.5

an immediate charge transfer occurs. This is converted to a voltage signal proportional to the energy of the incoming x-ray. These voltages are then sorted by a multichannel analyzer and fed to the computer. This new generation of hand-held spectrometers incorporates new electronics, including a patented digital signal processor.

The detector is thermoelectrically cooled to -25 °C to lower the leakage current and, thus, reduce noise. (In laboratory XRF spectrometers the detector

typically is cooled using liquid nitrogen.) The lower background provided by the reduced noise enhances performance by improving resolution and providing lower limits of detection.

X-ray Intensities to Concentration

There are several steps in the measurement sequence from the measured x-ray intensities across the energy spectrum to elemental concentrations. Initially, regions of interest defining the x-ray energy peaks for the various ele-

ments are established and the x-ray intensities in these regions are counted (integrated). Next, the blank is subtracted. This spectrum of air is measured during the calibration process and accounts for scattering and fluorescence from the instrument itself.

The next step is spectrum deconvolution. During the calibration process, numerous pure metals are also measured, and the spectra stored. Factors are generated describing the effect of each of these elements in the other regions of

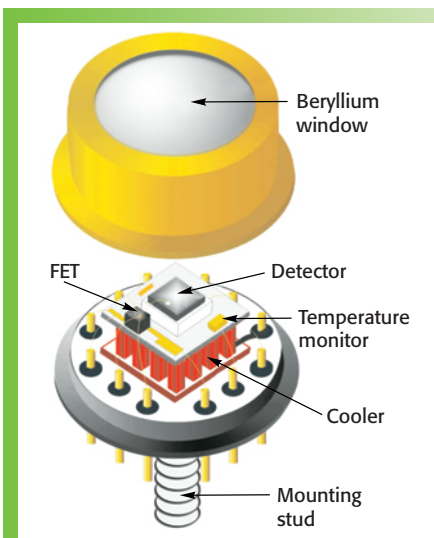
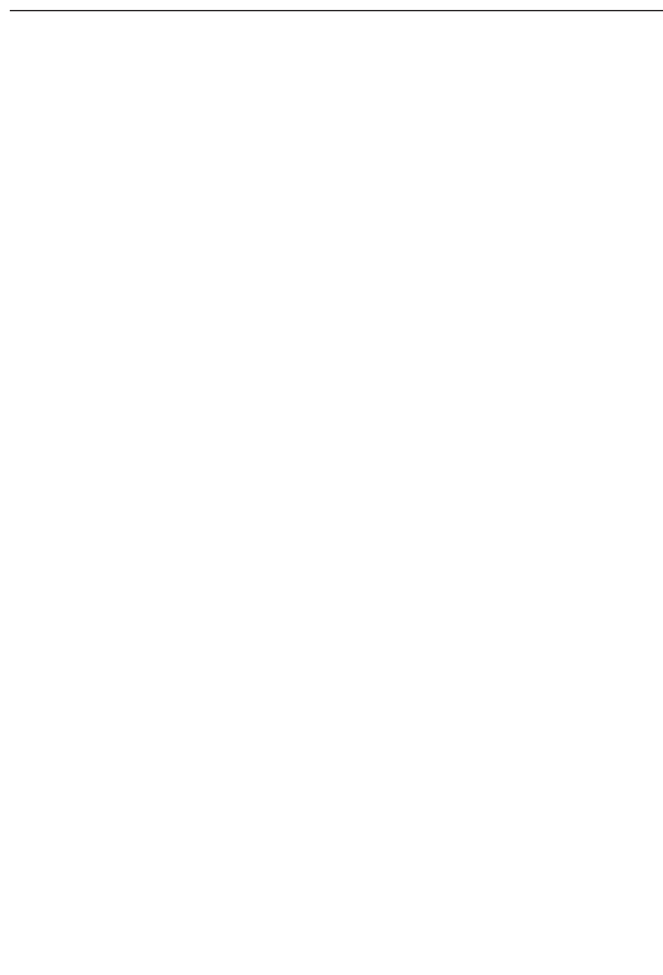


Figure 4. Diagram of silicon positive intrinsic negative (Si PIN) detector.

