X-ray Sources for Handheld X-ray Fluorescence Instruments

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This article discusses the current status of X-ray sources (tubes and power supplies) used in handheld X-ray fluorescence instruments. It outlines the basics of the tube and high-voltage power supply (HVPS) design and the functionality of X-ray sources designed specifically for handheld X-ray fluorescence (XRF). Further, the testing methodologies of the tubes and power supplies are discussed. Finally, the selection criteria for the X-ray source for common applications are presented.

1 BACKGROUND

Handheld XRF main advantage is taking the instrument to the sample, not the sample to the instrument.[1] The miniature tube-based X-ray source was a critical component in shifting the XRF technique from the laboratory to the field in handheld XRF. This portability has proved to be a very big advantage, demonstrated by the rapid growth of the handheld XRF market in 2004–2012. Handheld XRF absolutely needs small, lightweight, low-power components. All of these qualities are needed to make the entire instrument about the size of a handheld cordless drill. These constraints made the miniature X-ray source what it is today, with an 'X-ray source' defined to be composed of a miniature X-ray tube combined with a miniature HVPS. The tube has to be very small, consume a little amount of power, and robust to withstand shocks from dropping and temperature extremes found in the field (Figure 1). This is also true for the HVPS, which is often powered by a 9–18 V DC small portable battery with variable output. The tube and the HVPS both need to operate at voltages as high as 50 kV in a very small and sometimes sealed space, which is a very challenging engineering problem. All of these challenges have been attained with the miniature X-ray source used in handheld XRF today.

Historically, the radioisotopes were used in the handheld XRF instruments owing to their light weight, small size, and the monochromatic radiation with energies capable of exciting the K-lines in most materials of interest.[2] The handling of radioactive materials severely limited handheld XRF based on radioisotopes owing to strict and continual tightening regulations on their handling and transportation.

About the year 1999, Moxtek developed its first few miniature X-ray tube-based X-ray sources, funded by a NASA SBIR for the CHEMIN XRD/XRF instrument for Mars missions.[3] This X-ray source had the required small size and low power, which was needed to replace isotopes in handheld XRF. This was a huge advantage because it freed up legal restrictions with an X-ray source that could be turned on and off. Other advantages included having the flux output level adjustable to maximize the

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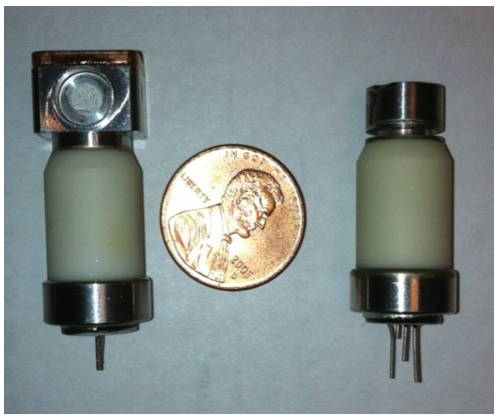

(a) (b)

Figure 1 Transmission window (b) and side window (a) tubes. The tube body is ceramic; the cathode and anode assemblies are metal alloys. (Reproduced with permission from www.moxtek.com © Moxtek, Inc.)

signal from the detector and the high voltage adjustable to change the range of elements detected. The limitation on the miniature X-ray tube was the high-voltage range, this was restricted to 35–50 kV owing to needed X-ray shielding. Therefore, most analyses for elements with atomic number higher than 50 (Sn) are done based on the L-lines that hinder the accuracy and precision of measurements.

The rapid growth of the handheld XRF market in 2004–2012 required that the X-ray sources be mass produced at ever-decreasing costs and at the same time satisfying the demand for ever-increasing performance. In the second decade of the twenty-first century, the global demand for the miniature X-ray sources reached 10 000 units per year level, far surpassing the market for the bench top and analytical XRF instruments. The market driving applications put the XRF instruments in scrapyards, mines, deserts, high mountains, and arctic conditions in the hands of non-XRF experts. From the start, there has been a demand for reducing the size and weight of both the tubes and high-voltage power supplies. Figure 2 shows the reduction is size and weight over the period from 2001 until 2014. It also shows the increasing high voltage and power of the miniature X-ray sources.

2 THE MINIATURE X-RAY SOURCE

An X-ray source is composed of a miniature X-ray tube and a miniature HVPS; sometimes, the HVPS is also called a generator. Figure 3 gives a schematic of the main parts of both an X-ray tube and the HVPS. The following two sections describe the X-ray tube and the HVPS. In the final section, we go over some specific examples of miniature X-ray sources.

2.1 The X-ray Tube

The miniature X-ray tube used in handheld XRF is the standard hot-cathode tube design used since William Coolidge original X-ray tube[4]; the main difference is the extremely small size achieved by the use of advanced materials and processing methods (Figure 1). The tube has a tungsten filament cathode that provides a source of electrons, an anode target for the electrons to decelerate in which generates X-rays, and passive electron optics to guide the electron beam to the anode. Some important aspects of the miniature tube include the following:

Year	Weight	Voltage & current	Tube power
2001	(763 gm)	35 kV 100 μA	3.5 W
2004	(320 gm)	40 kV 100 μA	4 W
2006	(533 gm)	50 kV 200 μA	10 W
2009	(335 gm)	50 kV 200 μA	4 W
2012	(250 gm)	50 kV 200 μA	4 W
2013	(750 gm)	60 kV 1000 μA	12 W

Figure 2 X-ray source weight and size reduction in 2001–2012 and a transition from cabled to monolithic design. The pen at the top of the image is shown as a size reference. (Reproduced with permission from www.moxtek.com © Moxtek, Inc.)

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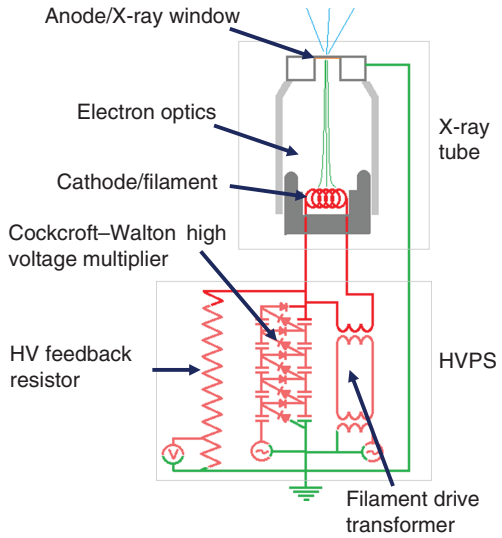

Figure 3 A schematic of an X-ray source with all its major parts labeled.

- A very small filament so it takes a low amount of input power to heat the filament to about 1800°C. The low-power filament is needed to extend the time of battery operation.
- A ceramic/metal vacuum envelope providing robustness over a glass vacuum envelope. This helps in keeping the tube from breaking in the event of both mechanical and thermal shocks experienced by this tube when used in the field.
- A 'simple diode' or unipolar design allowing for a single variable high voltage to run the X-ray tube. The beam current can only achieved when the cathode is lower voltage then the anode, and the filament is heated enough to emit electrons; thereby it is a diode, a one-way current device. There are no other components, such as a 'gate' for turning the tube on and off, or steering the electron beam, which are fairly common on many X-ray tubes.[5] The passive electron optics design is challenging and is simply achieved by shaping of metal components of the tube. The passive electron optics need to work over a large range of 4–60 kV and keep the electron beam at nearly the same location and size on the anode, with no active feedback. All of this effort functionally simplifies the X-ray tube and the HVPS so that the entire X-ray source can be smaller and the function of the HVPS can be simplified.
- The most popular 'transmission-window' design combines the anode of the tube and the X-ray window of the tube into the same part. The beryllium window (usually 100–250-μm thick) is coated with a thin ~1 μm layer of the desired anode material. Details on the anode layer thickness are very application dependent. This allows for closer source-to-sample distance, which is a large advantage for miniature X-ray sources for XRF (this is discussed extensively in Section 5).

All of these efforts result in a very small and robust miniature X-ray tube well suited for applications that need a very small source such as handheld XRF.

Functionally, an X-ray tube produces X-rays with an electron beam at the anode with two general types of interactions, bremsstrahlung radiation and electron beam-induced characteristic X-ray radiation.[5–10] Bremsstrahlung radiation, also known as 'braking' radiation, is caused by the impinging electrons interacting with the nucleus of an atom. As the electron approaches the atom, it is deflected and possibly stopped by the strong electric field surrounding the atom. This deceleration of the electron produces the bremsstrahlung radiation. The broadband radiation produces fewer photons at higher X-ray energies; with the intensity of bremsstrahlung X-rays approaching zero in kiloelectron volts at the tube's high-voltage setting in kilovolts.

Characteristic radiation is based on impinging electrons interacting with the electrons surrounding an atom. Kossel,[6–10] Moseley,[11,12] and Barkla[13] presented the theoretical and experimental foundation for the quantum theory of producing characteristic X-rays. For induced characteristic radiation, an electron of high energy may ionize an atom by displacing an electron from one of the inner atomic shells. An electron from an outer shell may fall into the shell vacancy emitting either another electron from the atom or a photon, the photon being the desired reaction for the X-ray tube. The energy of the X-ray is dependent on the energy levels of the shells participating in the process and therefore is 'characteristic' to the material of the target.

The spectrum of X-rays from two different materials, which shows both bremsstrahlung radiation and electron induced characteristic radiation, is shown in Figure 4, with no low-energy filters except for air absorption. To tailor a spectrum for a specific XRF application, the high-voltage setting on the tube is changed or a variety of filters are put in front of the anode to filter out lower energy X-rays from the source. Many techniques are used to modify the X-rays hitting the sample to get a desired spectrum from the X-ray source for XRF.

2.2 The High-Voltage Power Supply

The HVPS used in based on the Cockcroft–Walton high-voltage (HV) generator.[14] This device generates a DC HV based on an oscillator coupled with a ladder of capacitors and diodes (HV multiplier) (Figure 3). The type of

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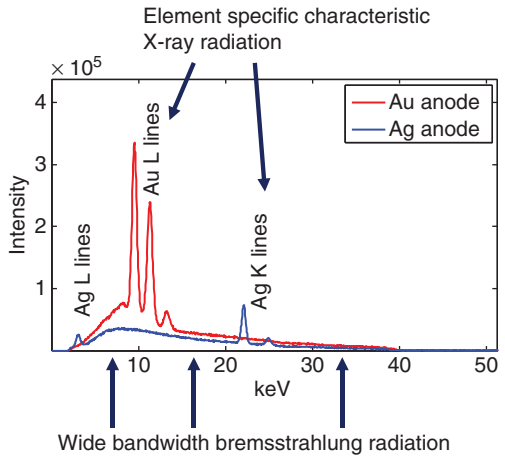

Figure 4 An X-ray spectrum from both a gold and silver anode X-ray tube that shows both the bremsstrahlung and the characteristic X-ray radiation.

Cockcroft–Walton HV generator uses most often the half-wave rectifier design, shown in Figure 3. The half wave design has the advantage of the least amount of components but does have the disadvantage of an HV AC ripple of a few hundred volts on the output. This slight HV ripple does not affect XRF. To achieve the needed HV of 4 kV up to 60 kV, the input oscillating transformer has HV oscillation amplitude of a few hundred volts to a few thousand volts, and a frequency of several kilohertz. The capacitor-diode ladder consists of between 8 and 15 stages. The Cockcroft–Walton HV generator generates the HV and provides the emission current needed to drive the electron current through the X-ray tube.

The next critical component is the HV feedback resistor, which allows for monitoring the HV, and for controlling the HV on the Cockcroft–Walton HV generator. XRF requires the X-ray source to have a stable output spectrum shape (Section 4.3). A stable X-ray spectrum shape requires a very stable high voltage, which in turn requires having a very stable and a predicable HV feedback resistor. Figure 5 outlines the simple circuit that shows how the HV is measured, by a simple ratio of the resistance of the entire resistor to just a smaller section of the resistor.

The final component of the HVPS is the filament drive transformer. Miniature X-ray sources are run with the anode at ground, and the cathode is at HV. The filament is driven with an AC current provided by a series of transformers. As the filament is at high voltage, the AC drive is achieved by a series of two or more transformers to isolate the HV.

One other critical design issue is achieving HV without arcing. This is extremely critical and difficult, especially in the very small packages and weights needed for miniature

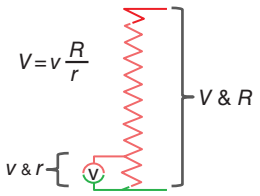

Figure 5 A schematic of the HV feedback resistor. '*V*' is the HV of the HVPS calculated by knowing '*R*' the resistance of the entire resistor, '*r*' the resistance of the resistor section, and '*v*' the measured voltage of this resistor section.

X-ray sources. Both the tubes and the HV power supplies are potted in a highly insulating material to prevent arcing. The layout of the HV components is also optimized for reducing the field gradients and providing enough HV standoff.

