X-RAY FLUORESCENCE

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ABSTRACT

X-ray fluorescence (XRF) spectrometry is an elemental analysis technique with broad application in science and industry. XRF is based on the principle that individual atoms, when excited by an external energy source, emit X-ray photons of a characteristic energy or wavelength. By counting the number of photons of each energy emitted from a sample, the elements present may be identified and quantities.

Keywords: X-ray fluorescence, Sources, Detectors and Applications.

INTRODUCTION

Henry Moseley was perhaps the father of this technique, since he, building on W.C. Roentgen's discovery of the high-energy radiation dubbed X-rays, built an X-ray tube which he used to bombard samples with high-energy electrons. Moseley in 1912 discovered a mathematical relationship between the elements emitted X-ray frequency and its atomic number. In 1925 Coster and Nishina were the first to use primary X-rays instead of electrons to excite a sample. After Glocker and Schreiber were the first to perform quantitative analysis of materials using XRF in 1928, detector technology had to catch up in order to make the technique practical, which didn't begin to happen until the 1940's. The 1950's saw the first commercially produced X-ray spectrometers. In 1970, the lithium drifted silicon detector was developed, and this technology is still in use today.

Modern XRF instruments are capable of analyzing solid, liquid, and thin-film samples for both major and trace (ppm-level) components. The analysis is rapid and usually sample preparation is minimal or not required at all.

Principle

X-ray is a type of electromagnetic waves such as visible light ray, but the key difference is its extremely short wavelength, measuringfrom 100A to 0.1A. And compared to normal electromagnetic waves, X-ray easily passes through material and it becomes stronger as the material's atomic number decreases. X-ray fluorescence analysis is a method that uses the characteristic X-ray (fluorescent X-ray) that is generated when X-ray is irradiated on a substance. The fluorescent X-ray is the excess energy irradiated as electromagnetic field, which is generated when the irradiated X-ray forces the constituent atom's inner-shell electrons to the outer shell and the vacant space (acceptor) falls on the outer-shell electrons. The generation of fluorescent X-ray is shown in Figure 1. These rays possess energy characteristic to each element, and qualitative analysis using Mosley's Equation and quantitative analysis using the energy's X-ray intensity (number of photons) are possible.

X-ray fluorescence analysis can be considered as spectrochemical analysis of an X-ray region. It has the same characteristics as atomic absorption spectrometry and optical emission spectrometry which conduct measurement by putting the sample into solution. For example, in flameless atomic absorption spectrometry (FLAAS), elements in the sample are atomized in 2000 to 3000C flame and in ICP atomic emission spectrometry (ICP-AES), sample is excited in 6000 to 9000C plasma flame. X-ray fluorescence likewise excites the sample using X-ray to obtain information [1].

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Instrumentation

Most of the XRF instruments in use today fall into two categories: energy-dispersive (ED) and wavelength-dispersive (WD) spectrometers. This paper will cover the most common types of instruments, with forays into the more advanced or specialized components where they are of interest. A diagram of a WD system is shown in Figure 2. The instrument operates based on the principle of Bragg diffraction of a collimated X-ray beam, in this case the beam emanating from the sample [2]. A typical ED spectrometer is diagrammed above. Here the entire polychromatic spectrum from the sample is incident upon a detector that is capable of registering the energy of each photon that strikes it. The detector electronics and data system then build the X-ray spectrum as a histogram, with number of counts versus energy.

X-Ray Source

The "front end" of both types of instruments is the X-ray source. The source consists of an evacuated chamber with a heated cathode, which is usually a tungsten wire, and an anode, which is held at a potential difference of several tens of kilovolts relative to the cathode. Thermal electrons are released from the cathode and accelerated toward the anode. When the electron beam impinges upon the anode, bremsstrahlung radiation as well as X-ray lines characteristic of the anode material are emitted. These photons escape through a beryllium window built into the side of the tube [3].

