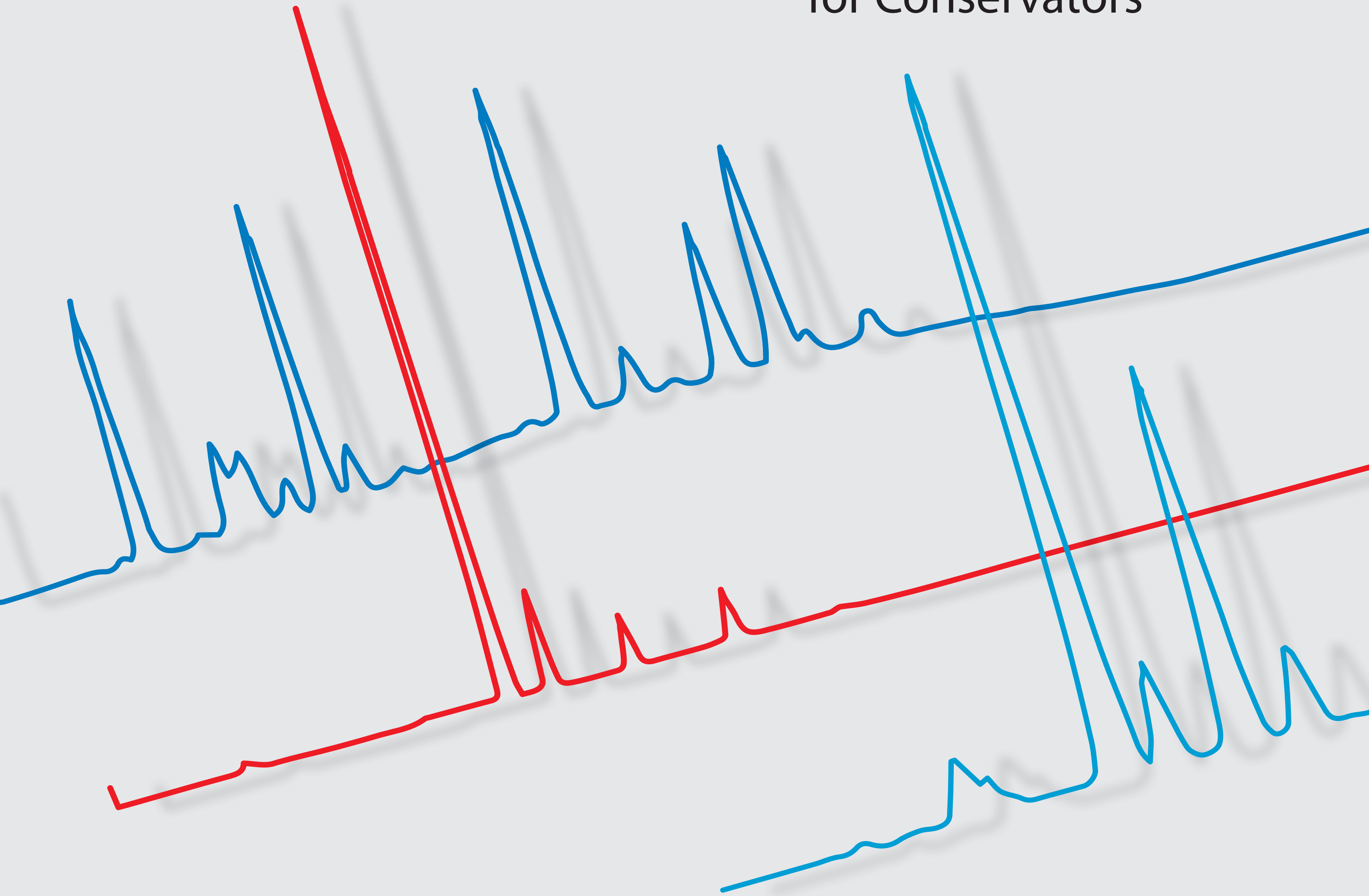
Handheld XRF In Cultural Heritage

A Practical Workbook for Conservators



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Getty Conservation Institute

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A collaboration of the Getty Conservation Institute and the Institute for the Preservation of Cultural Heritage at Yale University

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The Getty Conservation Institute (GCI) works internationally to advance conservation practice in the visual arts—broadly interpreted to include objects, collections, architecture, and sites. The Institute serves the conservation community through scientific research, education and training, field projects, and the dissemination of information. In all its endeavors, the GCI creates and delivers knowledge that contributes to the conservation of the world's cultural heritage.

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Museum

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Acknowledgments

In 2013 we developed and taught the first XRF Boot Camp, an intensive four-day workshop for conservators that combined theory with project-based learning in a practical manner. Subsequent Boot Camps were held in 2014 and 2016, each building on the last while incorporating a new special topic. Our experiences with the Boot Camps made it clear that a workbook designed for independent study would help participants review what they had learned and could serve as a training resource for new users. This workbook is the result. Like the Boot Camps, it provides basic background information on the principles of X-ray fluorescence spectroscopy (XRF), and the main focus is the use of practical exercises that exemplify common challenges encountered in the study of cultural heritage materials.

Many people have helped along the way. We thank the Getty Conservation Institute (GCI) and Yale Institute for the Preservation of Cultural Heritage (IPCH) for providing financial and staff support for both the workbook and the XRF Boot Camps. Also, our gratitude goes to the host institutions of the three Boot Camps and the museums that allowed access to their collections: Yale IPCH, Yale University Art Gallery, Yale Peabody Museum of Natural History, University of California, Los Angeles (UCLA) Fowler Museum, UCLA-Getty Conservation IDP, Stichting Restauratie Atelier Limburg, and the Bonnefantenmuseum.

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1. Radiation Safety

1.1 Basic Safety Considerations

X-rays are invisible to the human eye and likewise undetectable by other senses (hearing, taste, smell, and touch). Because of their high level of energy, X-rays are classified as ionizing radiation, which means they can cause damage to cells and tissue. Therefore, their safe use requires that extra precautions be taken.

Creating a safe working environment—both for humans and for the objects being analyzed—is the first and most important step that must be taken in the use of X-ray fluorescence (XRF) spectroscopy. Most institutions are required by local ordinances to carry out training in X-ray radiation safety for all operators of the equipment, as well as the completion of a test to ensure that you, as the operator, have understood the safety information provided. Requalification on a yearly basis may also be prescribed. In many countries, instrument manufacturers are required to provide radiation safety information with their instruments and include radiation safety considerations in standard operating procedures for the units. These could include radiation dosimeter badge requirements and/or the appointment of a radiation safety officer. Familiarity with the manufacturer's safety recommendations and operation guidelines is particularly important if you are self-employed or if the institution or business you are working for is not providing X-ray radiation safety training. Equipment vendors are required to inform you of local restrictions that apply to the equipment they sell, but it is your responsibility to be aware of and comply with all local regulations governing the use of X-ray generating equipment. Both the equipment and user may require a permit. Your country of residence and/or your employer may require additional precautions to those outlined here. Before using any X-ray generating device, make sure you comply with all local regulations and rules. Links to select national and international regulation websites can be found in the bibliography at the end of this chapter.

This section reviews information regarding the nature of X-ray radiation, how X-rays interact with the human body, and steps to take to minimize your exposure as an operator and the exposure of others who may be in your vicinity during analysis. Following this section is a series of short exercises designed to further help you understand the basics of X-ray safety.

FOR YOUR SAFETY, READ THIS SECTION AND COMPLETE THE EXERCISES BEFORE MOVING ON. ALWAYS FOLLOW YOUR INSTITUTION'S GUIDELINES AND PROTOCOLS FOR X-RAY SAFETY.

What Are X-rays?