2.3 Functional Examples of Miniature X-ray Sources

Table 1 and Figure 6 show examples of Moxtek's most recent X-ray sources.[15,16] The table gives some key metrics for each of these sources. The ULTRA-LITE® source, which uses Moxtek's Magnum® X-ray tube, is meant specifically for handheld applications, being very small, very light, and lower power. The MAGPRO® X-ray source is meant to go into small benchtop instruments and has potential to replace larger 50 W X-ray sources (Section 5). The MAGPRO® X-ray source is one-fifth the weight and a one-quarter the size of the typical 50 W X-ray source; yet, it has all the same functionality in an XRF instrument in many cases.

2.3.1 Characteristics of Miniature X-ray Sources

There are several characteristics of the X-ray source that needs to be known depending on the application. The most important attribute for XRF is the flux coming off of

Table 1 The basic parameters of both the ULTRA-LITE® and the MAGPRO X-ray sources

Parameters	ULTRA-LITE®	MAGPRO®
HVPS output kilovolt range	4–50 kV	4–60 kV
HVPS emission current range	5–200 μA	10–1000 μA
Anode material	W, Rh, and others	W, Rh, and others
HVPS power limit on X-ray tube	4 W	12 W
HVPS power input-voltage	6–18 V DC	24 V DC
Total weight	250 g (8.8 oz)	700 g (25.0 oz)

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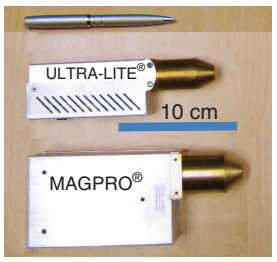

Figure 6 Image of the ULTRA-LITE® and the MAGPRO X-ray source. (Reproduced with permission from www.moxtek.com © Moxtek, Inc.)

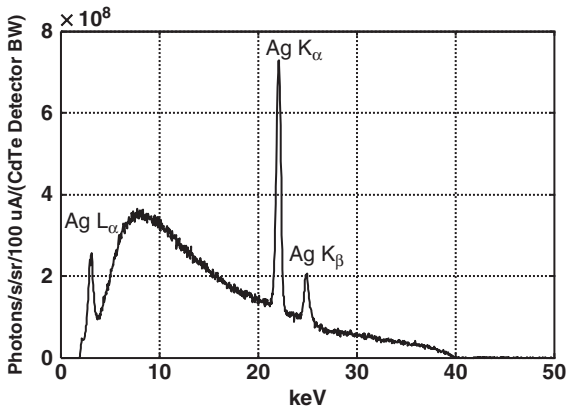

Figure 7 An example of a spectral radiant intensity curve from a silver anode X-ray tube. The tube was run at 40 kV, measured through 100 mm of air (air is filtering out the lower energy X-rays).

the source, including the X-ray energy distribution – the spectra – and the total intensity of the X-rays. Because the X-ray flux attributes are so central to XRF, we will focus on different X-ray flux attributes from a variety of perspectives such as flux stability, target material selection, and flux wattage maps specifically for XRF in the following sections.

In this section, we are going to define X-ray flux and give a few insights into measuring the X-ray flux. The following section covers the flux output in radiation dose. The final section covers the spot size measurements on the anode and the radiation cone angle coming off of the source. Spot size and cone angle are good information for X-ray imaging applications but are not nearly as critical for XRF.

2.4 X-ray Flux and Spectra

The flux coming from an X-ray tube-based X-ray source is often giving by stating the HV (spectral information), the emission current (flux information), and the anode material (spectral information), e.g. a 50 kV, 0.2 mA tungsten anode X-ray source. If higher flux is needed, one just acquires an X-ray tube that can achieve higher emission current. This is sensible for many X-ray applications, but it is not useful for comparing miniature X-ray sources to larger X-ray tubes. Miniature X-ray source achieve equivalent or higher fluxes on the sample by having a small X-ray tube-to-sample distance. In addition, a spectrum coming from the X-ray source tells one a great deal about the source. Most often, the spectra – the energy distribution of the radiation – is presented using the unitless 'intensity' labeled on the *y*-axis (Figure 4). In any event, the spectrum and flux information still needs to be conveyed for miniature X-ray sources, using a bit more than just the HV, the emission current, the anode material, or a spectrum.

For the flux, the two units of flux we have found to be useful for miniature X-ray sources is the *spectral radiant intensity* and the *radiant intensity*. The spectral radiant intensity is very much like a spectrum, it just has units of *photons/s/sr/100* μ*A/Detector BW* for the *y*-axis (Figure 7). The radiant intensity is just a sum of spectral radiant intensities; giving a single number for the flux in units of *photons/s/sr/100* μ*A*. The radiant intensity is much like the 'kilovolt' and 'milliampere' numbers commonly used for X-ray tubes; it is a number that can be used to compare the flux off different X-ray sources. We will first define the units and then explain why we use them for miniature X-ray sources.

To break down these units, the *photons/sec* is simply the input count rate 'ICR' per channel from the detector or the amount of photons hitting the detector per second per channel. The unit *Detector BW* means 'detector band width' and is just there to remind someone that different detectors have different energy resolutions and different quantum efficiency's at different energies; for example, it reminds us not to directly compare a spectrum from a CdTe detector, a 400-μm-thick SDD, or a 2-mm-thick Si(Li) detector. The unit '100 μA' simply normalizes to the emission current, if you double the current you double the flux; just like the emission current metric normally used with X-ray sources. The final unit 'sr' is the solid angle in sterradians of the flux and is the unit to really pay attention to for miniature X-ray sources, as it contains the geometrical information. For example, if the emission current on a miniature X-ray source is 10 times smaller than a larger X-ray source, you will get an equivalent flux on the sample if the solid angle is 10 times as large; this insight is critical for properly using miniature X-ray sources.

Both *spectral radiant intensity* and the *radiant intensity* are good units to compare X-ray tubes against each other. Table 2 shows a table of *radiant intensity* values as a function of the anode thickness; thereby showing

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Table 2 Table of radiant intensity from a few different types of transmission window sources, showing the total output photons at a few different high voltages

	Anode thickness (μm)	30 kV	50 kV	60 kV
Magnum® W	1.1	16	25	—
MAGPRO W	3.5	7.7	26	37
		10 kV	20 kV	30 kV
Magnum Rh	1.0	0.51	3.5	7.4
MAGPRO Rh	0.6	0.68	4.2	7.3
Magnum® Ag	0.75	0.65	3.8	6.9

$\times 10^{10}$ photons/s/sr/100 μA.

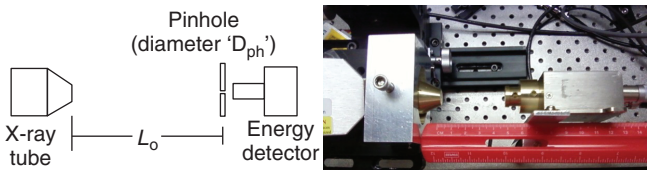

Figure 8 On the left is a schematic for measuring the spectrum from an X-ray source. On the right is an image of a setup to measure the flux (the brass part on the detector holds a tungsten pinhole).

relations such as higher flux is achieved with a thicker anode layer at higher kilovolt, and higher flux is achieved with a thinner anode layer at lower kilovolt.

One fairly direct way to measure the spectra is with an energy-dispersive (ED) detector, such as a PIN-diode or a silicon drift detector (SDD), which is extensively used in XRF instruments. The radiation directly from an X-ray source is much too intense to measure the spectrum but that can be overcome by putting a small pinhole of 10–200 μm in front of the detector to decrease the flux hitting the detector (Figure 8). This setup can give results like the spectra in Figure 4.

If the *spectral radiant intensity* (Figure 7) is desired to cross-compare the spectra on different sources, then the intensity axis scale can be calculated from the collected spectra with this equation:

$$I_{\mathrm{SRI}} = \frac{C[\mathrm{counts}]}{T[s]4\pi\sin^2\left(\frac{D_{\mathrm{ph}}[\mathrm{mm}]}{4L_{\mathrm{o}}[\mathrm{mm}]}\right)\frac{I_{\mathrm{e}}[\mu\mathrm{A}]}{100}} \times \left[\frac{\mathrm{photons}}{\mathrm{sec}\cdot sr\cdot 100\,\mu\mathrm{A}\cdot \mathrm{Detector\,BW}}\right] \quad (1)$$

C is the counts in each detector channel and T the live time of the detector, together they give the ICR from the detector as a function of the detector channels. D_{ph} is the pinhole diameter in millimeter, L_{o} the anode-to-pinhole distance in millimeter, and I_{e} the tube emission current in microampere. This equation works as long as $L_{\mathrm{o}} \gg D_{\mathrm{ph}}$, which should always be the case. In addition, the sine angle in this formula is in radians.

To generate a *radiant intensity*, you simply sum or integrate the *spectral radiant intensity* graph into a single number.

2.5 Radiation Dose from Miniature X-ray Sources

In an enclosed XRF system, the sample chamber is designed to be radiation tight. The radiation dose outside the sample chamber due to the X-ray source being 'on' should be zero. In addition, these instruments have interlocks that shut off the X-ray source if the sample chamber is opened to keep X-ray exposures from happening. For a handheld system, there is more of a chance for X-ray exposure, but there are a number of safety protocols for these devices as well (not discussed here).

Focusing on the X-ray source, just this single component, the X-ray source is considered radiation safe if the radiation is strictly coming out of the window opening. Radiation should not come out in other directions through other structures of the source. Repeating in another way, if the window opening of the X-ray source is blocked from emitting radiation, the X-ray source will emit $<0.5\,\mathrm{mrem\,h^{-1}}$ ($5\,\mu\mathrm{Gy\,h^{-1}}$) in any direction when turned on at the maximum kilovolt and power. For reference, natural background radiation is $\sim 0.3\,\mathrm{Rem\,h^{-1}}$.

Another frequent question is 'What the radiation dose is if the X-ray source window opening is not covered'. Tables 3 and 4 outline the radiation dose for both the Magnum® tube and the MAGPRO source. These values were measured with a Black Piranha radiation meter, which is a common radiation dose meter used in the medical field. The Piranha radiation meter can be used with a small ion chamber, which is used for lower kilovolt tubes. At the distance of 30 cm, the dose rate is covering a circular area with a diameter of about 25 cm. At the distance of 1 mm, it is basically the dose achieved touching the window opening of the X-ray source, covering a very limited area of a few square millimeter; you could cause a very localized radiation burn on your skin if you held the tube right on your skin and left it on for a few minutes at full power.

The full body limit of radiation per year is <5000 mrem (50 mGy) for a radiation worker. An unfiltered miniature X-ray source can reach this limit in a localized area in just a few minutes at a 30 cm distance, so even though these sources are small and low power, they still need proper radiation protection.

2.6 X-ray Spot Size

The X-ray tube's spot size is the spatial distribution of X-rays produced on the tube's anode. The spot size on an

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Table 3 Table of radiation dose from a tungsten anode miniature x-ray source, at two different distances of 1 mm, right at the window opening, and 30 cm away.

Tungsten sources	No filter					
	@ 30 cm			@ 1 mm		
	30 kV	50 kV	60 kV	30 kV	50 kV	60 kV
Magnum @ 4W	1.6 @ 133 μA	1.3 @ 80 μA	—	120 @ 133 μA	90 @ 80 μA	—
MAGPRO® @ 12W	2.1 @ 400 μA	3.4 @ 240 μA	3.9 @ 200 μA	90 @ 400 μA	150 @ 240 μA	177 @ 200 μA
	With 2 mm Al filter					
Magnum @ 4W	0.03 @ 133 μA	0.03 @ 80 μA	—	2.8 @ 133 μA	4.5 @ 80 μA	—
MAGPRO® @ 12W	0.06 @ 400 μA	0.14 @ 240 μA	0.16 @ 200 μA	5 @ 400 μA	15 @ 240 μA	19 @ 200 μA

Tungsten anode tubes are often used in imaging with a 2 mm Al filter; therefore the radiation dose rate is given with a 2 mm Al filter as well.
Units in mGy/sec ×100 for mRem/sec

Table 4 Table of radiation dose from a 'light element' silver and rhodium anode miniature X-ray source, at two different distances of 1 mm, right at the window opening, and 30 cm away

Light element sources	No filter			
	@ 30 cm		@ 1 mm	
	12 kV	20 kV	12 kV	20 kV
Magnum 'Ag 2' at full power (2.4 and 4 W)	0.03 @ 200 μA	1 @ 200 μA	108 @ 200 μA	260 @ 200 μA
MAGPRO® 'Rh3' at 12 W	0.8 @ 1000 μA	2.2 @ 600 μA	282 @ 1000 μA	430 @ 600 μA

Units in mGy $s^{-1} \times 100$ for mrem s^{-1}.

X-ray source is critical for many X-ray applications, such as X-ray imaging. For XRF, the spot size is less critical but is still important to maintain a stable flux; the spot needs to be a consistent size and position for the very critical flux stability.

There are many ways to both measure and evaluate a spot size from an X-ray source.[5,17,18] We are going only discuss one measurement technique. One very good way to measure the spot on the X-ray tube anode is with a pinhole camera (Figure 9). A pinhole camera creates a true two-dimensional representation of the X-ray spot from the X-ray tube (Figure 10). These images are very useful in making sure that the tube is functioning as desired. If the focal spot is missing, distorted, or moving position, the image will identify these problems and give vital clues as to what went wrong when manufacturing a particular X-ray tube.