There is no one-size-fits-all approach for source selection in XRF. X-ray tube powers may be set up at very different levels, from a fraction of a watt for EDXRF instruments with high detection efficiencies to several kilowatts for WDXRF instruments. In this latter case, the tube must be liquid-cooled since the majority of the power is dissipated as heat. The anode materials must be carefully chosen as well, since the wavelength of their characteristic lines is important for proper excitation of the sample. Some example single-element anode materials are aluminum, chromium, tungsten, palladium, or gold. For detection of light elements, a high intensity of low energy, i.e. 1-10 keV, radiation must be available, while heavy elements require excitation at higher energies up to 50 keV. It is also important to keep in mind that the primary source of detector background will be the intense primary radiation from the tube, above which the secondary sample radiation must be detected. A tube anode material is chosen to give a high bremsstrahlung or continuum output, which is used to excite a secondary fluorescer, or *target*, which gives off its own characteristic lines without the continuum. The sample is then excited by the emission from the target, which is chosen to efficiently excite elements in a certain Z range. A system may be set up to change targets automatically during the analysis so that the low, middle, and high end of the sample spectrum may be sequentially boosted. When an EDXRF instrument uses such a system,

tube powers must be increased dramatically since most of the original X-ray intensity is lost.

Certainly XRF excitation is not limited only to X-ray tubes. Less common excitation sources include gamma-emitting radioisotopes (241Am, 109Cd, 153Gd, and others), electron sources where the sample is the tube anode, and synchrotrons, which produce highly intense, coherent, monochromatic X-ray beams.

Sample Chamber

Up to this point, little has been said regarding what kinds of samples may be analyzed by XRF. The development of portable XRF (PXRF) instruments has greatly expanded the range of samples suitable for analysis. There is no longer a need to fit a sample into a small chamber. In the case of PXRF, it is possible to analyze the samples with the instrument in a stand or the instrument can be moved to the sample, as in the case of analyzing an exposed rock outcrop or a large painting. The majority of the samples analyzed by XRF at MURR are small obsidian artifacts that are placed on the nose of the instrument. We have recently acquired an automated sample changer that allows us to load up to 20 samples at a time and operated much like the sample changers on large lab-based instruments.

Monochromators

The common feature of Monochromators is the maintenance of a symmetrical geometry between the sample, the crystal and the detector. In this geometry the Bragg diffraction condition is obtained. The X-ray emission lines are very narrow, so the angles must be defined with considerable precision. This is achieved in two ways [4]

Flat crystal with soller collimators

The Soller collimator is a stack of parallel metal plates, spaced a few tenths of a millimeter apart. To improve angle resolution, one must lengthen the collimator, and/or reduce the plate spacing. This arrangement has the advantage of simplicity and relatively low cost, but the collimators reduce intensity and increase scattering, and reduce the area of sample and crystal that can be "seen". The simplicity of the geometry is especially useful for variable-geometry Monochromators.

Curved crystal with slits

The Rowland circle geometry ensures that the slits are both in focus, but in order for the Bragg condition to be met at all points, the crystal must first be bent to a radius of 2R (where R is the radius of the Rowland circle), then ground to a radius of R. This arrangement allows higher intensities (typically 8-fold) with higher resolution (typically 4-fold) and lower background. However, the mechanics of keeping Rowland circle geometry in a variable-angle Monochromators is extremely difficult.

In the case of fixed-angle Monochromators (for use in simultaneous spectrometers), crystals bent to a logarithmic spiral shape give the best focusing performance. The manufacture of curved crystals to acceptable tolerances increases their price considerably.

Detector Systems

Detectors used for wavelength dispersive spectrometry need to have high pulse processing speeds in order to cope with the very high photon count rates that can be obtained. In addition, they need sufficient energy resolution to allow filtering-out of background noise and spurious photons from the primary beam or from crystal fluorescence. There are four common types of detectors are, 1. Gas flow proportional counters, 2. Sealed gas detectors, 3.Scintillation counters and 4.Semiconductor detectors [5].