X-rays are part of the electromagnetic spectrum (fig. 1.1), which includes radio waves, microwaves, infrared radiation, visible and ultraviolet light, and, at higher energies, X-rays and gamma rays. Short wavelength ultraviolet light, X-rays, and gamma rays produce ionizing radiation capable of causing damage to organic compounds and living tissue. In a vacuum, all of these different forms of radiation travel at 3.00×10^8 $\mathrm{ms^{-1}}$

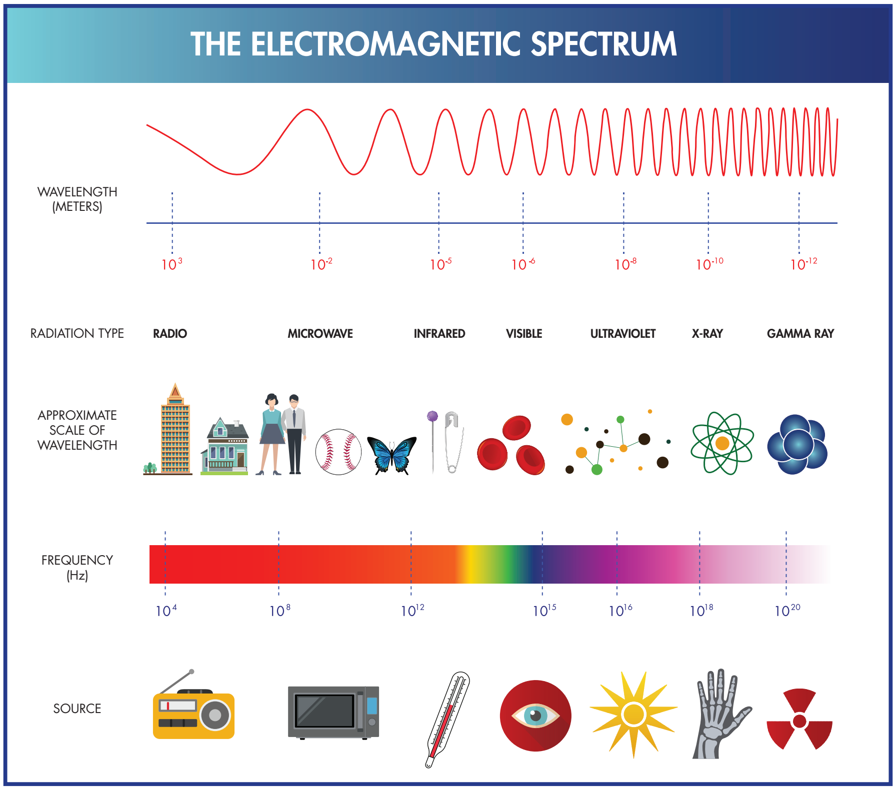


FIGURE 1.1. The electromagnetic spectrum, showing the relationship between wavelength and frequency of the seven bands of radiation: radio waves, microwaves, infrared radiation, visible/UV light, and X-rays and gamma rays.

(the speed of light) and differ only in their wavelength/energy. The energy of an X-ray, E, is related to its wavelength, λ, through the Duane-Hunt law:

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

where h is Planck's constant (4.14×10^{-15} eV·s) and c is the speed of light. The energy of an X-ray photon is typically expressed in kilo-electron volts (1 keV = 1000 eV) and the wavelength in nanometers (nm), which reduces this relation to:

$$E\left(\text{keV}\right) = \frac{1.24}{\lambda\left(\text{nm}\right)}$$

X-rays have wavelengths ranging from 0.01 to 10 nm, which corresponds to a wide range of energies from 124 keV to 0.124 keV, respectively. In practice, handheld XRF spectroscopy utilizes a much smaller range of energies from about 1 keV (the lowest practical detectable XRF emission line being Na Kα at 1.04 keV) to slightly over 30 keV (the Ba Kα line is at 32 keV).

Ionizing radiation can excite atoms and molecules, which makes them useful for X-ray spectroscopy, but it also can induce biological effects, including causing damage to cells and DNA. Low doses of ionizing radiation can cause nausea and changes in blood cells and, in higher doses, result in symptoms such as hair loss and sterility. Extreme exposures can be fatal. Special attention should be taken to protect the eyes, as the retinas are extremely susceptible to radiation damage. Thus, it is extremely important to know how to protect yourself from exposure to radiation.

Measuring Radiation Exposure

Biological radiation damage is approximately proportional to the amount of radiation absorbed by the target tissue, so it is important to monitor your exposure. Radiation exposure can be measured in terms of the total amount of radiation absorbed by a material (such as human tissue), called absorbed dose, and expressed in units of rad (US unit) or gray (Gy) (SI unit); 1 rad is equivalent to 0.01 Gy. Effective (or equivalent) dose takes into account tissue sensitivity to a particular type of radiation, such as beta, gamma, X-ray, or alpha radiation. Because it incorporates biological effectiveness, effective/equivalent dose is more useful than absorbed dose for assessing the effects from exposure to radiation. Effective/equivalent dose is expressed in units of rem (roentgen equivalent man; US unit) or Sv (sievert; SI unit), often expressed in mrem (1/1000 of a rem) or mSv (1/1000 of a sievert); 1 Sv = 100 rem.

It is important to maintain perspective on the relative dangers of radiation. When proper safety protocols are observed, radiation levels can be readily controlled so that work may continue at a level of risk comparable to or less than exposure received through commonly encountered sources (table 1.1). For example, you would receive approximately 5 mrem of exposure on a round-trip flight between Los Angeles and New York. By contrast, the normal exposure from a portable XRF spectrometer properly configured, shielded, and used, is less than 0.1 mrem/hour.

Your exposure to radiation in the workplace can be monitored using dosimeter badges. There are two types of dosimeter badges: whole body (worn between the neck and waist) and ring (worn on the hand). Since XRF spectrometers are used near the hands, both types of dosimeters are generally recommended. Check with your institution's radiation safety officer and/or local radiation regulations for specific guidance as to the type of radiation monitoring required.

TABLE 1.1. Typical levels of radiation exposure from background sources and XRF instruments, along with US regulatory exposure limits.

Exposure from Background Radiation Sources		
Scenario	**Exposure Amount**	**Units**
Dental X-ray (full mouth)	4 to 7	mrem/X-ray
Transatlantic flight (one way)	2.5	mrem/flight
Chest X-ray	10	mrem/X-ray
Ionizing radiation exposure of the population of the United States	625	mrem/year
Whole-body CT scan	1000	mrem/scan
Nuclear worker annual dose limit	5000	mrem/year
Exposure Limits Set by Regulatory Agencies		
Max permissible limit during pregnancy	500	mrem/9 months
Max permissible limit for entire body	5000	mrem/year
Max permissible limit for an extremity (e.g., finger)	50,000	mrem
Exposure from Normal Operation of XRF Analyzer in Sample Stand		
Left/right/behind analyzer	<0.1	mrem/hour
Exposure from Unacceptable Use of XRF Analyzer Outside Sample Stand		
4 feet directly in front of analyzer window	14	mrem/hour
1 foot in front of analyzer window	186	mrem/hour
Directly in front of analyzer window	20,000	mrem/hour

Sources: CDC 2015; Center for Scientific Information 2018; HPS n.d.; NCRP 2009; NRC 2018a, 2018b; PHE n.d.; US NRC 1980.

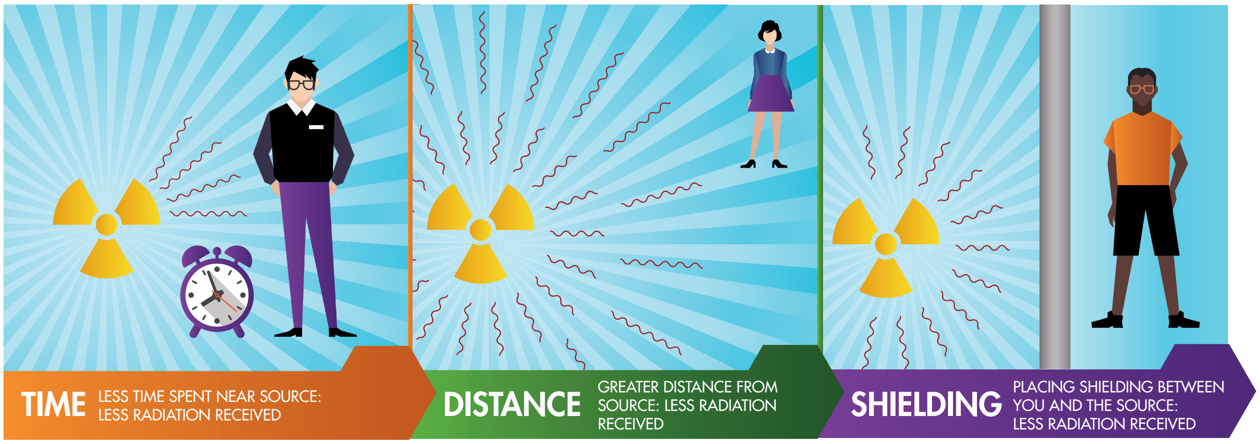


FIGURE 1.2. ALARA (As Low As Reasonably Achievable) provides a guide for minimizing exposure to radiation through the principles of time, distance, and shielding.