One very critical detail to consider in using a pinhole camera setup is the pinhole size. The pinhole size needs to be at least 3–4 times smaller than the source size to capture a representative image. If the pinhole size is too large, the resulting spot represents the pinhole size and not the X-ray spot on X-ray tube anode. The lower manufacturable limit in pinhole sizes is about 10 μm, in a 500-μm-thick tungsten foil. This foil thickness is needed to effectively block the X-rays under about 50 kV. This small 10 size μm pinhole makes very sharp, detailed images that are valuable, but the trade-off is a very low intensity that is hard to work with. Larger pinholes are much easier to work with and are able to characterize the X-ray spot size suitably (Figure 11).

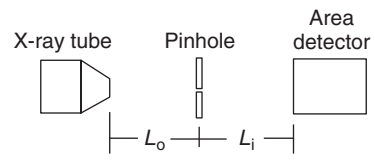

Figure 9 A basic schematic of the pinhole camera setup. The setup we have uses an object 'L_o' distance of about 3 cm and an image distance 'L_i' of about 12 cm.

The magnification or the size calibration of the spot on the 2D imaging detector can be estimated by taking the

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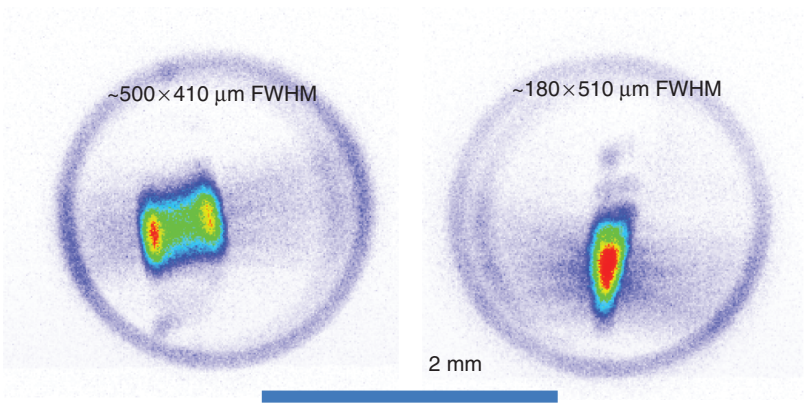

Figure 10 Two X-ray spot images from two miniature X-ray sources. The two images are shown to emphasize that spot size and locations vary from tube to tube.

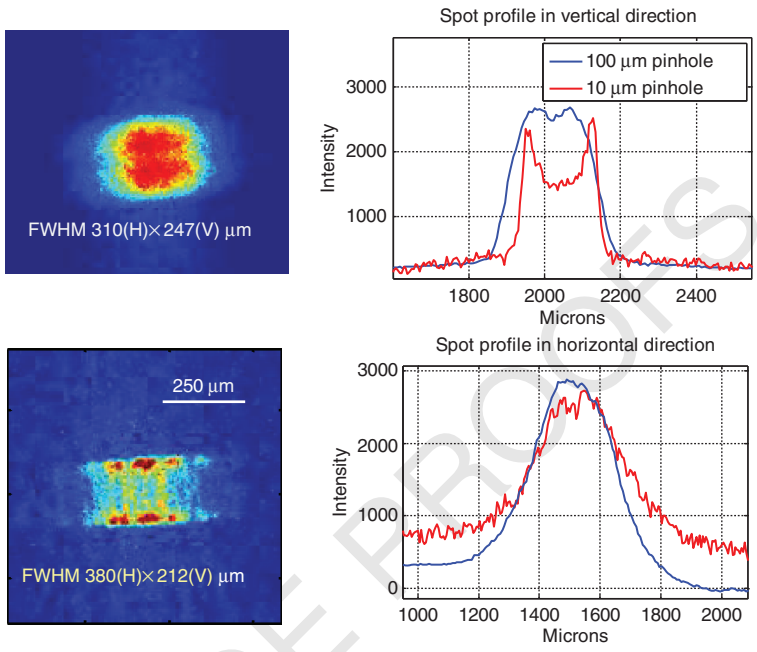

Figure 11 The two images on the left are from the same tube. The bottom image used a 10-µm pinhole (4.6 magnification), and the top image used a 100-µm pinhole (3.4 magnification). The 10-µm pinhole resolved the fine details. The 100-µm pinhole conveys the overall shape and size but lacks the fine detail. The graphs on the right give the spot profiles from the 100- and 10-µm images.

ratio of the object distance L_o to the image distance L_i (Figure 9). In practice, when the exact size is critical, we do not recommend estimating the magnification, the off-center, size of the spot should be physically calibrated. There are two straight forward methods for calibrating the source size to the image size:

- Use a known size reference in the image. For example, the ring around the spot in the images in Figure 10 has a diameter 2 mm. This ring is caused by back-scattered electrons off the anode hitting a drift tube inside the tube that has a diameter of 2 mm.
- Take an image of the source, then translate the source a known distance perpendicular to the pinhole, and then take a second image of the source. The features in the two images are offset by this known distance, giving you a size reference. For miniature X-ray sources that are only a few hundred grams, this is very easy to do with standard optomechanical hardware.

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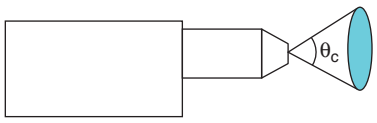

Figure 12 A basic schematic showing the radiation cone coming out of an X-ray.

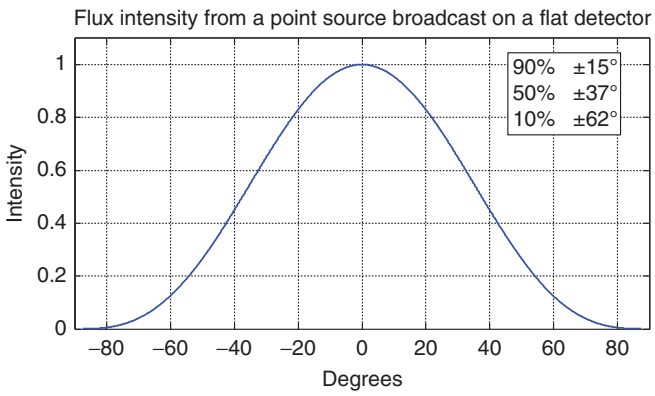

Figure 13 A graph that shows what flux intensity is expected from a spherically symmetric X-ray source when broadcast onto a flat surface, such as an imaging detector. If the intensity needs to remain flat to within 90%, a cone angle of 30° is required. If the intensity needs to remain flat to within 50%, a cone angle of 74° is required.

From the image, the spot size can be estimated. A standard way of presenting the spot size is a full-width-half-maximum (FWHM). Our preferred way of converting a two-dimensional image into a one-dimensional profile for each direction is to sum up the two-dimensional array into two graphs representing the *X* and *Y* directions. The peaks created by this summation give a profile to calculate the FWHM from in the *X* and *Y* directions (Figure 11).

2.7 X-ray Radiation Cone Angle

The X-ray radiation cone angle is the spread of radiation coming out of the X-ray source (Figure 12). The angular spread of the radiation is defined by the cone angle θ_c. The radiation cone angle is constrained by various parts of the X-ray tube and is very often further constrained by apertures outside the tube. In the case for XRF, the spot on the sample is often constrained to just a few millimeters by external apertures, giving a cone angle from the source of 10° or less. Without any external collimators, the transmission window tube has a cone angle of ∼130° (Figure 13). The side-window tube has a cone angle limit of about 45°, owing to the anode being inside the tube instead of right on the X-ray window.

In handheld XRF, only a very narrow cone angle is needed. For X-ray imaging applications, a very broad radiation cone angle is needed. The radiation coming off of the sources is by nature spherically symmetric; meaning that the intensity is constant at a given radius from the source. For imaging, it is desirable to have a flat field of X-rays hitting the flat X-ray imaging detector, which is strictly impossible to do with a spherically symmetric source. Figure 13 shows what level of intensity you are able to get from the spherically symmetric X-ray source with no radiation constraining apertures. This is very good information to know for imaging applications and any other applications requiring a wide cone angle from an X-ray source.

Figure 14 shows a measurement of the X-ray intensity from a side window tube compared to the ideal, aperture-free curve in Figure 13. For this graph, the red line represents the radiation fall off from an ideal aperture-free source broadcast on a flat surface. The green line and blue line represent the radiation fall off measured from a MAGNUM® side-window tube in two orthogonal directions. From Figure 13, it should be very apparent that calculated intensity follows the measured intensity very closely up to the edge of any physical aperture. In addition, the cone angle from the side-window source can be seen to be about 45°, and the cone angle from the source is not perfectly symmetric, owing to the spot on the anode not being exactly in the center of the X-ray tube's anode.

3 THE SELECTION OF A TARGET ANODE MATERIAL FOR X-RAY FLUORESCENCE

The basic premise of XRF is that high-energy X-rays are aimed at a sample and then the atoms in the sample may absorb an X-ray. This ionizes the atom by displacing an electron from one of the shells close to the atom. The next step is an electron from an outer shell may fall into the shell vacancy, emitting the excess energy in the form of characteristic X-ray radiation. The energy of the X-ray is dependent on the energy levels of the shells participating in the process and therefore is 'characteristic' to the material of the sample. For handheld XRF, the X-ray source is limited to 40 or 50 kV (mostly due to radiation safety and difficulty in shielding higher energy X-rays); therefore, handheld sources are only capable of exciting the L lines of elements above Lanthanum. More details in using XRF for material identification may be found in Van Grieken,[19] Jenkins.[20]

A critical detail for the X-ray source used for XRF is the X-ray source needs to produce X-rays at energies higher than absorption edge of the element in order to ionize the atom. As every element has different absorption edges

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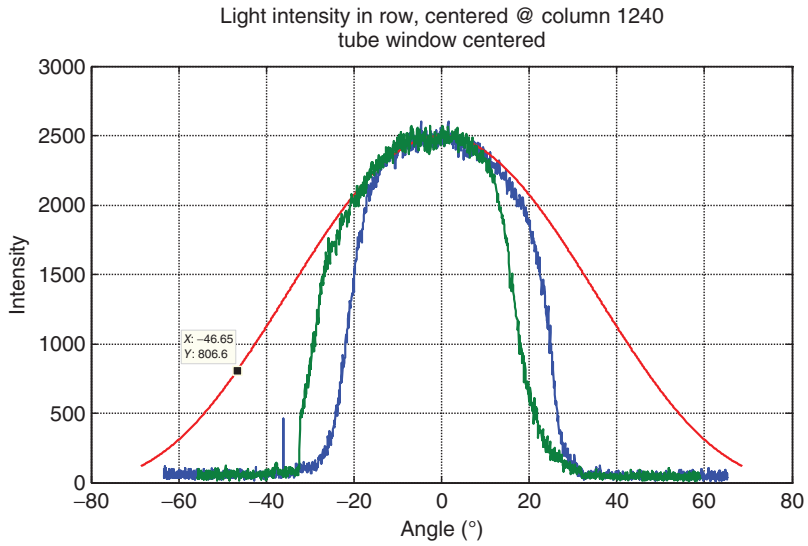

Figure 14 The calculated ideal flux curve broadcast on a flat surface (red curve) compared the measured intensity fall of from a MAGNUM® side-window tube in two orthogonal directions (green and blue curves).

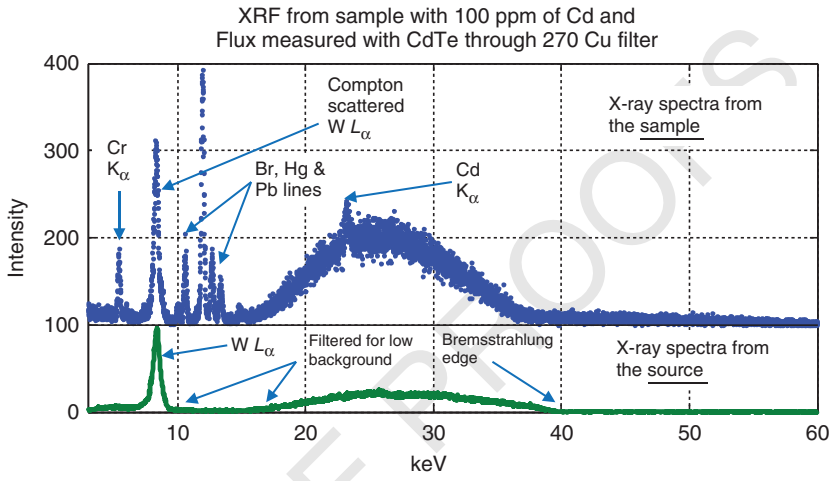

Figure 15 Two resulting spectra using a tungsten anode source at 40 kV with a 270-μm-thick copper filter with a CdTe detector. The lower graph shows the spectrum from the X-ray source through 270-μm filter combination. The upper graph shows the spectrum from a polyethylene sample with 750 ppm Cr, 400 ppm Br, 75 ppm Hg, 250 ppm Pb, and 100 ppm Cd. These figures show that the copper filter both lets the W L_α line from the source through to excite Cr and suppresses the background under the Br, Hg, and Pd lines.

just like they have different characteristic X-ray lines, the X-ray source needs to be tuned for different elements.