Gas flow proportional counters

Gas flow proportional counters are used mainly for detection of longer wavelengths. Gas flows through it continuously. Where there are multiple detectors, the gas is passed through them in series, then led to waste. The gas is usually 90% argon, 10% methane ("P10"), although the argon may be replaced with neon or helium where very long wavelengths (over 5 nm) are to be detected. The argon is ionized by incoming X-ray photons, and the electric field multiplies this charge into a measurable pulse. The methane suppresses the formation of fluorescent photons caused by recombination of the argon ions with stray electrons. The anode wire is typically tungsten or nichrome of 20–60 μm diameters. Since the pulse strength obtained is essentially proportional to the ratio of the detector chamber diameter to the wire diameter, a fine wire is needed, but it must also be strong enough to be maintained under tension so that it remains precisely straight and concentric with the detector. The window needs to be conductive, thin enough to transmit the X-rays effectively, but thick and strong enough to minimize diffusion of the detector gas into the high vacuum of the monochromator chamber. Materials often used are beryllium metal, aluminized PET pans and aluminized polypropylene. Ultra-thin windows (down to 1 μm) for use with low-penetration long wavelengths are very expensive.

Sealed gas detectors

Sealed gas detectors are similar to the gas flow proportional counter, except that the gas does not flow through it. The gas is usually krypton or xenon at a few atmospheres pressure. They are applied usually to wavelengths in the 0.15–0.6 nm range. They are applicable in principle to longer wavelengths, but are limited by the problem of manufacturing a thin window capable of withstanding the high pressure difference.

Scintillation counters

Scintillation counters consist of a scintillating crystal (typically of sodium iodide doped with thallium) attached to a photomultiplier. The crystal produces a group of scintillations for each photon absorbed, the number being proportional to the photon energy. This translates into a pulse from the photomultiplier of voltage proportional to the photon energy.

The crystal must be protected with a relatively thick aluminium/beryllium foil window, which limits the use of the detector to wavelengths below 0.25 nm. Scintillation counters are often connected in series with a gas flow proportional counter: the latter is provided with an outlet window opposite the inlet, to which the scintillation counter is attached. This arrangement is particularly used in sequential spectrometers.

Semiconductor detectors

Semiconductor detectors can be used in theory, and their applications are increasing as their technology improves, but historically their use for WDX has been restricted by their slow response.

Wavelength-Dispersive Spectrometers

More collimators, usually made from a series of closely spaced parallel metal plates, are needed to direct the beam in order to closely control the diffraction angle of all detected photons. The analyzing crystal angularly disperses incident radiation of wavelength l according to Bragg's Law ($n\lambda = 2d \sin\theta$, n = 1, 2, 3,… where d is equal to the crystal lattice spacing). In the instrument shown, the analyzing crystal may be rotated with the detector assembly simultaneously revolving around it to scan through the possible wavelengths.

To resolve wavelengths in all regions, different crystals must be used, since crystals with large spacing's must be used for long wavelengths but they make the short wavelengths irresolvable at low. The system in the diagram utilizes two detectors in series. The first, a gas-flow proportional detector, is efficient for detecting long-wavelength radiation (> 0.15 nm). Most high-energy X-rays pass through it, however, and are counted by the NaI(Tl) scintillation detector. The gas-flow proportional detector works by placing a high voltage across a volume of gas (usually Ar with methane). An X-ray photon will ionize a number of Ar atoms proportional to its energy. The freed electrons are accelerated in the high voltage, ionizing other Ar atoms and creating an electron cascade which is controlled by the quench gas methane. The freed charges are measured in the circuitry as a voltage pulse whose height is proportional to the energy of the photon that initiated the cascade.

With WDXRF systems, it may be possible to have several detector assemblies placed at fixed angular locations in order to analyze for a few selected elements over and over. WDXRF spectrometers often offer more flexibility for the researcher as well as very good

sensitivities. The detector outputs are also simpler to use directly and do not generally require heavy use of electronics and computer algorithms in order to deconvolute. Disadvantages include the inability to quickly acquire the entire X-ray spectrum for full-element analyses, higher hardware costs, and a larger instrumental footprint when compared to EDXRF systems [6].