Minimizing Radiation Exposure

X-rays must always be treated responsibly. To minimize risk, the ALARA principle (**A**s **L**ow **A**s **R**easonably **A**chievable) is followed. ALARA relies on three principles: time, distance, and shielding (fig. 1.2).

Time. Dose equals the rate of exposure multiplied by time. By minimizing your time around the radiation source, you can reduce your exposure. While conducting XRF measurements, observe this principle by turning off the instrument or closing the shutter when not actively collecting data.

Distance. From a point source, radiation spreads out in all directions, and the intensity follows Newton's inverse square law, which states that intensity (I) is inversely proportional to the distance (*d*) from the source, squared:

$$I \propto \frac{1}{d^2}$$

This relationship is illustrated in figure 1.3, which shows that by doubling the distance from an X-ray source, the intensity is reduced by a factor of 4, and by tripling the distance, the intensity is reduced by a factor of 9. The relationship between the intensity at two different distances can be expressed as:

$$I_1 \times d_1^2 = I_2 \times d_2^2$$

While it may not be possible to increase the distance from a portable XRF spectrometer if it is being used in the handheld mode, use of remote triggers when possible can help increase your distance from the X-ray source.

Because the radiation from a handheld XRF spectrometer is collimated, the highest level of radiation is found along the main direction of the tube output (i.e., the primary beam). The direction of the primary beam will depend on the specific form factor of your instrument. You will need to consult your instrument manual to determine the geometry of your instrument and the tube orientation so you can position yourself away from the direction of the primary beam and any possible reflections. The amount of radiation varies according to distance and angle with respect to the direction of the primary beam, but the area where the manual trigger is located will have a higher amount of radiation due to its proximity to the nose; thus, the user should be aware and take necessary precautions, such as using an external trigger if provided by the manufacturer.

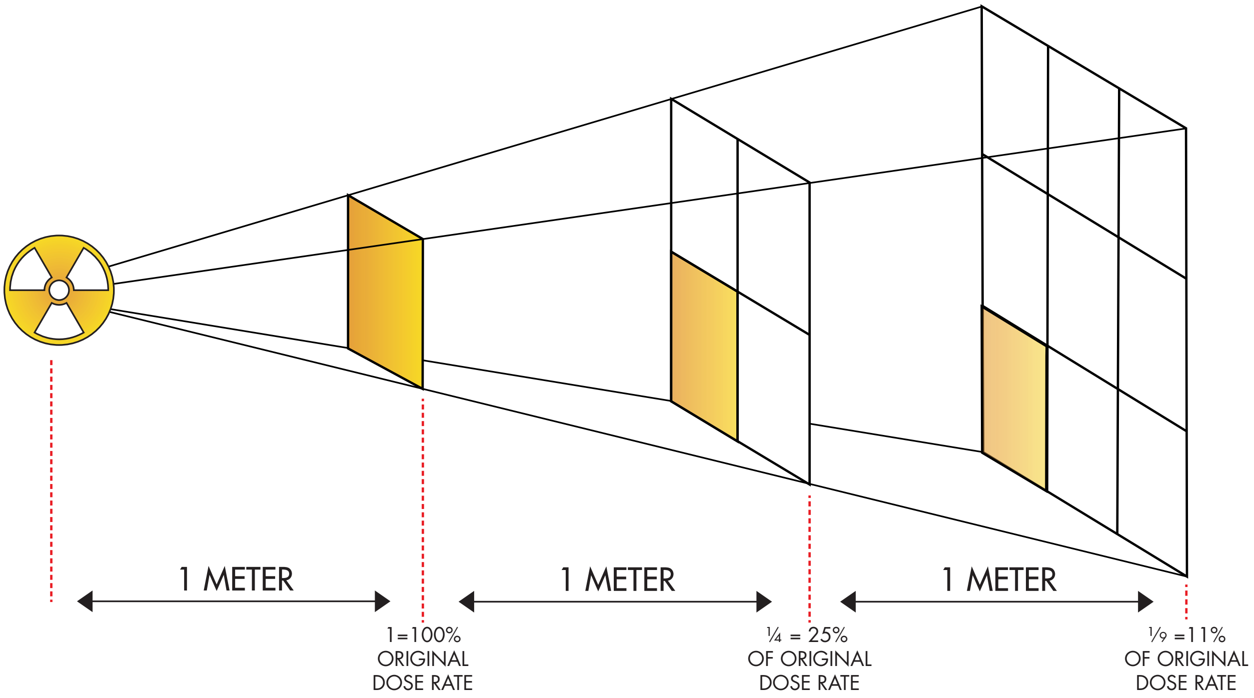
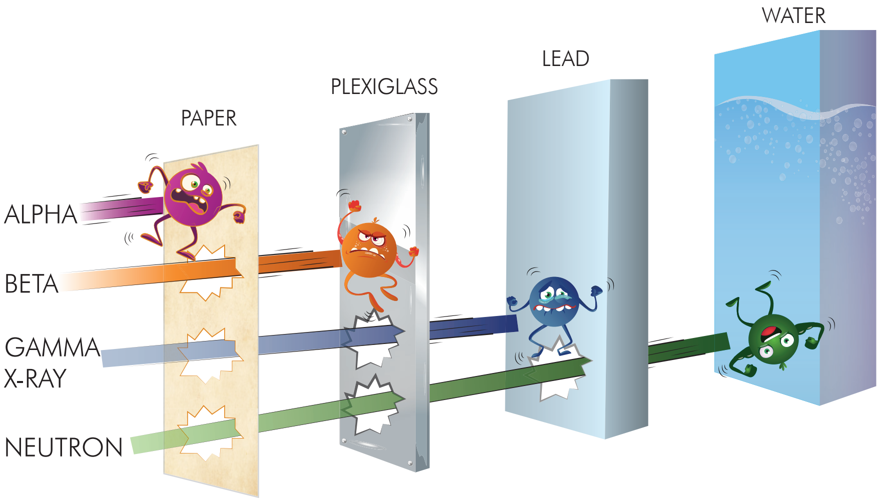


FIGURE 1.3. Diagram illustrating Newton's inverse square law, in which the intensity of radiation is inversely proportional to distance from the source, squared.

Shielding. Placing a physical barrier between you and the radiation source can block some or all of the radiation. The amount and type of barrier material needed is dependent on the energy of the X-ray source (fig. 1.4). In general, the more radio-opaque material there is between you and the source of ionizing radiation, the smaller the dose of radiation you will receive. When operating a portable XRF spectrometer in the handheld mode, it may not be possible to place a physical barrier between you and the instrument. However, if you are using a stand, you can use a barrier such as a nose cap (if provided with your instrument) or place a sheet of lead or leaded glass between you and the instrument.

Always follow the operation guidelines provided by your instrument manufacturer. Incorrect operation can have adverse effects, but when used as stipulated, the dangers are negligible. In general, handheld XRF spectrometers are designed to maximize shielding of the fingers and hands when holding the instrument or operating the trigger. As an extra precaution, a dosimeter ring should be worn on the hand holding

FIGURE 1.4. Illustration showing types of radiation shielding using different materials, dependent on the energy of the source.



or operating the instrument. Another area requiring extra precaution is the eyes. When positioning the instrument over an area of interest for analysis, it may be necessary to look closely at the nose to check the positioning. Always make sure the instrument is off before placing your eyes anywhere near the nose of the instrument. Eyes are very sensitive to radiation, and the threshold dose for radiation-induced cataracts is 200 rad (2 Gy) delivered to the lens of the eye in a single occurrence.

WARNING: NEVER LOOK DIRECTLY INTO THE PRIMARY BEAM OF THE HANDHELD XRF ANALYZER.