There are three basic methods for tuning the spectrum shape from the X-ray source:

- Setting the HV on the X-ray tube.
- Putting X-ray filter between the X-ray source and the sample.
- Selection of the anode material on the X-ray tube.

Setting the voltage is used to either include or exclude elements from the XRF analysis. The source is often run at the maximum voltage in order to excite the most elements possible. Often, for detecting light elements under 3 keV, the HV is set to a much lower voltage of about 10 kV. This effectively turns off the detection of elements with lines above about 10 keV so that signal of X-rays under 3 keV is more pronounced. From an instrument perspective, setting the HV on the X-ray source is an easy change to make by changing a setting on the HVPS. Therefore,

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for any particular application, the HV can be changed to optimize for that application quite easily.

The use of X-ray filters in front of the X-ray source is application specific. Most often, the filters main function is to eliminate lower energy X-rays from the spectrum, thereby making the signal to background lower. The details for using a particular filter can be wide ranging depending on exactly what elements are of interest. Figure 15 shows an example of using a filter for the restriction of hazardous substances (RoHSs). RoHS specifically is looking for the elements Cr, Br, Hg, Pb, and Cd. For this application, a tungsten anode on the X-ray source is desirable. A copper filter blocks all the lower energy X-rays, with the exception of some of the tungsten L_α line, which is just below the absorption edge at 9.0 keV of the copper foil. The tungsten L_α is above the Cu K edge and provides a good excitation source for Cr. In addition, the tungsten L_α is below the K lines for Br and the L lines for both Hg and Pd; therefore, the tungsten L_α does not interfere with these desired signals. From an instrument perspective, changing the filter is independent from the X-ray source; therefore, changing a filter is not too hard to do. Very often, several filters are mounted on a wheel and depending on the exact XRF application, the X-ray source's HV adjusted and filter type is selected for a particular XRF application.

The selection of the anode material on the X-ray tube is very commonly asked question. The anode material for the source cannot be changed, unlike setting the HV, or changing the filter. Therefore, the choice of anode material on the X-ray tube in many ways defines the application capabilities of the XRF instrument. The choice of anode material strongly depends on exactly what XRF application or elements one is most interesting in detecting. For XRF, there are two classes of anode types, 'light element' anodes for specifically exciting light elements below about 3 keV and 'general use' anodes for exciting everything higher than about 3 keV.

Light element anodes are most commonly made of either silver or rhodium. These elements are ideal for light element excitation in a sample because they both have L lines that are near 3 keV. Silver has L lines between 2.9 and 3.4 keV and rhodium has L lines between 2.7 and 3.0 keV. The L line at close to 3 keV strongly excites lines just under 3 keV, such as S, P, Si, Al, and Mg, which are the specific elements of interest for light element XRF. In light element applications, there is no filter used and the source is run between 8 and 12 kV; in addition, X-ray sources meant for light element analysis use a very thin 125 μm beryllium window for the purpose of minimizing X-ray absorption of the Rh or Ag L lines. In some instruments used for light element XRF, a helium purge or a vacuum chamber is sometimes used to eliminate absorption owing to the air. Often, light element sources are used for other applications as well, which require running the X-ray source at an HV of 40–50 kV. Therefore, the silver or rhodium anode layer is optimized to run at about 30 kV, which means that at 30 kV, the silver is thick enough to stop and adequate number of the impingent electrons on the anode for higher energy kilovolt work. The drawback to this higher thickness is adding some filtering of the L line for light element applications. This compromise is due to only one anode available on miniature X-ray sources, neither application can have an optimized anode thickness on the X-ray window so an in-between compromise is used.

General use anodes are most commonly made of tungsten, but other materials such as gold or tantalum can be used as well. These anodes produce more flux per unit current, the reason being that the bremsstrahlung radiation production scales with the atomic number 'Z' of the target [5], this is also somewhat evident from Tables 2, 3, and 4. These anode thicknesses are optimized for the highest kilovolt the source can produce, and they have a beryllium window thickness of 250 μm or more. They are very good for heavier element XRF but do not work for light element XRF.

Outside XRF applications, such as X-ray imaging, tungsten is the anode of choice owing to tungsten having both a high atomic number and being a refractory metal that can take a very high amount of heat. Both of these advantages allows for a high flux output from the X-ray tube wanted for X-ray imaging. In addition, most imaging applications use a 2-mm Al filter or more because lower energy X-rays are absorbed and damaging to live samples. For X-ray diffraction, a tight single energy of X-rays is desired. Common anode materials are chromium (5.4 K_α), copper (8.0 K_α), and molybdenum (17.5 K_α). For X-ray diffraction, only a single characteristic line is desired, and the wide band of bremsstrahlung not wanted because it contributes to the background noise. Often, these sources are run at a kilovolt that is 3–4 times the kiloelectron volt of the desired line.

The anode selection for a source is quite important to consider and depends strongly on the application, with different anodes desired for different XRF applications.

4 FUNCTIONALITY OF X-RAY SOURCES FOR HANDHELD X-RAY FLUORESCENCE

The functionality of an X-ray source has a number of needed attributes. The source needs to operate over a fairly large temperature and humidity ranges as it is meant for field use. It also needs to produce a very stable spectrum shape or a stable output flux, which is required for

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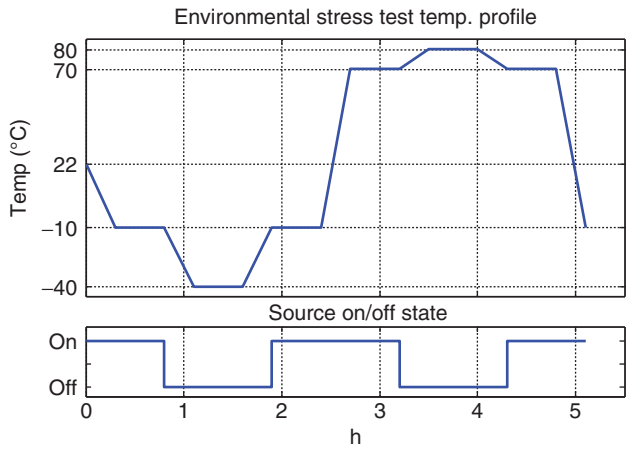

Figure 16 The temperature profile from a single cycle of the environmental stress test and a profile showing the on/off state of the X-ray source. This cycle is repeated 20 times for the full environmental test. (Reproduced with permission from Ref. 15 © ICDD, 2013.)

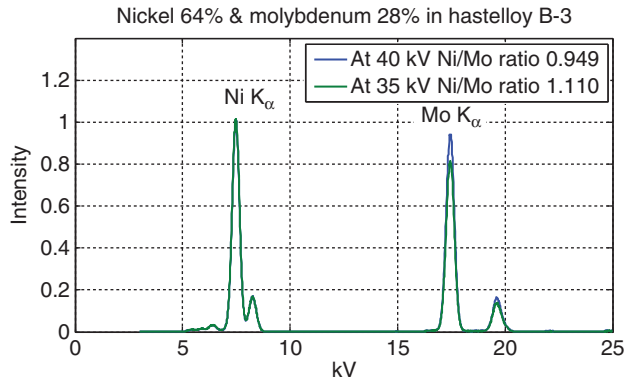

Figure 17 Two resulting spectra from a Hastelloy B-3 sample excited with a silver anode tube with a 70-μm Cu filter. The two spectra were taken with the tube set to 40 and 35 kV. This high-voltage shift changed the ratio between the peaks by 16%. In this setup, the nickel to molybdenum ratio can be changed by 0.5% by changing the voltage by just 200 V. This demonstrates that a very stable high voltage is needed to maintain a consistent ratio between elemental X-ray lines.

XRF. It is also intended to run over an extended operational range from low kilovolt to high kilovolt and operate as well as every setting in between. In the following sections, we explain each of these needed attributes for miniature X-ray sources for handheld XRF.

4.1 Environmental Stress Testing

One of the more critical constraints on portable X-ray sources is the environment. These small X-ray sources need to operate in the field, wherever they are taken. This translates into having a storage temperature range of −40 to 80 °C and an operational range of −10 to 60 °C. While developing a miniature X-ray source, the design is considered to be robust when the X-ray source can survive a 120-h environmental test during which the temperature profile in Figure 16 is repeated 20 times. When developing an X-ray source for handheld XRF, several iterations of this environmental test are performed. Each testing cycle is meant to find any weaknesses in the design, and when failure points are found, they are renovated.

4.2 X-ray Spectrum Stability

The X-ray flux, as defined in Section 2.4, needs to be very stable for XRF. More specifically, the *spectrum shape* should not change in an XRF instrument over time (Figures 4 and 7). The X-ray source needs to output the same spectrum shape at the same settings for months to years to maintain the calibration on a calibrated XRF instrument.

How Do You Change the Spectrum Shape from the X-ray Source?

- Change the HV – this is very changeable; the core of this section
- Change the anode target material or the anode thickness – this is stable for each source in normal operation
- Change the X-ray filter – this is outside the control of the X-ray source
- Change the emission current – this does change the X-ray intensity but should not change the spectrum shape.

The HV stability of the X-ray source is extremely critical for XRF. Changing the HV on the X-ray source changes the spectrum shape that changes the ratio of X-ray counts between each element's X-ray lines from a sample. The ratio between the different characteristic lines gives information about the elemental concentration of each of these elements, so if this ratio changes the XRF calibration is compromised (Figure 17).

Because HV stability is so critical to the source's spectrum-shape stability, and the spectrum-shape stability is so critical to XRF, we look directly at the spectrum from the source and measure the bremsstrahlung edge to insure the X-ray source has a stable HV (see the following section).

The anode thickness also affects the spectrum shape, in that it stops the electrons generating X-rays and also acts as an X-ray filter for the generated X-rays. Having tightly controlled thicknesses on the anode material is important to maintain an analogous spectrum shape between two different sources. This is also true for any X-ray filter, having tightly controlled thicknesses on the filter material is important to maintain an analogous spectrum shape

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through the X-ray filter. This is somewhat less of a concern then the HV, in that an anode material and thickness as well as a filter thickness are not variable once the X-ray source is built. This means that if an XRF instrument is calibrated with a specific source and set of X-ray filters, the anode and filters for this instrument should not change, thereby the calibration should not change. There are ongoing efforts to control anode thicknesses, the filter thicknesses, and the source's HV tightly enough that the spectrum shape is virtually the same between different X-ray sources. Controlling these features tightly will allow for an XRF equivalent X-ray source, in which an X-ray source can be exchanged for another X-ray source and the calibration on the XRF instrument is unaffected.

One last way to affect the spectrum shape is with the emission current on the X-ray tube. Changing the emission current only changes the intensity of the X-rays from the source, it does not really change the spectrum shape, and therefore, it does not change the resulting ratios between X-ray lines in XRF from a sample. All the emission current affects is the time it takes to get a desired number of events and if the data collection time is limited, it affects the precision and accuracy of the analysis. The emission current is important; setting it allows getting counts on an XRF detector as efficiently as possible, but it is not as critical as things that affect the spectrum shape such as the HV.

4.3 X-ray High-Voltage Stability

To maintain a stable spectrum shape from an X-ray source, the HV on that X-ray source must remain constant over time and over on and off cycles of the X-ray source. Measuring the HV stability is accomplished by evaluating the X-ray spectrum, specifically the bremsstrahlung edge, over and over. The bremsstrahlung edge in kiloelectron volt coincides with the X-ray source's HV in kilovolts. If the bremsstrahlung edge moves, it means that the HV has shifted on the HV power supply. This technique is very sensitive; changes in the high voltage on the order of 50–100 V can be seen. Figure 18 shows a spectrum

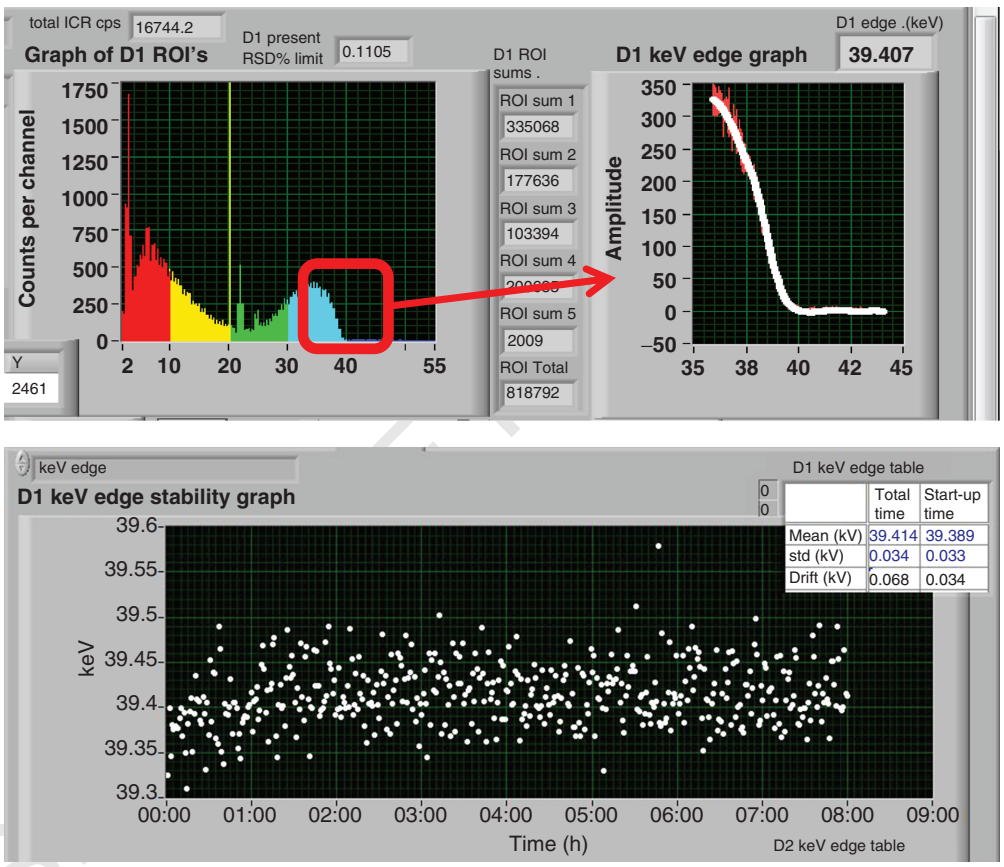

Figure 18 A high-voltage repeatability test from ULTRA-LITE source. The top left figure shows a single X-ray energy spectrum collected directly from the source. The top right figure shows the bremsstrahlung edge of the same spectrum. An algorithm finds the edge and records it for each of the 480 spectra taken over 8 h. This source achieved a voltage of 39.4 kV (set at 40 kV), with a standard deviation of 34 V.