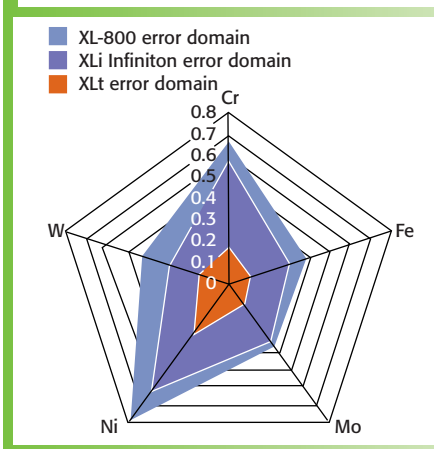


Figure 5. Comparison of measurement precision for alloy Hastelloy C-276.

interest. These factors are applied to the integrated signals in the various regions of interest of the unknown sample. In this way, we can correct for x-rays of one element that overlap the region of interest of another.

In alloy analysis, the deconvoluted intensities are subjected to a fundamental parameters (FPs) calculation based on x-ray physics and the relevant ele-

mental parameters that have been measured and tabulated through the years. (For more information on FPs and XRF see, for example, references 3 and 4). Note that empirical factor/offset corrections may be applied as necessary to fine-tune this theoretical calibration.

Analytical Aspects

The two hallmarks of any analytical

technique are precision and accuracy. Precision is defined as the reproducibility of repeat measurements, and may be quantified by the standard deviations of these results. Accuracy, on the other hand, is the relationship of the measured value to the true value. Perhaps the best way to evaluate the accuracy of an analytical method is to generate correlation curves between measured and certified values.

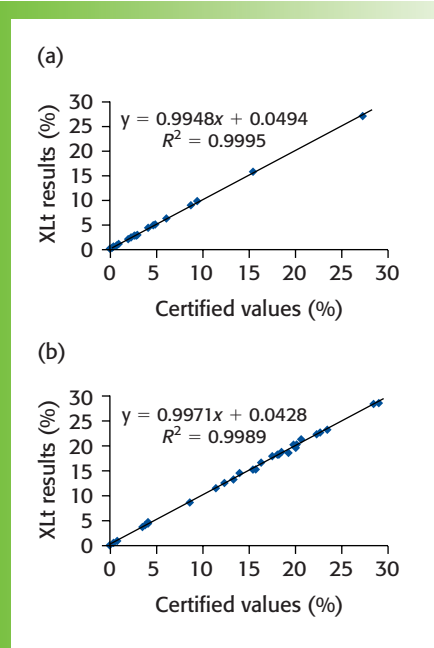


Figure 6. Correlation curves for (a) molybdenum and (b) chromium in alloys of iron, cobalt, and nickel.

Precision data are shown in Table 1 for an alloy reference material using two different isotope excitation sources. Standard deviations were calculated based on 11 measurements for 20 s each. The relative standard deviations were calculated as standard deviation divided by the mean and multiplied by 100. It should be noted that the precision shown here is worthy of laboratory instrumentation.

Figure 5 provides a graphical comparison of new-generation precision with that of the previous generation of instrumentation. Shown are two sigma values for five elements in the alloy Hastelloy C-276. The outer area connects the precision results from previous-generation instrumentation (XL-800) using 10 mCi ^{109}Cd excitation. The inner area shows results with the

miniature x-ray tube excitation (XLt), while the area in between shows new generation ^{241}Am (XLi) results. This shows that the single americium source performs slightly better than the traditional ^{109}Cd excitation across the range of elements of interest in this sample. It also shows significantly better precision achievable with x-ray tube excitation.

Correlation curves for two major alloying elements — chromium and molybdenum — in alloys of iron, nickel, and cobalt as measured using an instrument with x-ray tube excitation are shown in Figure 6. Some 30 alloys of iron, nickel, and cobalt were measured to generate these curves. The excellent agreement between certified and measured values should be noted.

One interesting aspect of these correlation curves is that they cover three matrices. The spectrometer itself determines the matrix element, which is displayed in about a second. All measurements are made in a single “alloy” mode, or calibration model. The high accuracy evidenced here is a demonstration of the quality of the fundamental parameters model used.

Finally, there are times when accuracy is not required — when a simple qualitative analysis will answer the question posed. Therefore, it is valuable to view the entire spectrum and identify element peaks. This is possible with a touch of the screen.

This new generation of instruments is very fast. It is difficult to assign a number to the improvement in speed of analysis; however, we note that these instruments provide an alloy grade identification in 1–2 s, compared with 6–8 s with the previous generation.

Conclusion

Advances in electronics and data processing coupled with higher x-ray fluxes have produced substantial improvements in the precision and speed of analysis of hand-held x-ray spectrometric instrumentation.

References

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