Special Considerations for Handheld XRF Spectrometers

- Only the operator(s) should be within a minimum of 1 meter of the instrument. The operator should never put any body part near the beam port or in the primary direction of the X-ray path. Ignoring this warning could result in unnecessary exposure to radiation.
- Avoid all risky operation of the spectrometer (fig. 1.5). Never hold a sample up to the X-ray port for analysis with your hand or any other part of the body; always hold the instrument up to the sample, and hold it *only* by the handles provided.
- All X-ray generating instruments are designed with a number of safety interlocks. A proximity sensor disables the instrument when no solid object is in front of the nose (this interlock can be mechanical, infrared, or laser based). Similarly, a backscatter interlock disables the instrument if it does not detect sufficient radiation scattered back from the sample (this is to ensure the instrument is kept in contact with or close to the sample to prevent unwanted scattered radiation from reaching the operator). Other safety systems include requiring a key to operate the instrument (stored in a separate, secure location when not in use), password protection (only higher-level logins can override proximity sensors), operator trigger interlock (instrument is operable only when the trigger is held down manually), red X-ray warning light, external X-ray warning lamps (optional), and operator time-out. An uninformed operator should never defeat the interlocks and safety systems. Defeating these safety features could result in overexposure to radiation.
- If possible, place the analyzer *in contact* with the sample when operating. Holding the analyzer away from the sample may result in excess backscattered radiation reaching you. In the case of cultural heritage objects, it is often not possible or desirable to place the instrument in direct contact with the object.

FIGURE 1.5. Illustrations of spectrometer handling that risk exposure to radiation. From left: holding the instrument too close to the body; holding the sample in the hand; holding the nose of the instrument too far away from the sample; having another person in the scattering angle of the radiation.

In such cases, it may be necessary to disable some of the safety interlocks to enable measurement. This should be done only if absolutely necessary and with great caution.

- Small samples that do not entirely cover the measurement window are potentially risky because part of the primary radiation may go unattenuated by the sample. To eliminate this risk, a safety cap should be placed over the sample to protect the operator from exposure (fig. 1.6).

FIGURE 1.6. Photo of the Bruker Tracer III-SD, showing a safety cap placed over the sample to be analyzed, to minimize risk of exposure.

Follow these common sense safety guidelines:

- **Never pull the trigger without a sample in place (or without a radiation cover).**
- **Keep an area of 1 meter (3 feet) minimum in front and to the sides of the analyzer free of all personnel not actively operating the instrument.**
- **Never point the device at another person or yourself.**
- **Only trained personnel should operate the instrument.**
- **Maintain all labels and safety interlocks.**
- **When in doubt, contact your supervisor or the equipment vendor or manufacturer.**

1.2 Exercises: Understanding Radiation Output from Your Instrument

The following exercises are designed to help you create a safe working environment. The first exercise helps you compile important radiation safety information in one place. The subsequent exercises encourage you to go beyond safety facts and put principles and relations into action.

Note: **After you have completed the exercises, compare your results with the findings in the Solutions section that follows.**

EXERCISE 1.2a:

Safety Checklist

☐ I have completed X-ray radiation safety class and/or I have read and studied the manufacturer's X-ray radiation safety operator training manual.

☐ I have gathered the necessary important contact information concerning radiation safety.

- ☐ For information about radiation safety, I contact: ____________________
- ☐ To report exposure to X-ray radiation, I contact: ____________________

☐ I know if I am required to wear a device to monitor the amount of radiation exposure I receive (dosimeter).

- ☐ I am required to wear a dosimeter badge (circle one): YES NO
- ☐ I know how frequently my dosimeter badge is checked and replaced (enter frequency, e.g., every *X* months): ____
- ☐ I keep my dosimeter badge (enter location): ____________________

☐ I know the effective dose limit values for occupationally exposed persons for my country or region:

- ☐ Whole-body annual limit (make sure to use the correct units, e.g., mrem/year or mSv/year): __________
- ☐ Skin: ____________________
- ☐ Hands: ____________________
- ☐ Internal organs: ____________________
- ☐ Eyes: ____________________

☐ I have a survey meter to help detect X-rays while my XRF instrument is in use and I know how to use it.

☐ There is a secure storage location for the XRF spectrometer and/or there is a way to prevent the use of the instrument by untrained and/or unauthorized users.

☐ If required, I have a sign to warn people of the possibility of X-ray exposure while I am using the instrument. See example shown in figure 1.7.

☐ I am aware of the direction X-rays travel when they exit my instrument (sketch your instrument in the space below and indicate direction of X-rays).

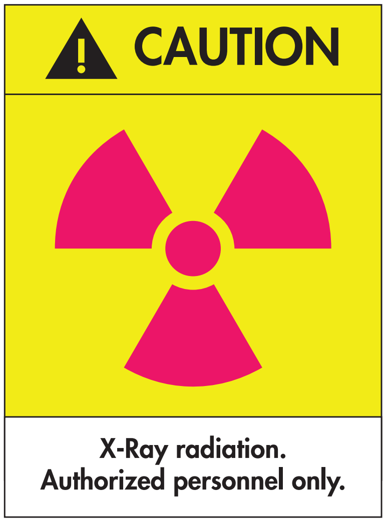


FIGURE 1.7. Sign warning of possible X-ray radiation exposure.

☐ I know what actions lead to the emission of X-rays from the instrument I am using:

____

____

____

☐ My instrument has safety features to reduce the chances of accidental radiation exposure:

- ☐ Proximity sensor (X-rays are emitted only if sensor is blocked by sample/object)
- ☐ Backscatter X-ray sensor (X-ray emission is stopped unless a sufficient quantity of X-rays is scattered back to the detector by sample/object)
- ☐ Safety shield
- ☐ Other: ________________________________

☐ In case of malfunction or other emergency, I know how to stop X-rays from being emitted by the instrument (indicate all options):

____

____

____

EXERCISE 1.2b:

Checking the Safety Interlocks of the System

Set up your instrument according to the manufacturer's directions. With a sample in place or a safety cover over the nose of the instrument, pull the trigger to activate the X-rays.

For your instrument, what indicates the X-ray generator is on and producing X-rays?

☐ Red light only

☐ Blinking red light

What light (if any) or other indication is given that the proximity sensor is active (armed)?

EXERCISE 1.2c:

Converting Radiation Dose Units

National Council on Radiation Protection and Measurements (NCRP) Report no. 160 indicates that individuals in the United States receive a total annual dose of about 620 millirem (mrem) from a combination of natural and man-made sources of radiation (NCRP 2009). Public Health England (PHE) has calculated that, on average, people in the United Kingdom are exposed to about 2.7 mSv of radiation a year (PHE n.d.).

- Calculate which country's residents receive a higher average total annual dose of radiation. Do these reports refer to radiation absorbed dose or effective dose?

EXERCISE 1.2d:

Reading Your Survey Meter

A Geiger-Muller pancake detector (also known as a probe) connected to a portable count rate indicator such as a Ludlum Model 3 survey meter, commonly used in the US (fig. 1.8a), is a highly sensitive way to survey your environment for background radiation exposure levels and to survey your work setup for radiation exposure from your instrument. Each has a range selector switch with the following options: ×100, ×10, ×1, and ×0.1 (fig. 1.8b). To arrive at the correct reading, multiply the number you see on the scale (fig. 1.8c) by the option you selected with the range selector switch.

- Which multiplier option is selected on the survey meter shown (see fig. 1.8b)?

  ____

- How many counts per minute is the survey meter measuring (see fig. 1.8c)?

  ____

- Which multiplier option allows you to monitor the lowest range of counts per minute?

  ____

FIGURE 1.8a. A Geiger-Muller pancake detector attached to a Ludlum Model 3 portable survey meter (count rate indicator).

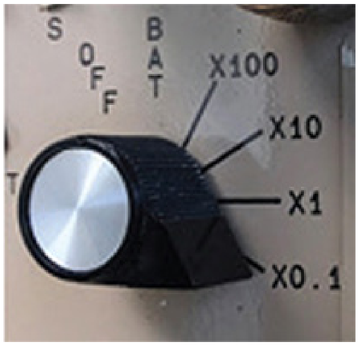


FIGURE 1.8b. Range selector switch on the Ludlum Model 3 survey meter.

FIGURE 1.8c. Display on the Ludlum Model 3, showing cpm, milliRoentgen per hour (mR/hr) measured.

EXERCISE 1.2e:

Calculating the Effect of Distance on Dose Rate

You have set up your XRF instrument on a tripod to analyze a photograph. After selecting the appropriate parameters, you test your work setup using a survey meter and find that your meter is reading 300 counts per minute (cpm) by your laptop, which is located 100 cm from the nose of the instrument. You have been advised by your radiation safety officer to arrange your instrument setup so that you detect only 100 cpm where you are standing or working.