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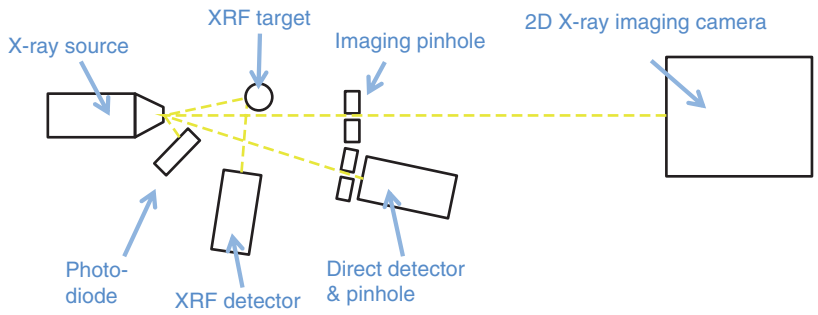

Figure 19 A simple schematic of the stability and repeatability test showing all the major instruments, three flux detectors, and an imaging detector, simultaneously measuring and evaluating the X-ray source. (Reproduced with permission from Ref. 15 © ICDD, 2013.)

from a silver anode source measured every minute for 8 h, with the setup in Figure 19. The bremsstrahlung edge is enhanced using a pinhole that is slightly too thin, in this case, a 50-μm-thick tungsten foil, which lets some of the higher energy X-rays through. Having a few higher energy X-rays helps the algorithm that calculates the bremsstrahlung edge achieves more accuracy.

We will again stress that a stable HV is very critical for an XRF instrument; XRF needed a very stable spectrum shape from the X-ray source. The HV stability results in Figure 18 are exactly what an XRF instrument needs from its X-ray source.

4.4 X-ray Flux Stability and Spot Stability

Having a stable and repeatable flux from the X-ray source is also needed for XRF. Measuring the flux in a stability or a repeatability test is a very useful indicator for finding any issues with the X-ray source, but it is not able to directly sort out what the is the cause. Types of issues that affect the flux stability are changes in the HV, spot movement on the X-ray tube, and changes in the emission current. As an X-ray source warms up when used there are inevitable small changes in both the X-ray tube and the HV power supply that will shift the X-ray flux around. The aim for designing these X-ray sources is to make the source as stable as possible throughout any changes that are expected.

The stability and repeatability test evaluates how the X-ray source operates over time. For the stability test, the X-ray source is left on for the entire test. For the repeatability test, the X-ray source is periodically cycled on an off, typical off cycles are 2–10 s, and typical on cycles are 30–120 s. The test durations can be from an hour to days. For the stability and repeatability tests, several detectors and instruments are simultaneously measuring and evaluating the X-ray source. Figure 19 shows our current X-ray source testing setup that incorporates the tests outlined in Figures 8 and 9, an XRF instrument, and a simple photodiode. Testing the stability and repeatability source involves several detectors and instruments simultaneously measuring and evaluating the X-ray source. Having all these instruments evaluating the X-ray source simultaneously effectively pinpoints any issues that cause the flux to be unstable.

For both the stability and repeatability tests, we measure the flux directly from the source, which gives the flux stability (Figure 20), and from the same spectrum information the HV stability is measured using the bremsstrahlung edge (Figure 18). XRF flux is measured a second way from a 316 stainless steel secondary target, simulating XRF instruments stability. The flux output is measured a third way with a photodiode. Each of these methods gives flux stability information and differences between each measurement give vital clues as to what the causes any flux instability, if there is any. We measure a time series of pinhole images of the X-ray tube's anode for X-ray spot stability (Figure 21). In addition to four ways used to evaluate the flux from the source, we have five thermocouples on different locations of the source's tube and HV power supply, and we monitor every signal and power line going into and out-of the HV power supply. Collecting all this information simultaneously allows for finding correlations in the data, which is critical for trouble shooting issues as problems are found. This stability and repeatability testing verifies that the X-ray source has a stable HV, a stable flux, and a stable X-ray spot needed for a handheld XRF instrument.

4.5 Multi-settings Testing and Flux Linearity

The stability and repeatability testing verifies that an X-ray source is stable at one setting over time, and the multi-settings test verifies the X-ray source functions over its entire range of voltage and emission current settings. In the multisettings test, the X-ray source is turned on and

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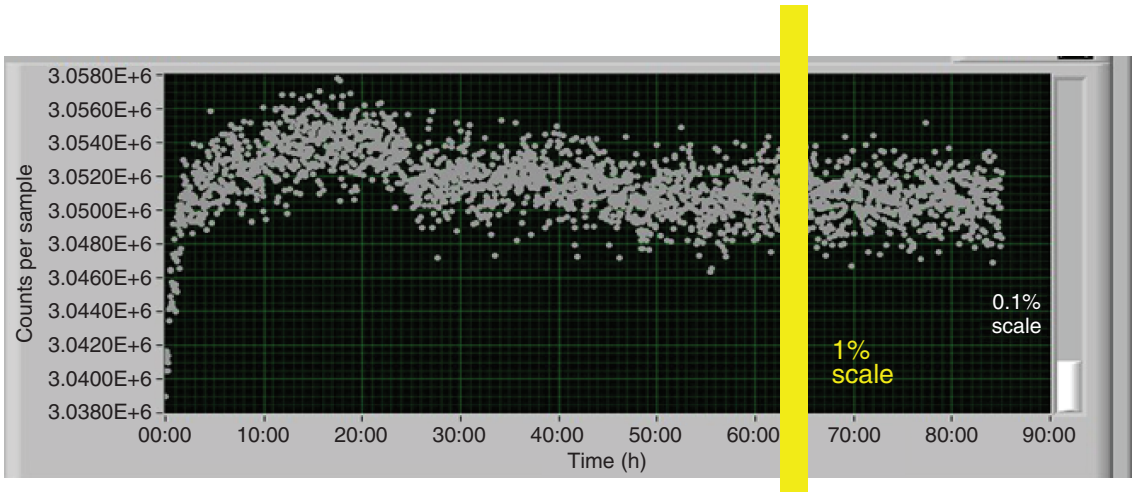

Figure 20 An X-ray flux measured directly from ULTRA-LITE source, set at 50 kV and 80 μA (the full 4 W) during a repeatability test, cycled on for 120 s and off for 5 s for 2400 cycles. This test measured an X-ray flux repeatability of 0.10% RSD over 85 h. During the source's warm-up time of 30–45 min, the X-ray flux drifted by 0.45%. (Reproduced with permission from Ref. 15 © ICDD, 2013.)

off for a few seconds over a few hundred to thousands of different HV and emission current settings. We record the flux value with a photodiode, and we monitor every signal and power line going into and out-of the HV power supply as well as four thermocouples on different locations of the X-ray source. All of this information provides several ways to evaluate the X-ray source. We will present data collected with the just photodiode, which gives information on:

- the flux turn-on time
- the flux stability for a few seconds at each setting
- the flux linearity over many settings.

For handheld XRF, a quick turn-on time of about a second is desired. Figure 22 shows the signal flux, measured by the photodiode, as the X-ray source is turned on. The turn-on time can be measured over all the settings evaluated. Table 5 outlines the turn-on speed on an ULTRA-LITE® X-ray source showing a range of turn-on times over different current and voltage settings on the X-ray source. The most demanding settings are at very low voltages as this requires more power delivered to the filament to compensate for lower electron flow toward the anode.

The flux stability for a few seconds at each setting is very valuable as well, showing if there are any settings that have an unstable flux. Figure 23 shows photodiode flux stability over a few seconds at each setting on an early prototype ULTRA-LITE® X-ray source. This was a very extensive test, with the source tested in 1 μA steps (ranging from 0 to 200 μA) and 0.5 keV steps (ranging from 4 to 50 data keV) resulting in data taken over 13 000 individual settings, with the entire test taking about 24 h. A low standard deviation in the flux signal represents the desired stable flux output and is represented in blue dots in the plot of Figure 23. A high standard deviation in the flux signal represents the undesired unstable flux output, and is represented in either red or yellow dots in the plot of Figure 23. The settings with unstable flux stability are

Table 5 This shows the ULTRA-LITE source turning on time over a few selected settings

	@ 50 kV	@ 40 kV	@ 30 kV	@ 20 kV	@ 10 kV	@ 6 kV	@ 5 kV
Maximum emission current	~0.5 s @ 80 μA	~0.5 s @ 100 μA	~0.5 s @ 133 μA	~0.7 s @ 200 μA	~0.9 s @ 200 μA	~1.2 s @ 200 μA	~2.3 s @ 200 μA
5 μA emission current	~0.7 s @ 5 μA	~0.6 s @ 5 μA	~0.6 s @ 5 μA	~0.5 s @ 5 μA	~0.8 s @ 5 μA	~1.1 s @ 5 μA	~1.4 s @ 5 μA

A turn-on speed of <1 s is considered an adequate turn-on time for a handheld XRF instrument. This time is defined as the time between the HV TTL being enabled to the X-ray flux coming on to 99% of its maximum value.[15]
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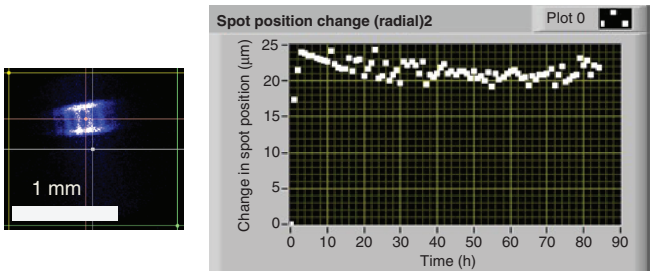

Figure 21 An X-ray spot repeatability test from ULTRA-LITE source, taken simultaneously with information in Figure 20. To the left is a single pinhole camera image of the X-ray spot, with a spot size of 390 × 340 µm FWHM. The small white dot in the center of the image represents the physical center of the anode. The graph to the right shows the drift of the spot over time; it drifts ~20 µm as the source warms up over the first 30–60 min and has a constant position thereafter over 85 h. (Reproduced with permission from Ref. 15 © ICDD, 2013.)

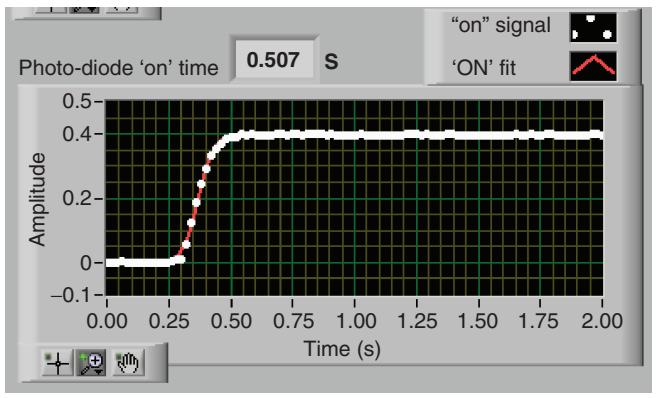

Figure 22 An X-ray flux signal measured over time by the photodiode as the source turns on. For this setting of 50 kV and 80 µA, the flux is fully on after 0.51 s. (Reproduced with permission from Ref. 15 © ICDD, 2013.)

clearly identified in the region circled in red. This mapping procedure insures that the X-ray source is functional with a stable flux output over all the available high voltage and emission current settings that may be needed to a given XRF application.

Lastly, with the information from the photodiode, the flux linearity over several different high voltages is measured. The flux output should be linear with the emission current on the source when the source is held at a constant high voltage (Figure 24). Measuring the X-ray flux at several emission current settings verify this relationship. For handheld XRF, the flux linearity is needed because the handheld XRF instrument adjusts the current on each sample to maximize the usable signal from the detector and for the calibrated measurements.