Energy-Dispersive Spectrometers

While simpler in terms of the positioning of the detector versus the sample, EDXRF spectrometers require sophisticated electronics and computer software in order to interpret the detector output. Nowadays this is less complicated, though, due to important technological advances in multichannel analyzers and faster computers, and EDXRF is often the technique of choice for fast multielement analyses.

Dispersion in EDXRF is accomplished through the use of a semiconductor-type detector. Although germanium detectors are utilized, the most common type in service is the Si(Li), or lithium-drifted silicon, detector. A semiconductor detector operates based on the principle that an X-ray photon incident upon the diode material will give up its energy to form electron-hole pairs, the number of which is proportional to the energy of the photon [7].

The high voltage applied across the diode quickly collects the released charge on a feedback capacitor, and the resulting proportional voltage pulse amplified by a charge-sensitive preamplifier. The output of the preamp is fed to a main amplifier system. The pileup rejector, part of this system, deals with the probable event that two pulses will arrive very close together in time. From this point, the pulse is converted to a digital signal and processed in the multichannel analyzer (MCA).

For both of the Bruker Tracer instruments we use we have incorporated a secondary target made of thin sheets of copper, aluminum and titanium to optimize the spectra for the analysis of obsidian and any other analyses focusing on elements with fluorescent energies between about 10 and 20 kV.

Sample Preparation for XRF

Sample preparation is highly variable depending on the matrix and goals of the analysis. Most of the materials we analyze (obsidian, metals, and ceramic paints) do not require any sample preparation. The choice of sample preparation depends on the nature of the X-ray beam relative to the sample. For example, a piece of obsidian that is 1 cm thick and has a clean, flat surface will provide ideal results. As samples get smaller, thinner, or less homogenous it is necessary to understand the nature of the X-ray beam and how it interacts with the sample.

The Bruker Tracer III instruments have a beam size of only about 2 x 3 mm. This small beam is fine for homogenous materials, but heterogenous material such as crystalline rocks and tempered pottery may need to be analyzed multiple times in numerous areas to generate a representative average composition. The small beam size is ideal for isolating specific painted elements on the surface of ceramics and also aids in the analysis of very small obsidian artifacts. Homogeneous solid samples such as metals may be machined and smoothed to form disks. Whatever type of preparation is done, the surface roughness of the sample should be taken into account. A rough surface causes the penetration layer to look heterogeneous to the spectrometer. In general, the surface roughness (measured in μm) should not exceed the path length for 10% absorption of the radiation being measured [8].

Extracting analytical results

At first sight, the translation of X-ray photon count-rates into elemental concentrations would appear to be straightforward: WDX separates the X-ray lines efficiently, and the rate of *generation* of secondary photons is proportional to the element concentration. However, the number of photons *leaving the sample* is also affected by the physical properties of the sample: so-called "matrix effects". These fall broadly into three categories:

- X-ray absorption
- X-ray enhancement
- sample macroscopic effects

All elements *absorb* X-rays to some extent. Each element has a characteristic absorption spectrum which consists of a "saw-tooth" succession of fringes, each step-change of which has wavelength close to an emission line of the element. Absorption attenuates the secondary X-rays leaving the sample.

Enhancement: Occurs where the secondary X-rays emitted by a heavier element are sufficiently energetic to stimulate additional secondary emission from a lighter element. This phenomenon can also be modeled, and corrections can be made provided that the full matrix composition can be deduced.

Sample macroscopic effects: It consists of effects of in homogeneities of the sample, and unrepresentative conditions at its surface. Samples are ideally homogeneous and isotropic, but they often deviate from this ideal. Mixtures of multiple crystalline components in mineral powders can result in absorption effects that deviate from those calculable from theory. When a powder is pressed into a tablet, the finer minerals concentrate at the surface. Spherical grains tend to migrate to the surface more than do angular grains.

In machined metals, the softer components of an alloy tend to smear across the surface. Considerable care

and ingenuity are required to minimize these effects. Because they are artifacts of the method of sample preparation, these effects cannot be compensated by theoretical corrections, and must be "calibrated in".