- Calculate how far away you need to move to achieve this:

EXERCISE 1.2f:

Using a Survey Meter to Check for Scatter

Set up a measurement for three objects: one metal, one glass, and one plastic. If using a handheld instrument or small-format instrument, use a tripod mount. Ensure that you are either in contact or at the right distance for the measurement, depending on the type of instrument you are using. Choose a measurement mode or measurement parameters that employ a high voltage (40 kV or higher).

First, with the instrument turned off, use a survey meter to determine the level of your environmental background radiation. Next, with the instrument turned on, measure and record the intensity of radiation scattered by each of the three different materials, at three different angles (the specular reflection angle from the primary beam; perpendicular to the surface of the sample; and in the plane of the surface of the sample), holding the meter as close as possible to the sample for each measurement. At each angle, move the meter away from the material and record the distance from the measurement point at which no more signal due to scattered radiation is detectable. Enter your results in table 1.2 and keep for future reference; this marks the minimum safe distance from the instrument.

TABLE 1.2. Table to record radiation counts from your instrument

Instrument:						
	Specular angle		**Perpendicular to surface**		**Parallel to surface**	
	Counts by sample	**Distance from sample for zero counts**	**Counts by sample**	**Distance from sample for zero counts**	**Counts by sample**	**Distance from sample for zero counts**
Metal object						
Glass bottle or drinking glass						
Plastic bottle or drinking glass						

1.3 SOLUTIONS

EXERCISE 1.2c: Converting Radiation Dose Units

To compare the two numbers, they need to be in the same unit. 1 mSv = 100 mrem, so

$$620 \text{ mrem} \times \frac{1 \text{ mSv}}{100 \text{ mrem}} = 6.20 \text{ mSv}$$

$$6.20 \text{ mSv} > 2.7 \text{ mSv}$$

$$\text{US total annual dose} > \text{UK total annual dose}$$

The units “mrem” and “mSv” are used to express the amount of *effective dose*, or the dose equivalent, which is a measure that combines the amount of radiation absorbed by a person and the medical effects of that type of radiation.

EXERCISE 1.2d: Reading Your Survey Meter

Which multiplier option is selected on the survey meter shown? x0.1

How many counts per minute is the survey meter measuring? 4800 cpm × 0.1 = 480 cpm

Which multiplier option allows you to monitor the lowest range of counts per minute? x0.1

EXERCISE 1.2e: Calculating the Effect of Distance on Dose Rate

Newton’s inverse square law allows you to calculate how distance from the source impacts the intensity of radiation at that location (see the section “Minimizing Radiation Exposure”):

$$I_1 = 300 \text{ cpm},\ I_2 = 100 \text{ cpm},\ d_1 = 100 \text{ cm},\ d_2 = ?$$

$$I_1 \times d_1^2 = I_2 \times d_2^2$$

$$d_2 = \sqrt{\frac{I_1 \times d_1^2}{I_2}}$$

$$d_2 = \sqrt{\frac{300 \text{ cpm} \times (100 \text{ cm})^2}{100 \text{ cpm}}} = 173.2 \text{ cm}$$

By increasing the distance between yourself and the instrument nose to 173.2 cm from 100 cm, you can reduce the intensity to the desired level.

EXERCISE 1.2f: Using a Survey Meter to Check for Scatter

X-rays are scattered more strongly by materials with lower average atomic numbers. The three materials in this exercise can be ranked according to their ability to scatter X-rays:

Metal << Glass << Plastic

Based on the relative ability to scatter X-rays, the distance between the measurement point and a location where scattered X-ray signals can no longer be measured should be the longest for plastic and the shortest for metal.

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2. X-ray Fluorescence Spectroscopy

2.1 Fundamental Principles

X-ray fluorescence (XRF) spectroscopy is an analytical technique that can be used to determine the elemental composition of many kinds of materials. It is noninvasive and requires no or only minimal preparation of the material to be analyzed. Because the technique itself is nondestructive, it lends itself ideally to the study of works of art and cultural heritage artifacts. The fundamental principles of XRF presented in this chapter and throughout this book by no means constitute a comprehensive treatise of the topic. Selected concepts are elucidated to enable optimal use of the equipment and completion of the exercises. For a more thorough treatment of XRF theory, refer to the texts listed in the bibliography at the end of this chapter.

What Is X-ray Fluorescence?

When an X-ray strikes a material, it can be either absorbed, scattered, or transmitted. For XRF spectroscopy, the most important of these interactions is absorption. An X-ray is absorbed by an atom when all its energy is transferred to an inner-shell electron. When a high-energy X-ray photon collides with an inner-shell electron in an atom and has enough energy to overcome the binding energy of that electron, the electron can be expelled. This is called the photoelectric effect and leaves the atom in an excited state. In an attempt to stabilize the atom, an electron from a higher shell will move into the vacancy created in the lower shell. In the higher shell this electron has more energy than in the lower (inner) shell into which it moves, and the excess energy is emitted as a fluorescent photon as the transition occurs. Because it was an X-ray photon that was initially absorbed by the atom, this process is called X-ray fluorescence (fig. 2.1).

The electronic orbital structure of each atomic element is unique, and so the energies of the X-ray fluorescent photons produced are also unique and are characteristic of the individual electronic transition and of the atom. The detection and examination of these fluorescent X-rays is the basis of XRF spectroscopy, which allows this process to be used as an analytical technique to determine the elemental composition of materials.

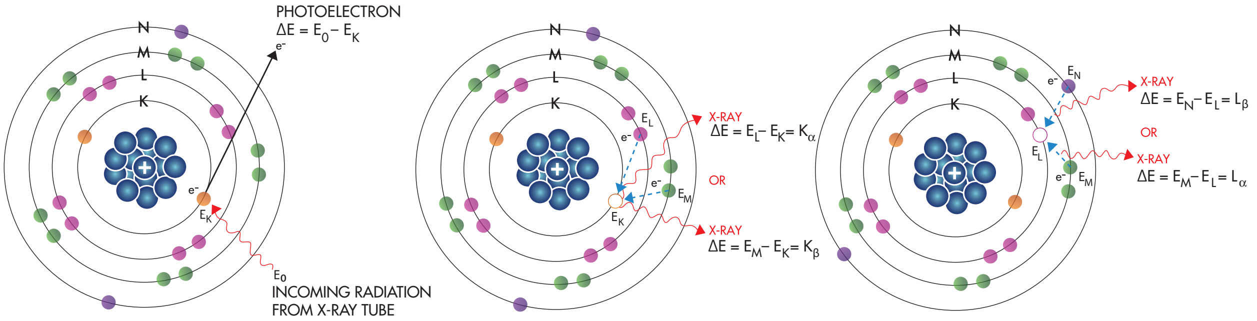


FIGURE 2.1. Diagrams illustrating the X-ray fluorescence process. Left: incoming radiation from the X-ray tube ejects an inner-shell electron, creating a vacancy. Center: L- and M-shell electrons fill a vacancy in the K shell, emitting Kα and Kβ fluorescent X-rays and creating vacancies in the L or M shells, respectively. Right: M- or N-shell electrons fill a vacancy in the L shell, creating L fluorescence emission lines.

FIGURE 2.2. XRF spectrum of a sample containing multiple inorganic pigments, showing the energies of fluorescent emission lines corresponding to different elements.

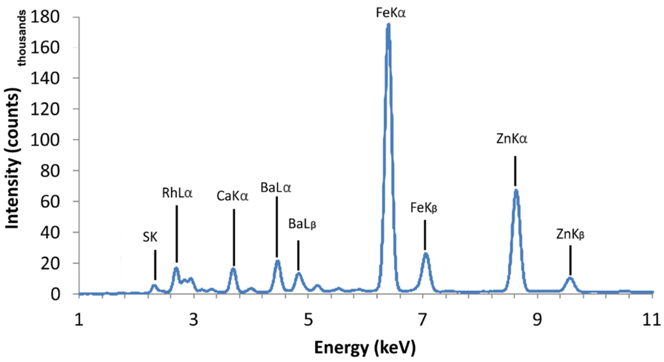


Figure 2.2 shows an XRF spectrum collected from a painting containing multiple inorganic pigments. Each peak in the spectrum corresponds to XRF emission from an element, but note that a single element can produce multiple emission peaks. By measuring the energies of these fluorescent X-rays and knowing which energies are characteristic of which element, it is possible to identify the elements present in a sample, that is, to perform a qualitative analysis. If, in addition, the intensity of the fluorescence emission produced at each energy is also examined, it may be possible to make some qualitative judgments as to relative abundance of different elements. However, this must be done with caution, as intensity does not always directly correlate to abundance. Many factors can affect the production of fluorescent X-rays, including the characteristics of the X-ray source, the detector, and the sample itself (particularly true for inhomogeneous materials such as mixtures and layers); therefore, true quantitative analysis is beyond the scope of this workbook. Interested readers are referred to the entries in the bibliography—Willis, Turner, and Pritchard (2011) in particular—at the end of this chapter to learn more.