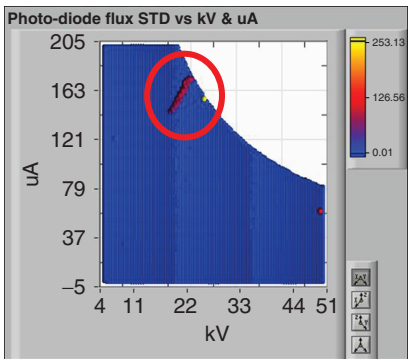

Figure 23 An example of data collected from the multisettings test where the set voltage and the set current are plotted against the standard deviation of the X-ray flux measured with a photodiode. An unstable flux output region is clearly seen inside the red circle. (Reproduced with permission from Ref. 14 © The Royal Society, 1932.)

Substantial effort has been taken to fully characterize the miniature X-ray sources under these three categories: environmental stress tests, X-ray flux and spot stability and repeatability tests, and multisettings tests. This intent of this testing is to provide confidence for those using these X-ray sources in a variety of applications and environments. XRF needs a stable spectrum shape and the critical HV stability test verifies the source has stable spectrum shape.

5 FLUX COMPARISONS WITH MINIATURE X-RAY SOURCES: X-RAY FLUORESCENCE WATTAGE MAPS BY APPLICATION

Choosing the most appropriate X-ray source is sometimes complex, involving the energy of the X-rays examined, the possible geometries for the measurement and the maximum count rate for the detector. This section explores the trade-offs between geometry, detector choice, and X-ray source power for a few XRF applications, including nonaluminum metal alloy identification, trace element XRF in a low *Z* matrix, aluminum metal alloy identification, and light element XRF. We have created 'wattage maps' in an effort to describe the geometry needed for X-ray sources in some typical handheld and bench top EDXRF applications. A wattage map is a map of the wattage needed to achieve a fixed count rate as a function of the tube-to-sample distance and the sample-to-detector distance. These maps provide a good estimate for what conditions and which X-ray source is needed for a particular application. The wattage map can enable a practical, data-driven approach to evaluating some of the trade-offs required in any instrument design.

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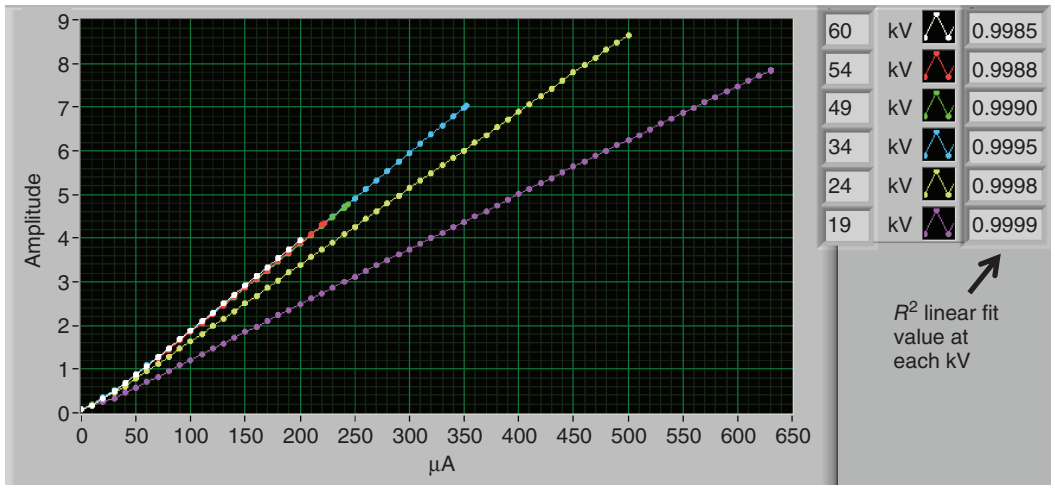

Figure 24 The flux linearity from a MAGPRO tungsten X-ray source at a few selected high voltages. For settings from 60 to 19 kV, the source flux is very linear, with R^2 values all under 0.998. Several of the higher voltage linear curves are on top of each other due to the photodiode not detecting higher energy X-rays.

5.1 Experimental Setup

The testing described here uses a standard XRF setup, shown in Figure 25. Using this setup, XRF experiments were performed on a number of samples, over an array of tube-to-sample distances ranging from 15 to 100 mm and sample-to-detector distances ranging from 8 to 35 mm. Both the X-ray source and the detector are at about 45° from the sample; the source and detector are about 90° to each other. The HV on the X-ray source and the choice of X-ray filters were held constant for each application; these settings are specified in their respective sections. The emission current of the X-ray source was varied to maintain a constant total count rate on the X-ray detector. The exception to this was the light element application for which a constant voltage and current were maintained. An aluminum sleeved brass collimator was mounted on the front of the X-ray source which was 11 mm long and had a diameter of 3.8 mm. The resulting X-ray spot on the sample was 4 × 6 mm, with the longer 6 mm dimension the result of the beam hitting the sample at an angle. The aluminum sleeve is necessary to eliminate the stray XRF signal from the brass and to ensure that the XRF signal is coming exclusively from the sample.

In this study, we used two detectors, a 6-mm^2 silicon PIN detector from Moxtek (XPIN-BT) and a 42-mm^2 SDD detector from Hitachi (Vortex). The XPIN detector has a 25-µm-thick beryllium window and the SDD has an 8-µm-thick beryllium window. The signal from both detectors was processed by Moxtek's MXDPP-50 digital pulse processor. All the tests using the XPIN detector were run at a 12-µs peaking time and all the tests using the

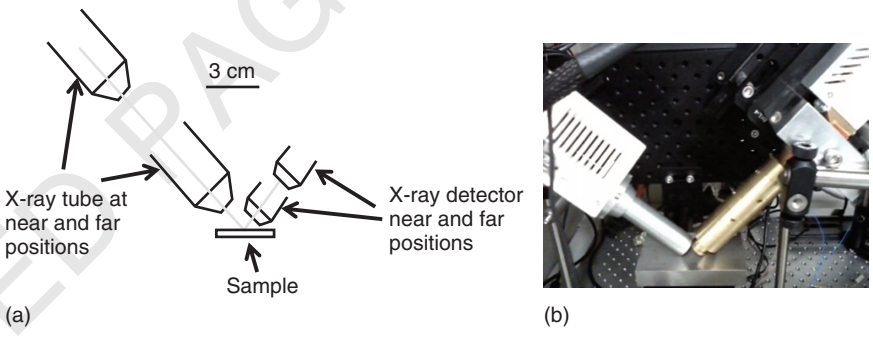

Figure 25 (a) Sketch of the XRF setup, which is to scale with the reference marker shown. The double image represents the near and far positions of the X-ray source and X-ray detector, respectively. (b) Image of the setup, with the X-ray tube in the far position (a) and an SDD in the near position (b); the X-rays from the source are contained within the long brass tube, with the 3.8-mm collimator at the end near the sample. (Reproduced with permission from Ref. 16 © ICDD, 2012.)

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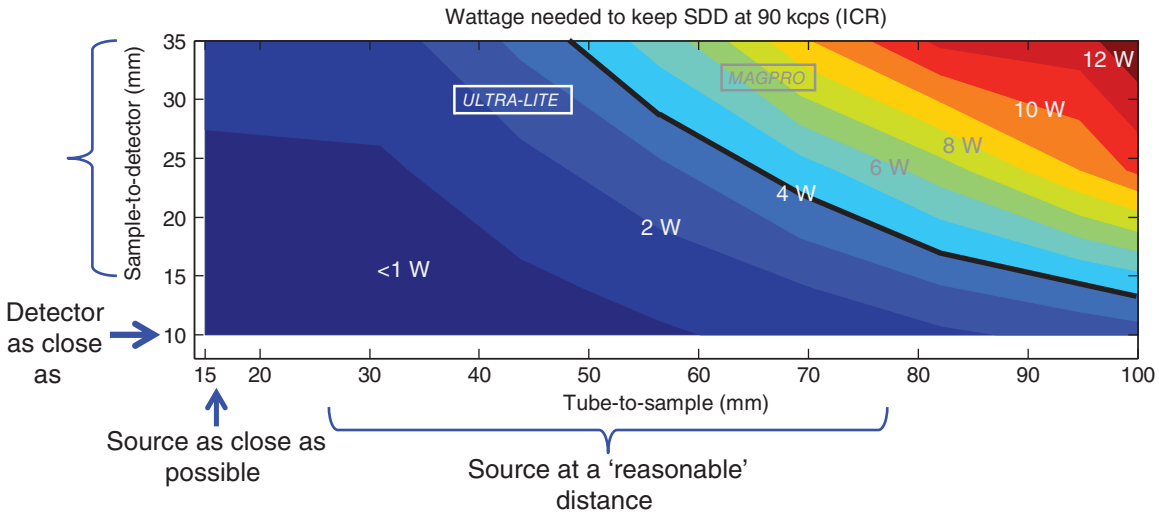

Figure 26 A wattage map created for nonaluminum alloy metals identification, which shows the wattage of the X-ray source needed to maintain a 90-kcps input count rate on the 42-mm^2 SDD detector. The dark line at 4 W shows the limit of capabilities of the ULTRA-LITE® source; the MAGPRO is limited to 12 W. Both of these sources are good to use for nonaluminum alloy identification with an SDD. (Reproduced with permission from Ref. 16 © ICDD, 2012.)

SDD were run at a 1-μs peaking time. These are typical peaking times used for each detector type. The SDD can process X-ray events at a much faster rate compared to a PIN detector, and both detectors have an energy resolution of about 170–180 eV at the Fe^{55} line.

5.2 X-ray Fluorescence Wattage Maps

A wattage map is a map of the wattage needed on the X-ray source for a given XRF application, as a function of the tube-to-sample distance and the sample-to-detector distance. The wattage map is quite useful in understanding what is needed for an EDXRF instrument because the wattage map provides a framework to address two items:

- Which miniature X-ray source is appropriate for a particular geometry and a particular XRF application?
- What is the best geometry to optimize an XRF instrument for a particular miniature X-ray source and X-ray detector for a given XRF application?

As the tube-to-sample and sample-to-detector distances are changed, the emission current on the X-ray tube was changed to maintain the chosen ICR. The emission current on the X-ray tube was multiplied by the HV to convert the data to a wattage map, which is more in line with the base metrics of 'wattage' that describes X-ray source types. Wattage plotted versus the tube-to-sample and sample-to-detector distances can then be assembled in a wattage map.

Figure 26 shows a wattage map created for the application of identifying nonaluminum metal alloys such as stainless steel, iron alloys, and brass. As expected, as the X-ray source is moved away from the sample, the X-ray source power must be turned up to maintain a constant count rate. Similarly, as the detector is moved away from the sample, the X-ray source power must be turned up to maintain the ICR. In these tests, the closest tube-to-sample distance is 15 mm, and the closest sample-to-detector distance is 8 mm for the PIN or 10 mm for the SDD. Physically, this is the point that the X-ray source and detector just touch the sample. In practice, this close spacing is not usually practical. The detector is often moved back to protect the X-ray window from damage and the X-ray tube is often moved back to provide space for a collimator and an X-ray filter. Figure 26 outlines more reasonable ranges of tube-to-sample and the sample-to-detector distances.

The ULTRA-LITE® is limited to 4 W, indicated by the thick black line at the 4 W contour. In Figure 26 from this map, it is clear that a miniature X-ray source, such as the ULTRA-LITE®, can provide a total ICR of 90 kilo-counts per second (kcps) for the SDD that was determined to be sufficient for this application. A benchtop source such as the MAGPRO will clearly work as well, but the higher power capability of the MAGPRO® is not needed for this application.

For both sources, the low-power limit of operation is typically <0.2 W (or under 5 μA of emission current). Below this low emission current level, the HV power supplies are typically not able to control the emission

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current across the X-ray tube accurately. Moving the detector and source as close as possible to the sample may actually be a disadvantage because of this issue.

As an example of how wattage maps can be used as a starting point in designing an XRF system, we consider an XRF instrument intended for use on metals identification that has a tube-to-sample distance of 25 mm, a sample-to-detector distance of 35 mm, and a 25 mm^2 SDD. According to Figure 26, about 1 W of power is needed to maintain a 90 kcps ICR. If a different configuration is required, the wattage map can often still be applied through a simple scaling factor. As an example, if the desired count rate is 25 kcps (instead of 90 kcps), the collimation diameter is 1 mm (instead of 3.8 mm) and the detector is 25 mm^2 in size (instead of 42 mm^2), an adjustment of the power level will likely be needed. As the count rate is different by a factor of 25 kcps/90 kcps = 0.28, the area of the collimator is different by the ratio of the collimator areas, $\pi(3.8\,mm/2)^2/\pi(1\,mm/2)^2 = 14.4$, and the detector size is different by the ratio of the detector areas, $42\,mm^2/25\,mm^2 = 1.68$, the estimated wattage needed for this new system is simply 1 W * 0.28*14.4*1.68 = 6.8 W. If this exceeds the available power (e.g., for a handheld XRF device limited to 4 W), then either the geometry needs to be tighter or the collimator on the X-ray tube needs to be larger. This example shows the power of these wattage maps for tuning into a particular geometry for a low-wattage X-ray source.