This means that the calibration materials and the unknowns must be compositionally and mechanically similar, and a given calibration is applicable only to a limited range of materials. Glasses most closely approach the ideal of homogeneity and isotropy, and for accurate work, minerals are usually prepared by dissolving them in a borate glass, and casting them into a flat disc or "bead". Prepared in this form, a virtually universal calibration is applicable [9].

Applications of XRF Spectrometry

Currently XRF spectrometry is very widely applied in many industries and scientific fields. The steel and cement industries routinely utilize XRF devices for material development tasks and quality control.NIST utilizes XRF as one technique to quantitatively analyze and acceptance-test many of its standard reference materials (SRMs), from spectrometric solutions to diesel fuel to coal to metal alloys. The plastics industry is looking at a modified XRF spectrometer as an on-line wear monitor, taking advantage of its ability to detect particles of worn-off metal in extruded plastic pieces. Polish scientists are accomplishing XRF analyses on very thin films by placing the source and detector at very low angles with respect to the sample. This technique is being applied to trace element determinations in water samples that have been evaporated to a thin film of residue. XRF has been one of the tools of choice for geologists for many years, so much so that graduating geologists usually receive practical training with these devices, whereas graduating chemists probably haven't even heard of the technique. For geologists, the ability to determine major and trace components in one quick analysis with relatively little sample preparation has been a boon. Current basic research aimed at improving XRF analyses for geological and ecological samples focuses on methods for correcting for matrix effects, in which major components absorb some of the X-rays emitted from trace components [10].
Archaeometrists have applied XRF in order to solve their ancient mysteries. An example of this was the study of the composition of blue soda glass from York Minster, England, which distinguished three compositional groups, indicating this number of possible sources for the glass. Trace metal signatures also can effectively differentiate genuine artifacts from modern copies. Forensic scientists utilize XRF spectrometry to match samples associated with suspects (i.e. dirt or sand on clothing or shoes) to samples from crime scenes. As for other applications, here XRF can help elucidate an elemental fingerprint, without need to analyze the evidence destructively.

X-Ray fluorescence is used in a wide range of applications, including
- Research in igneous, sedimentary, and metamorphic petrology
- Soil surveys
- Mining (e.g., measuring the grade of ore)
- Cement production
- Ceramic and glass manufacturing
- Metallurgy (e.g., quality control)
- Environmental studies (e.g., analyses of particulate matter on air filters)

- Petroleum industry (e.g., sulfur content of crude oils and petroleum products)

- Field analysis in geological and environmental studies (using portable, hand-held xrf spectrometers)x-ray fluorescence is particularly well-suited for investigations that involve

- Bulk chemical analyses of major elements (si, ti, al, fe, mn, mg, ca, na, k, p) in rock and sediment

- Bulk chemical analyses of trace elements (in abundances >1 ppm; ba, ce, co, cr, cu, ga, la, nb, ni, rb, sc, sr, rh, u, v, y, zr, zn) in rock and sediment - detection limits for trace elements are typically on the order of a few parts per million(12).

X-ray fluorescence is limited to analysis of
- Relatively large samples, typically > 1 gram

- Materials that can be prepared in powder form and effectively homogenized

- Materials for which compositionally similar, well-characterized standards are available

- Materials containing high abundances of elements for which absorption and fluorescence effects are reasonably well understood