The Generation and Naming of Characteristic Lines

To initiate X-ray fluorescence, the atoms must first be excited by high-energy X-ray photons. Once the electron has been excited, leaving a vacancy in an electron shell, there are a multitude of different transition pathways by which that vacancy can be filled. Consider the example shown above (see fig. 2.1), in which a K-shell electron has been expelled, creating a vacancy. An electron from any higher-energy shell could fill the vacancy, but let's first consider that it is filled by an L-shell electron, emitting a fluorescent X-ray photon. This now leaves a vacancy in the L shell, which in turn can be filled by an electron from the M shell (emitting another fluorescent X-ray photon), which in turn leaves a vacancy in the M shell. This cascading process of electrons and fluorescent photon emission continues until the last outer orbital vacancy is filled by a loose photoelectron in the material and the atom is back in its ground state.

Therefore, the XRF spectrum from each element may consist of multiple emission lines, often referred to as characteristic lines. To keep track of and describe the X-ray spectral lines produced by all the different possible transitions, spectroscopists use the Siegbahn notation, named for Kai Siegbahn, the Swedish physicist who first measured characteristic lines from pure elements. In 1991, the Siegbahn notation was officially replaced by the IUPAC (International Union of Pure and Applied Chemistry) nomenclature, but in practice most X-ray spectroscopists still use the Siegbahn notation. Table 2.1 shows the Siegbahn notation for some of the more commonly encountered X-ray emission lines and the transition giving rise to each. In this notation, the primary designation of X-ray lines is the shell being *filled* (e.g., K, L, M) with a Greek letter (e.g., α, β, γ, sometimes with an additional numerical designation) used as a secondary notation to refer to the specific transition. A transition from an L shell to fill a vacancy in the K shell, for example, gives rise to a Kα photon, and a transition from an M shell to fill the K shell vacancy gives origin to a Kβ photon. Together, the Kα and Kβ lines constitute the K series. Transitions that fill vacancies in the L and M shells likewise constitute the L and M series. However, due to the multiple sub-orbitals that may be involved in the transitions, the secondary designation is not as straightforward as it is for the K series.

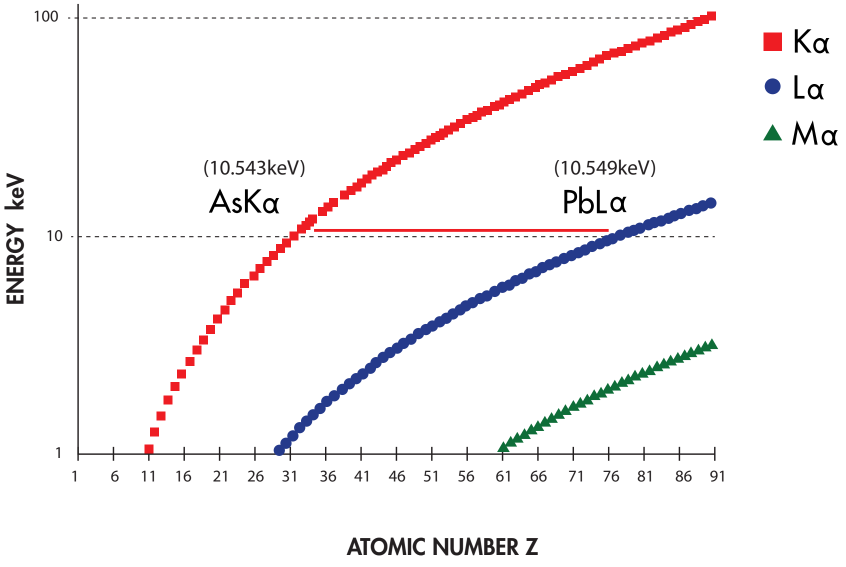
TABLE 2.1. Siegbahn notation of X-ray transitions giving rise to each emission line.

K Series		**L Series**		**M Series**	
Siegbahn	**Transition giving origin to the line**	**Siegbahn**	**Transition giving origin to the line**	**Siegbahn**	**Transition giving origin to the line**
$K\alpha_{1,2}$	$L_{2,3}$-K	$L\alpha_1$	M_5-L_3	$M\alpha_{1,2}$	$N_{6,7}$-M_5
$K\alpha_1$	L_3-K	$L\alpha_2$	M_4-L_3	$M\beta$	N_6-M_4
$K\alpha_2$	L_2-K	$L\beta_1$	M_4-L_2		
$K\beta_1$	M_3-K	$L\beta_2$	N_5-L_3		
$K\beta_{1,3}$	$M_{2,3}$-K	$L\gamma_1$	N_4-L_2		
$K\beta_{2,4}$	$N_{2,3}$-K	$L\eta$	M_1-L_2		
		$L\ell$	M_1-L_3		

Because the series represent *all* the possible transitions to fill a vacancy in a given shell, if one line in a series occurs, then *all* the lines in that series would occur. Not all transitions produce X-rays of the same intensity, though. In theory, their intensity is determined by the probability of the transition occurring, which in turn depends on the energy difference between the involved orbitals. For each element, the K series lines have the strongest intensity, with the L and M series lines having subsequently weaker intensities. Within each series, the lines designated by an alpha are generally the strongest, with the other lines being relatively weaker. However, it should be noted that in practice there are many factors that can influence the intensity of an XRF line, and so their interpretation must be done with great care. For example, it is possible that some spectral lines in a series may be masked by overlap from another line due to lack of detector resolution, or simply may not be detected if the intensity is too low. Nonetheless, examination of the relative intensity of X-ray fluorescence lines can, in some cases, provide information about the relative position of an element within a stratigraphy, as will be demonstrated in the exercises in chapter 3.

The energies at which the K, L, and M series lines appear increase with increasing atomic number Z, as shown in figure 2.3. Note that this plot shows only the most intense line (α) from each series, but it

FIGURE 2.3. Graph showing how the energy of K, L, and M series varies as a function of atomic number Z. Note that the As Kα line and the Pb Lα line overlap at nearly the same energy.



serves to illustrate that, in general, the energy of characteristic lines increases with increasing Z and, importantly, where spectral overlaps may occur. For example, the Kα line for As (Z=33) appears at 10.543 keV, almost exactly the same energy as the Lα line for Pb (Z=82), at 10.549 keV.

Mass Attenuation Coefficients, Absorption Edges, and Enhancement

There are multiple ways X-rays can be absorbed during the XRF process. As X-rays from the X-ray tube pass through the sample, part of the radiation is absorbed by atoms, ejecting electrons and initiating the photoelectric effect, as discussed above. As the excited atoms relax to fill the vacancies, characteristic fluorescent X-rays are produced. If they have enough energy, these fluorescent X-rays can, in turn, be absorbed by neighboring atoms. To reach the detector, fluorescent X-rays must pass back through the sample, and along the way some of them may be absorbed. The amount of absorption depends on the properties of the material through which the X-rays are passing.