5.3 Results for Nonaluminum Alloy Identification

To illustrate the use of wattage maps for a design intended for identification of nonaluminum alloys (stainless steel, iron alloys, copper alloys, etc.), a stainless steel 316 standard was used as a reference sample. Both an ULTRA-LITE® and a MAGPRO X-ray source with tungsten anodes were tested, each set at 50 kV and both with a 75-μm-thick copper filter to suppress lower energy X-rays. Figure 26 shows the wattage map using the SDD detector, and Figure 27 shows the wattage map using the XPIN detector. The SDD ICR was fixed at 90 kcps, as a detector at a 'reasonable' distance ideal case as it only produces a 20% dead time on the detector electronics. The XPIN was limited to 26 kcps, owing to the longer peaking time of 12 μs, producing 50% dead time on the detector. For metal identification, either detector generates enough counts for identification of the alloy in 2 s or less using either the 90 kcps from the SDD or the 26 kcps from the PIN. A spectrum that contains ~30 k total counts has enough data within the spectrum to identify the metal using fundamental parameters (FPs) XRF software. Fast detection of alloys is very desirable for metal identification in the handheld XRF market, and these count rates allow for rapid identification.

Even a much lower an ICR of 10 kcps is adequate for many less stringent alloy identification applications, allowing to identify the alloy in 5 s of more. In other words, nonaluminum alloy identification is exceptionally manageable using low-power miniature X-ray sources using either an SDD or a PIN detector.

The X-ray source needs 2–4 times more power when using the PIN detector compared to the SDD in the same geometry. Most of this difference in tube intensity is due to the SDD having a much larger detection area of 42 mm^2, with the PIN having seven times less area at 6 mm^2. Another affect between the SDD and PIN deals with the shaping time used for each detector, the SDD

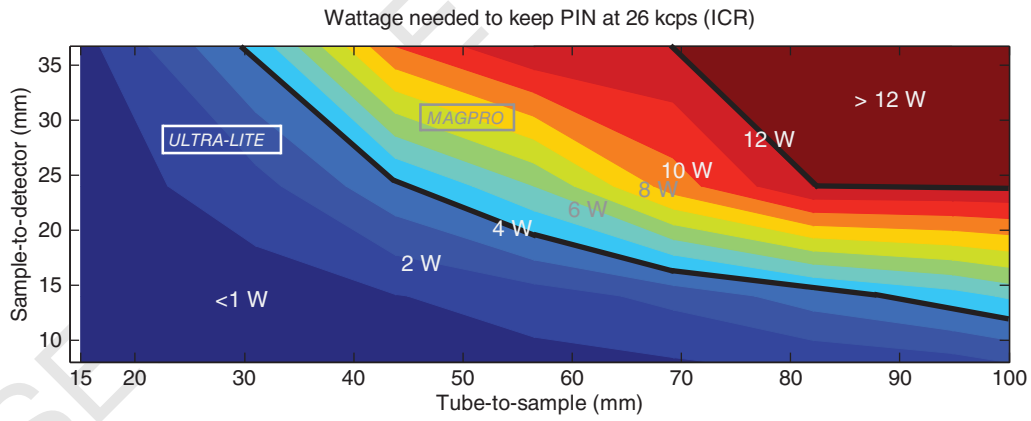

Figure 27 A wattage map created for nonaluminum alloy metals identification, which shows the wattage of source needed to maintain a 26-kcps input count rate on the 6-mm^2 XPIN detector. The dark lines show the limit of capabilities of the ULTRA-LITE® source (4 W) and the MAGPRO (12 W). Both of these sources are good to use for nonaluminum alloy identification with a PIN. (Reproduced with permission from Ref. 16 © ICDD, 2012.)

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has a better resolution at shorter peaking times; therefore, it can count X-ray events faster while maintaining about the same energy resolution. Despite these differences between detectors, both detectors are able to collect enough counts in a second or two and easily use a miniature X-ray source to excite the sample, in order to identify a nonaluminum alloy.

5.4 Results for Trace High Z Element X-ray Fluorescence Detection in a Low *Z* Matrix

We also explored trace element detection, which includes RoHS/WEEE, wear metals in oils, or any other trace high *Z* elements in a low *Z* matrix such as plastic and oils. We used an RoHS/WEEE standard that had 1250 ppm Cr, 500 ppm Hg, 250 ppm Pb, 100 ppm Br, and 125 ppm Cd in a polyethylene matrix purchased from Chemplex Industries, Inc. (*PL(PE)9-5E(D)*). Both an ULTRA-LITE® and a MAGPRO X-ray source with tungsten anodes were tested, each was set at 50 kV and had a 75-μm-thick copper filter to suppress lower energy X-rays. Figure 28 shows the wattage map using the SDD detector, and Figure 29 shows the wattage map using the XPIN detector. Trace element detection in light element matrices is often limited by the maximum count rate of the detector; one is looking for a small XRF signal superimposed on a large amount of background Compton X-ray scatter. A practical upper limit for the maximum count rate is overall rate that produces 50% dead time in the detector electronics. For the SDD, this count rate was 300 kcps. At this limit, the net count rates for elements of interest in the standard were 70 cps in the Pb L_α and 540 cps in the Cd K_α lines. For the XPIN detector, the maximum count rate producing 50% dead time was 26 kcps. This resulted in obtaining count rates of 12 cps in the Pb L_α and 65 cps in the Cd K_α lines.

For this application, both the ULTRA-LITE® and the MAGPRO will provide enough flux onto the sample to effectively saturate either the PIN or the SDD detector. In other words, the X-ray source does not limit this application; the limitations are due to the counting speed of each respective detector. Within the wattage map, it is evident that the lower power ULTRA-LITE® requiring a more tightly constrained geometry to be able to provide the needed X-ray flux from the source to saturate either the PIN or the SDD detector.

The application of trace elements in a low *Z* matrix and the nonaluminum alloy identification used identical setups. The nonaluminum application only needs a few seconds worth of data in order to have the X-ray events needed for identification. For trace elements, the detector counts as fast as the detector will allow, for several seconds up to minutes, depending on the users need on accuracy and error tolerance. This difference is evident in comparing Figures 26–28 for the SDD and Figures 27–29 for the PIN; the more flux demanding trace element analysis needs a tighter geometry compared to the nonaluminum application in order to provide the required flux from a miniature X-ray source for trace element detection.

5.5 Results for Aluminum Alloy Detection

A similar comparison of source capabilities was conducted for aluminum alloy identification. Aluminum 7075 was used as the representative sample for this class of materials and an ULTRA-LITE® with a silver anode and a MAGPRO® with a rhodium anode were

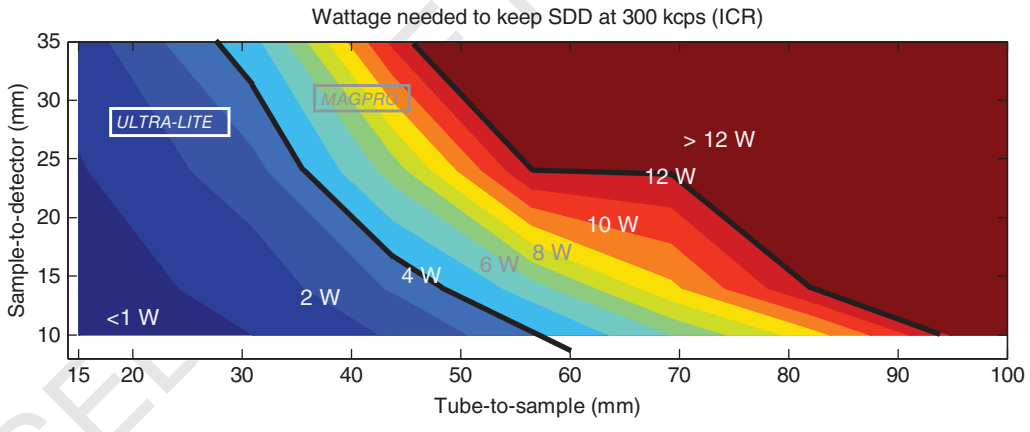

Figure 28 A wattage map for trace element detection on a polyethylene RoHS/WEEE standard, which shows the wattage of X-ray source needed to maintain a 300-kcps input count rate on the 42-mm^2 SDD detector. The black line at 4 W shows the limit of capabilities of the ULTRA-LITE® source; the MAGPRO is limited to 12 W, shown by the second black line. Both of these sources are useful for trace element detection with an SDD, with closer geometrical coupling needed for the ULTRA-LITE®. (Reproduced with permission from Ref. 16 © ICDD, 2012.)

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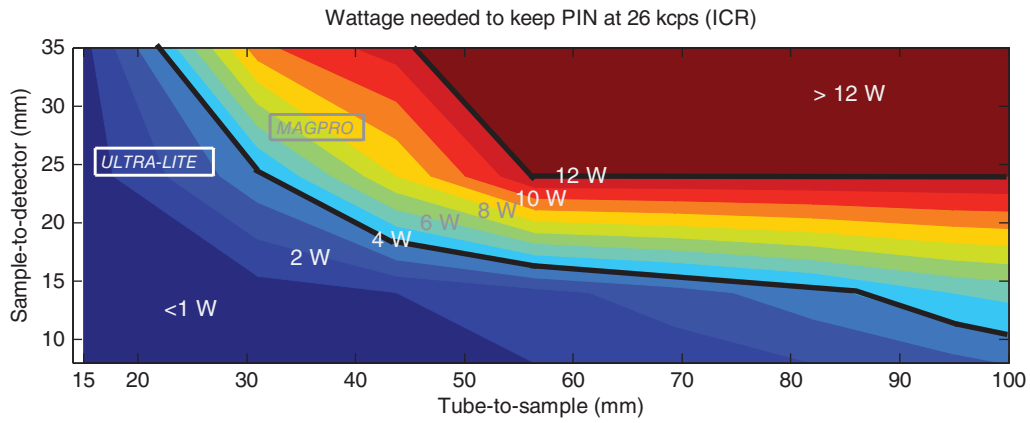

Figure 29 A wattage map for trace element detection on a polyethylene RoSH/WEEE standard, which shows the wattage of X-ray source needed to maintain a 26-kcps input count rate on the 6-mm^2 XPIN detector. The black line at 4 W shows the limit of capabilities of the ULTRA-LITE® source; the MAGPRO® is limited to 12 W, shown by the second black line. Both of these sources are useful for trace element detection with a PIN detector, with closer geometrical coupling needed for the ULTRA-LITE®. (Reproduced with permission from Ref. 16 © ICDD, 2012.)

compared. Each X-ray source was set at 12 kV and used no filter in front of the X-ray source. The ULTRA-LITE® has a maximum emission current of 200 μA, at 12 kV achieving 2.4 W. The MAGPRO® has a maximum emission current of 1000 μA and can achieve a full 12 W at 12 kV. Figure 30 shows the wattage map using the SDD detector, and Figure 31 shows the wattage map using the XPIN detector. For the SDD, the count rate was fixed at 90 kcps, with a 20% dead time on the detector electronics. For the XPIN detector, the count rate was fixed to 26 kcps, producing 50% dead time on the detector. These count rates were chosen to match the previous tests conducted on nonaluminum alloys. The nonaluminum alloys test used a tube with a different anode and filter; therefore, the results in Figures 26 and 27 are somewhat, although not directly, comparable to Figures 30 and 31. A minimum total of about 30 k counts total counts are needed to identify an alloy on the order of a second or two.

The major limitation in this application is the significant X-ray absorption in air of the low-energy X-rays in sample-to-detector path. The absorption of low-energy X-rays is not directly accounted for in the wattage maps in Figures 30 and 31; the ratio of light element X-rays to the higher element X-rays is changing even though the total counts in the spectrum is held constant. For 3.0 keV X-rays (~Ag L lines), half the X-rays are absorbed in 35 mm of air, which is the energy used to excite the sample.

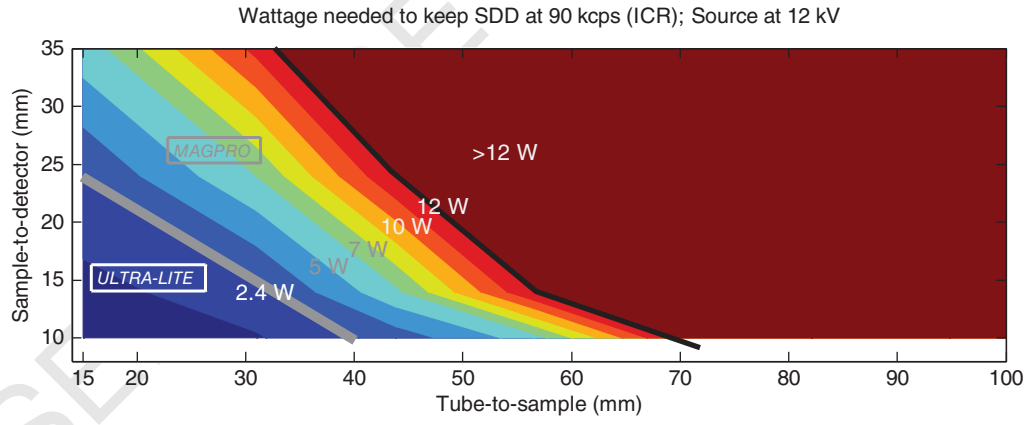

Figure 30 A wattage map created for aluminum alloy metals identification, which shows the wattage of X-ray source needed to maintain a 90-kcps input count rate on the 42-mm^2 SDD detector. The gray line at 2.4 W shows the limit of capabilities of the ULTRA-LITE® source; the black line at 12 W shows MAGPRO® is limited to 12 W. The MAGPRO® is the better source for aluminum alloy identification with an SDD. (Reproduced with permission from Ref. 16 © ICDD, 2012.)