In most cases for rocks, ores, sediments and minerals, the sample is ground to a fine powder. At this point it may be analyzed directly, especially in the case of trace element analyses. However, the very wide range in abundances of different elements, especially iron, and the wide range of sizes of grains in a powdered sample, makes the proportionality comparison to the standards particularly troublesome. For this reason, it is common practice to mix the powdered sample with a chemical flux and use a furnace or gas burner to melt the powdered sample. Melting creates a homogenous glass that can be analyzed and the abundances of the (now somewhat diluted) elements calculated.
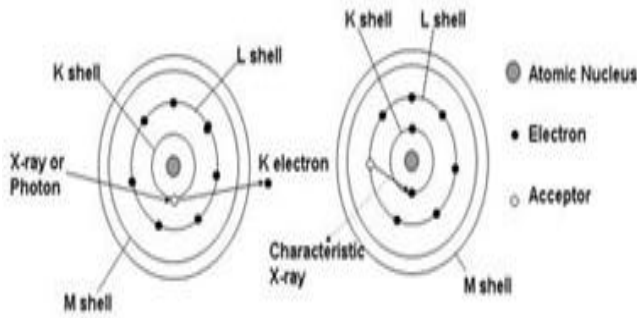
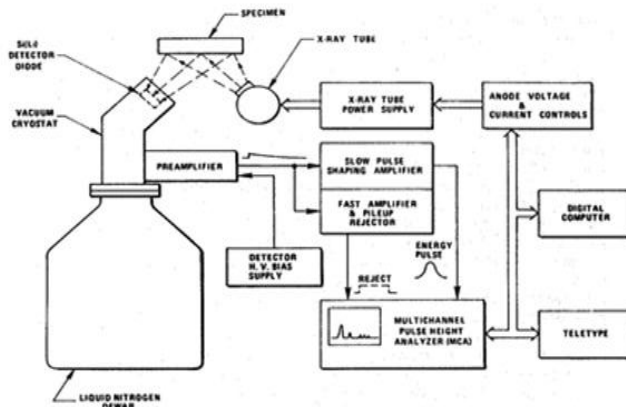**Figure 1. X-Ray**

Figure 2. Diagram of a wavelength-dispersive spectrometer

Figure 3. Block diagram of a typical EDXRF spectrometer

Figure 4. Flat crystal with Soller collimators

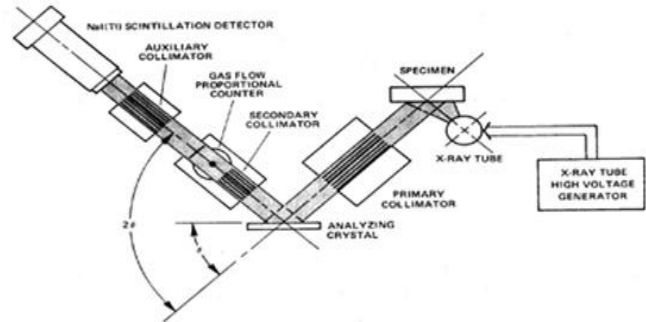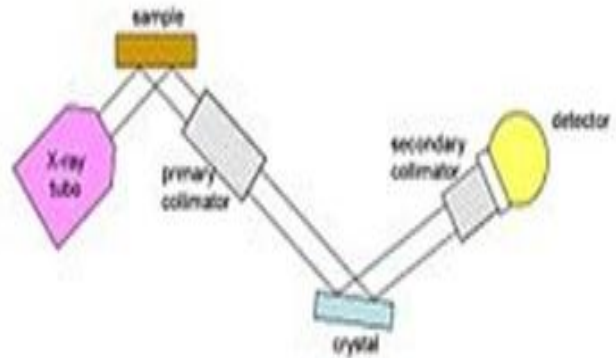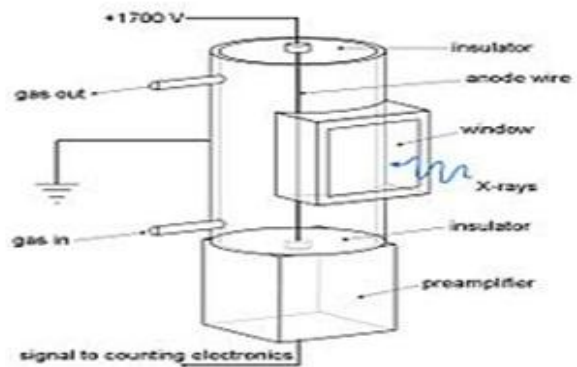**Figure 5. Curved crystal with slits**

Figure 6. Arrangement of gas flow proportional counter

CONCLUSION

With the help of both WDXRF and EDXRF spectrometer virtually all types of sample materials can be analysedand the higher degree of analytical accuracy and precision.Hence XRF is now recognised as a versatile laboratory tool which is useful for both infrequent and routine sample analysis and thus XRF certainly does hold an important position in the realm of analytical chemistry.

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