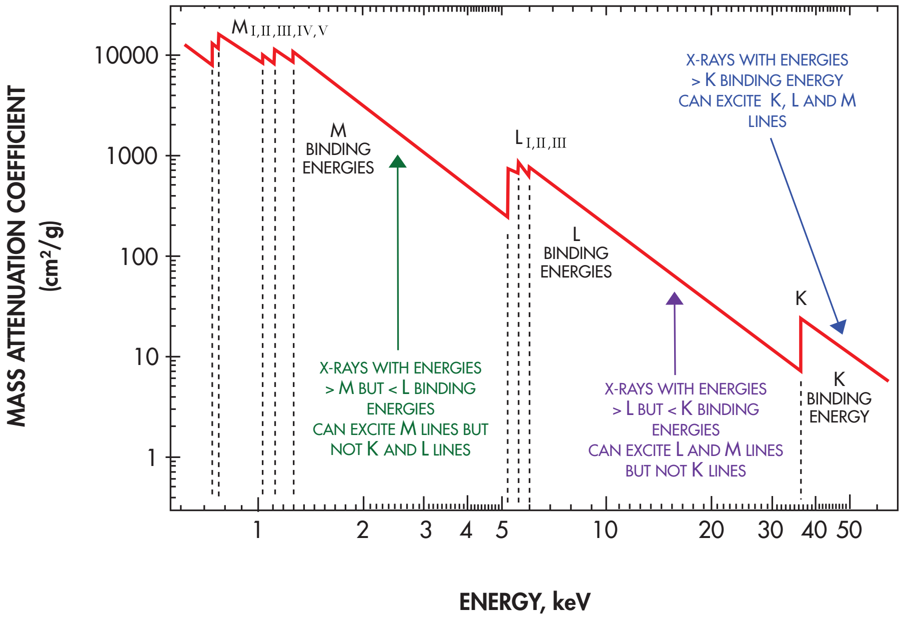
This absorption is described mathematically by the following relationship:

$$I = I_o e^{-\mu \cdot \rho \cdot t}$$

where I is the measured (transmitted) intensity, I_o is the incident intensity, μ is the mass attenuation coefficient (cm^2/g), ρ is the density of the absorbing material (g/cm^3), and t is the thickness (cm).

The mass attenuation coefficient (MAC), also referred to as the mass absorption coefficient, describes the absorption of X-rays by atoms. The MAC depends on the density of the atom—proportional to the atom's atomic number (Z)—and the energy of the X-rays being absorbed. In general, for each element the MAC decreases with increasing X-ray energy. However, as can be seen in figure 2.4, in which the MAC of barium (Ba, Z=56) is plotted as a function of energy, there are also sharp discontinuities. These are the absorption edges, which appear at the energies at which the incoming X-ray photon has enough energy to remove an electron from its shell, namely, the binding energy of the electron. Note that the absorption edge with the highest energy (37.4 keV for Ba) is for K-shell electrons, as these electrons are the most tightly held by the nucleus of the atom. Less energy is required to remove electrons from the L and M shells. For Ba, the absorption edges for the L and M shells are around 6.0 and 1.2 keV, respectively.

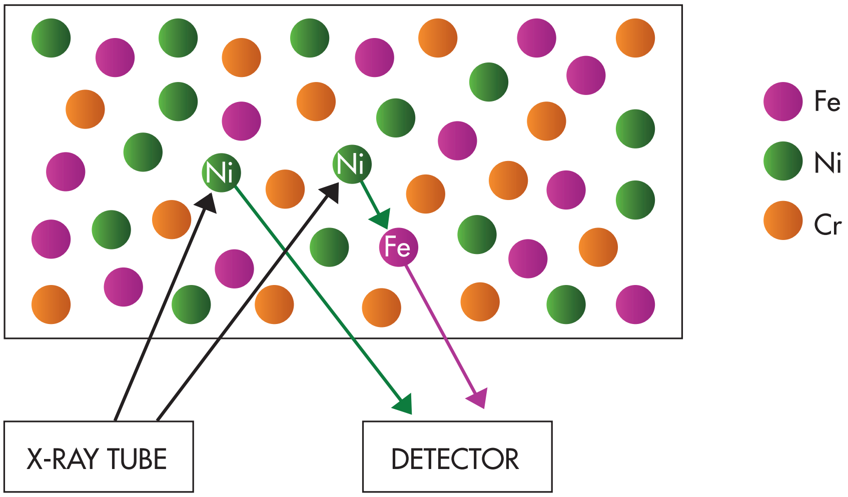
FIGURE 2.4. Plot of MAC of barium as a function of energy, showing the absorption edges, and illustrating the energy ranges that can excite K, L, or M lines.



In XRF spectroscopy, characteristic fluorescent X-rays from an element can be produced only if the *incoming* X-ray has more energy than the absorption edge for each shell of the analyte element. Excitation is most efficient when the energy of the incoming X-ray photon is just above (i.e., has slightly higher energy) the absorption edge of the electron to be expelled. In theory, one could use the absorption edges to determine the ideal energy of incoming X-rays to excite each shell of each element in a sample. In practice, incoming X-rays from the tube contain a sufficiently wide range of energies to excite the majority of possible elements in a sample.

More frequently, absorption edges are used to understand and predict inter-element matrix effects. As mentioned at the beginning of this section, X-rays generated from elements within the sample (primary fluorescence) may excite other atoms in the sample (secondary fluorescence) *if* the energy of the primary fluorescence is above the absorption edge of the second element. Figure 2.5 illustrates this effect in a stainless steel sample containing Cr, Fe, and Ni, which have K-shell absorption edges at 6.0, 7.1, and 8.3 keV, respectively. All three elements are excited by the X-rays originating from the tube and produce characteristic Cr Kα, Fe Kα, and Ni Kα lines at 5.4, 6.4, and 7.5 keV, respectively. While traveling out of the sample and to the detector, a Ni Kα photon could collide with an Fe atom and, because its energy is greater than the absorption edge energy of the Fe K-shell electrons, the Ni Kα photon can be absorbed by the Fe atom to produce an Fe Kα photon. Since the Ni Kα photon did not reach the detector, the intensity of the Ni Kα peak in the resulting XRF spectrum will not accurately reflect the quantity of Ni in the sample, but rather will be smaller than otherwise expected (i.e., it is suppressed). Likewise, the Fe Kα secondary fluorescence produced by the absorption of the Ni Kα photon will make the Fe Kα peak in the XRF spectrum appear larger than expected (i.e., it is enhanced). These matrix effects follow quantum mechanical laws and can be predicted and corrected for in the resulting spectra but, in most cases, are of concern only if quantifying the amount of each element present is of interest.

FIGURE 2.5. Schematic showing absorption/enhancement effects in a stainless steel sample containing Cr, Fe, and Ni: the Ni emission is suppressed by the excitation of Fe, which is enhanced (see text).



Scatter

Besides absorption, the other important interaction between X-rays and matter is scattering. In this process, X-ray photons interact with outer-shell electrons of an atom in one of two ways. If the X-ray photon is scattered off the atom, emerging in a new direction but without losing any of its energy to the atom, it is called Rayleigh (also referred to as coherent, or elastic) scattering. Alternatively, the X-ray photon can transfer some of its energy to an outer-shell electron of an atom, causing the electron to be ejected. However, since no transitions from higher orbitals can occur, no resulting fluorescence photon is created. Instead, the original photon, now with less energy, is scattered away from the atom. This process is called Compton (also referred to as incoherent, or inelastic) scattering (fig. 2.6). Scattering occurs more strongly in low Z elements, since these elements have fewer protons in the nucleus to hold on to the outer electrons which are more loosely bound. The intensity of the Compton scatter is proportional to the density and average atomic number of the matrix (reflected in the MAC) and can in some cases be used to correct for differences between the matrix of a reference material and an unknown sample.

Scattering can occur for X-rays generated from either the tube or fluorescent X-rays generated from the sample. However, in practice, scattering from the X-ray tube is of greater interest, since it often appears in the collected XRF spectrum. The types of X-rays generated by an X-ray tube are discussed in more detail in the section titled "Generating X-rays: X-ray Tubes." In brief, it consists of a broad continuum of radiation with sharp, superimposed characteristic lines from the anode. Although scattering can occur from the continuum, it is most noticeable in the characteristic lines from the anode. Figure 2.7 illustrates Rayleigh and Compton scattering of Rh K lines from a Rh anode X-ray tube. Because the amount of energy lost during the scattering process is not fixed, Compton peaks appear as broad peaks to the low-energy side of their corresponding Rayleigh line. Also note that the scattering is much larger for the low Z sample (polytetrafluoroethylene or "Teflon" in fig. 2.7) than for the higher Z sample (iron in fig. 2.7).

FIGURE 2.6. Diagram illustrating Compton scattering, or incoherent scattering, in which the X-ray photon is scattered upon losing some of its energy ejecting an outer-shell electron (Compton recoil electron) $\lambda_s > \lambda_i$.