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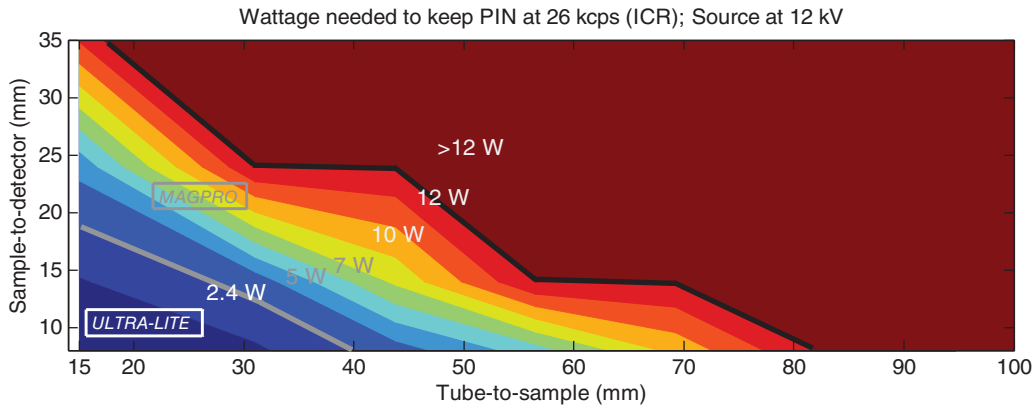

Figure 31 A wattage map created for aluminum alloy metals identification, which shows the wattage of X-ray source needed to maintain a 26-kcps input count rate on the 6-mm^2 XPIN detector. The gray line at 2.4 W shows the limit of capabilities of the ULTRA-LITE® source; the black line at 12 W shows that MAGPRO is limited to 12 W. The MAGPRO is the better source for aluminum alloy identification with a PIN detector. (Reproduced with permission from Ref. 16 © ICDD, 2012.)

For 1.5 keV X-rays (~Al K lines), half the X-rays are absorbed in just 4.5 mm of air, which is the energy we are want to detect. The SDD count rate of the Al K_α peak was 12 kcps at the very close sample-to-detector distance of 10 mm, and at a reasonable tube-to-sample distance of 31 mm and 240 μA of tube emission current. The count rate of the Al K_α peak dropped severely to 2.5 kcps, at a sample-to-detector distance of 24 mm, the same tube-to-sample distance, and a full 1000 μA of tube emission current. The PIN count rate of the Al K_α peak was 2.5 kcps at the very close sample-to-detector distance of 8 mm, and at a reasonable tube-to-sample distance of 29 mm and 80 μA of tube emission current. The count rate of the Al K_α peak dropped severely to 0.7 kcps, at a sample-to-detector distance of 29 mm, the same tube-to-sample distance, and a full 1000 μA of tube emission current. For both detectors, moving back just 14 mm made a huge difference in the Al K_α count rate. A short sample-to-detector distance is very critical for aluminum alloy detection in air. The tube-to-sample distance is also critical, but much less so compared to the sample-to-detector distance.

Despite the limitations described earlier, the ULTRA-LITE® will work for aluminum alloy detection if the sample-to-detector distance is kept quite small. In handheld instruments available today, which would use an ULTRA-LITE® X-ray source, sample-to-detector distances <20 mm have been achieved in order to allow for aluminum alloy detection, using low-power portable sources such as the ULTRA-LITE® source. The MAGPRO has sufficient amount of X-ray flux for this XRF application in a wider array of geometries; therefore, this is a functionally better for this application compared to the ULTRA-LITE®.

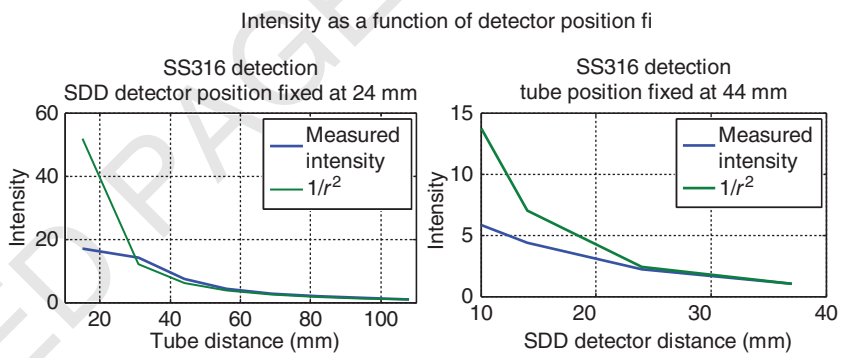

Figure 32 The figure on the left maps out the intensity of flux off an SS316 sample with the SDD detector held at a constant 24 mm from the sample and the tube moved between 15 and 108 mm away from the sample. The figure on the right maps out the intensity of flux off an SS316 sample with the tube held at a constant 44 mm from the sample and the SDD moved between 10 and 37 mm away from the sample. In both cases the intensity diverges strongly from the idealized inverse square law at tube-to-sample or sample-to-detector distances <30 mm. (Reproduced with permission from Ref. 15 © ICDD, 2013.)

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5.6 Wattage-map Comparisons to the Inverse Square Law

Many use the inverse square law as a rule of thumb in dealing with intensity in changing geometric issues in instrument design. We have found that at close spacing, often used with miniature X-ray sources, the inverse square law does not work very well because we do not have an idealized 'point' source. Figure 32 shows how the intensity departs from the inverse square law, using the same data that generated the wattage maps in Figure 26. At distances greater than about 30 mm, the inverse square law works relatively well. At distances <30 mm, in which miniature X-ray sources are commonly used, the inverse square law is compromised by very large factors in intensity. In addition, the inverse square law does not answer the question 'Which miniature X-ray source is appropriate for a particular geometry and a particular XRF application?', it only gives a reference to a relative change. The wattage maps do answer this question; giving the wattage needed in different geometries.

In addition, the inverse square law does not work at all with light element analysis in air because air absorption is a considerably stronger effect, as discussed in the previous section. The issue of air absorption is addressed in the wattage maps in Figures 30 and 31, noted by the much tighter coupling of both the tube-to-sample and sample-to-detector distances required.

5.7 Results for Light Element Detection in Portland Cement

We next explored light element detection using Portland cement powder as an example for light element detection (composition given in Table 6). In this experiment, detection of Al and Si was severely limited by X-ray air absorption. Without air path between the source, sample and detector, air does not absorb the light element X-rays, and this is much easier to do from a pure XRF centered standpoint. However, eliminating the air path is much harder from a practical instrument standpoint, requiring a vacuum system and an air tight sample chamber. We chose to do this experiment with the air path because it represents the worst-case scenario for light element XRF detection and therefore the worst case scenario

Table 6 Materials in Portland cement

Typical constituents of Portland Cement	Mass (%)
Calcium oxide, CaO	61–67
Silicon dioxide, SiO_2	19–23
Aluminum oxide, Al_2O_3	2.5–6.0
Ferric oxide, Fe_2O_3	0.0–6.0
Sulfate	1.5–4.5

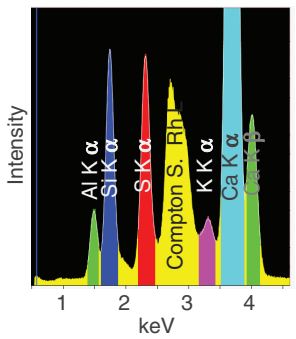

Figure 33 A spectrum from Portland cement with the X-ray source set to 6 keV. All the light element K lines can easily be seen. (Reproduced with permission from Ref. 16 © ICDD, 2012.)

for the MAGPRO source. The maximum power of the X-ray source was used for all the geometrical positions, so instead of a wattage map where the count rate on the detector is held constant, the X-ray source was held a maximum power and the count rate changes as the geometry changes. For this test, the X-ray source was set at 6 kV and 1000 μA (6 W) with no filter in front of the source. Only the MAGPRO with a rhodium anode was tested because the higher maximum current was a large advantage for this particular application. Because of the high concentration of Ca, the choice of excitation voltage is highly constrained; 6 kV was chosen because it maximized the number of X-ray counts in the Al, Si, S, and K peak lines. If the quantification of iron is needed, the measurement protocol could include two settings on the X-ray source, a low kilovolt setting to get the lighter elements and a second setting at a higher kilovolt to get the iron content in relation to the calcium content.

Figure 33 shows a spectrum taken from the Portland cement sample, showing all of the light elements and the calcium peak (off-scale). Figure 34 shows the count rate from the entire spectrum, which is dominated by the calcium peak. Figure 35 shows the count rate for just the silicon peak, which is a small fraction of the total counts. The Compton scattered lines from the X-ray tube's Rh target are needed to excite the K lines of lighter elements below Chlorine.

For this application, the MAGPRO has sufficient X-ray flux for detecting the light elements. To be effective, tight X-ray tube-to-sample and sample-to-detector distances are needed, for the same reasons discussed in the section about identifying aluminum alloys. Because of the high concentration of Ca, limiting its excitation is essential to managing the overall count rate. An SDD detector is essential for getting the needed higher count rate. Despite the constraints and limitations, it is clear that the MAGPRO miniature X-ray source is very effective for even this demanding application.

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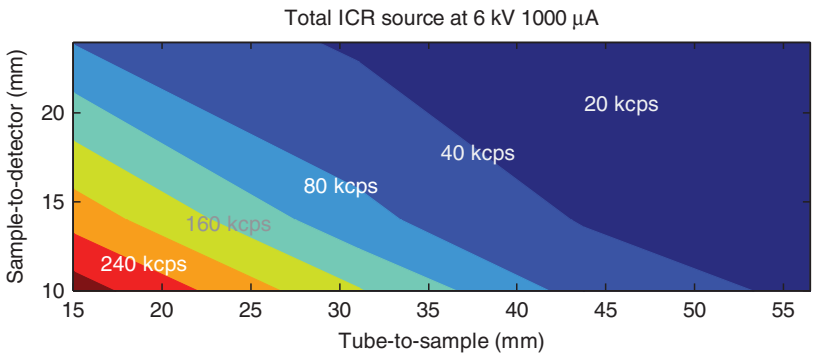

Figure 34 The total input count rate, using the 42-mm^2 SDD detector, as a function of detector and X-ray tube position. In this map, the X-ray source was set at the maximum setting of 1000 μA at 6 kV. The majority of the counts represent counts from the calcium peak. (Reproduced with permission from Ref. 16 © ICDD, 2012.)

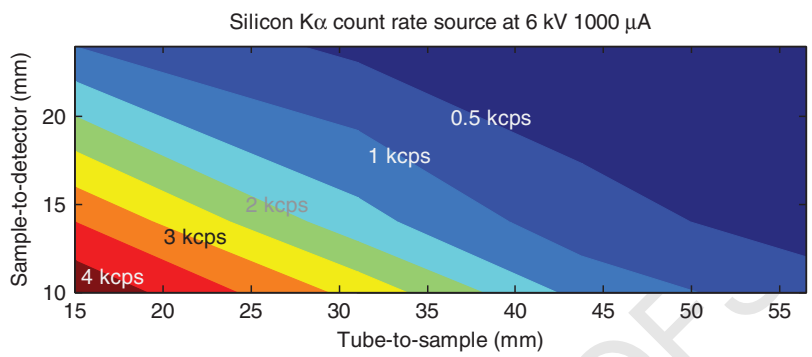

Figure 35 The count rate in the silicon peak, using the 42-mm^2 SDD detector, as a function of detector and X-ray tube position. In this map, the X-ray source was set at the maximum setting of 1000 μA at 6 kV. (Reproduced with permission from Ref. 16 © ICDD, 2012.)

Lower wattage X-ray sources such as the ULTRA-LITE® or the MAGPRO are effective solutions for many EDXRF applications. The smaller package and weight of miniature X-ray sources have the advantage of making much smaller and lighter XRF instruments or enable operation in constrained spaces, an obvious advantage in instrument design. The close source-to-sample distances possible with miniature sources are particularly advantageous for light-element detection, where air absorption can severely limit count rates. The 'wattage maps' allow for comparison of the geometries needed for X-ray sources in some typical EDXRF applications. These maps can provide a good illustration of the trade-offs in a particular application with regards to the geometry of the XRF setup and provide useful guidance in selecting the most appropriate source.

ABBREVIATIONS AND ACRONYMS

ED	Energy-Dispersive
FP	Fundamental Parameter
FWHM	Full-Width-Half-Maximum
HV	High-Voltage
HVPS	High-Voltage Power Supply
ICR	Input Count Rate
kcps	Kilo-Counts Per Second
RoHS	Restriction of Hazardous Substance
SDD	Silicon Drift Detector
XRF	X-Ray Fluorescence

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