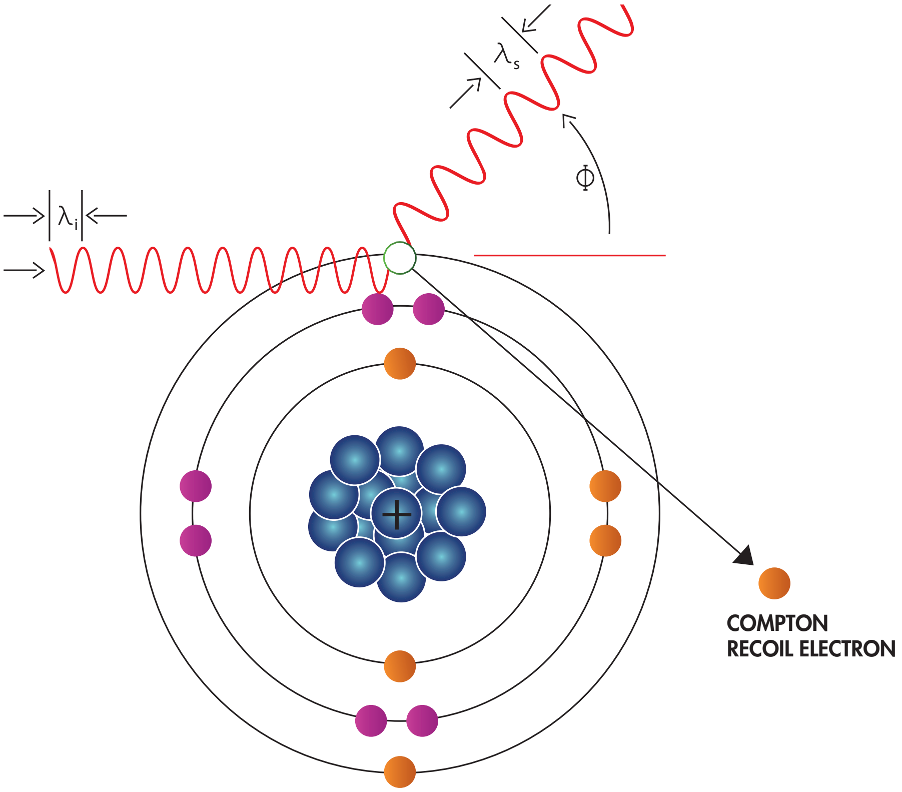
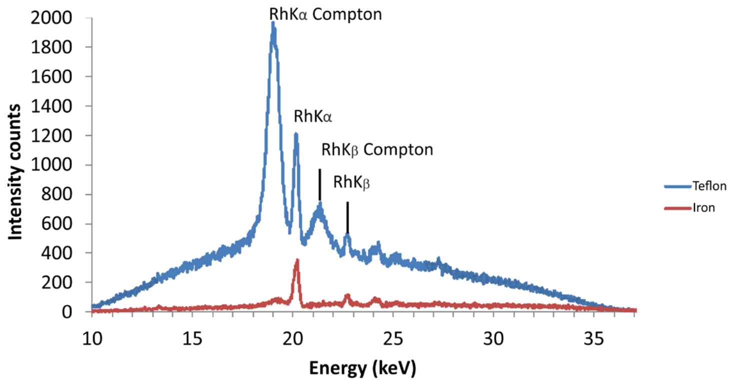


FIGURE 2.7. XRF spectrum showing Rayleigh and Compton scattering peaks for a Rh anode X-ray tube.

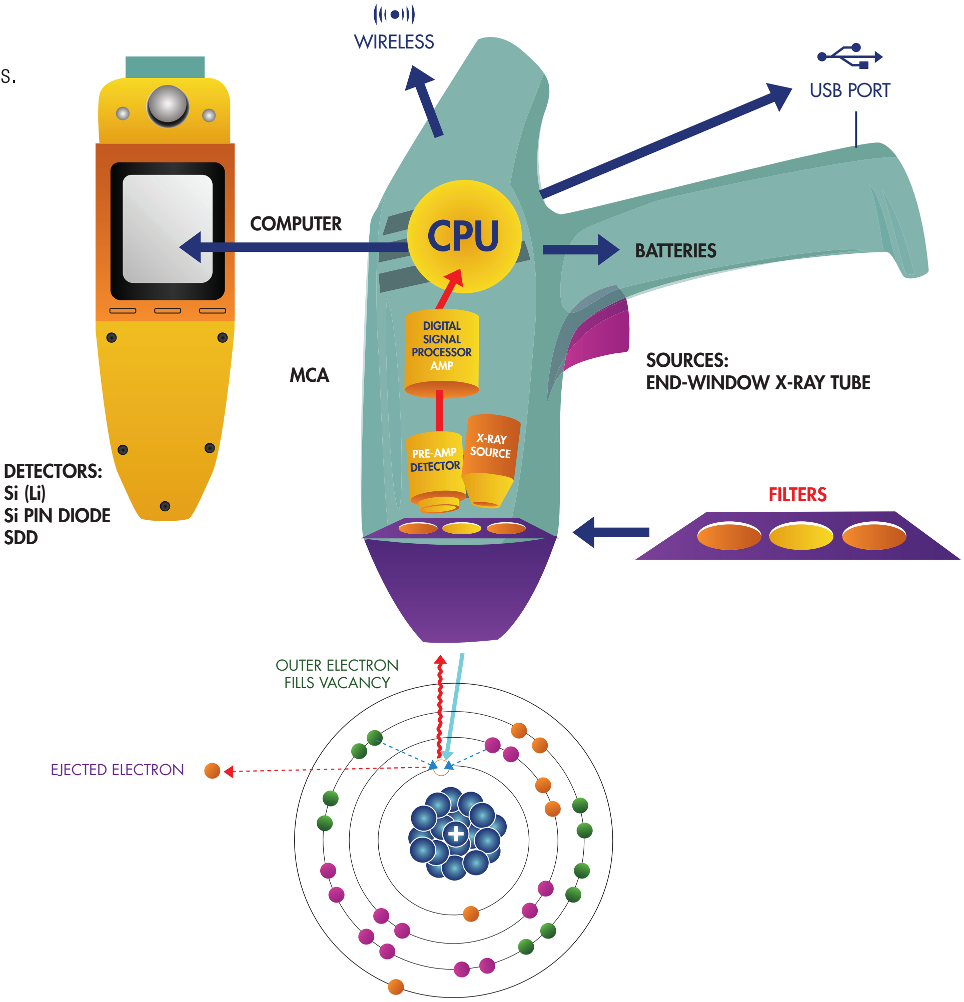


In XRF spectroscopy, scattering is usually undesirable, but it can be exploited to get an idea of the output of the X-ray tube. Taking advantage of the fact that scattering is strongest in low Z materials, the spectrum acquired from a "blank" sample (i.e., something with no analyte peaks as would be provided by a material containing only low Z elements such as C, O, and N; e.g., polyethylene foam) consists only of X-rays from the tube that have been scattered from the sample. As discussed below and explored in exercise 2.3a, this approach can help us to understand how the tube output is affected by the choice of target material, voltage, and current.

2.2 The XRF Spectrometer

All XRF spectrometers, whether handheld or laboratory based, have the same main components: an X-ray source, filters or other beam modifiers, a detector, signal processors, and a means of recording the data (a computer). A schematic illustration of a spectrometer appears in figure 2.8. Briefly, a low-amperage, high-voltage supply enables X-rays to be generated in the tube. These X-rays leave the tube through a beryllium window and pass through primary beam filters (if any) before irradiating the sample. Fluorescent X-ray photons generated in the sample—as described in the next section—are then detected, preamplified, and processed in the digital signal processor or multichannel analyzer (MCA). From here, data are collected and stored in the central processing unit (CPU) of a computer as an XRF spectrum. Each of these components is discussed in the following sections, with the processes occurring in each component described.

FIGURE 2.8. Diagram of a handheld XRF spectrometer illustrating its main components.



Generating X-rays: X-ray Tubes

X-rays are produced when a beam of electrons of sufficient energy interacts with matter. In an X-ray tube, the µA setting on the instrument controls the current that runs through a filament wire; through a process called incandescence, electrons form a cloud around the filament wire. Applying a potential difference—controlled through the kV setting on the instrument—between the filament wire (the cathode) and the target material (the anode) causes the electrons to be attracted toward the anode. When the electrons hit the target, X-rays are created through two atomic processes: bremsstrahlung (fig. 2.9) and fluorescence (fig. 2.10).

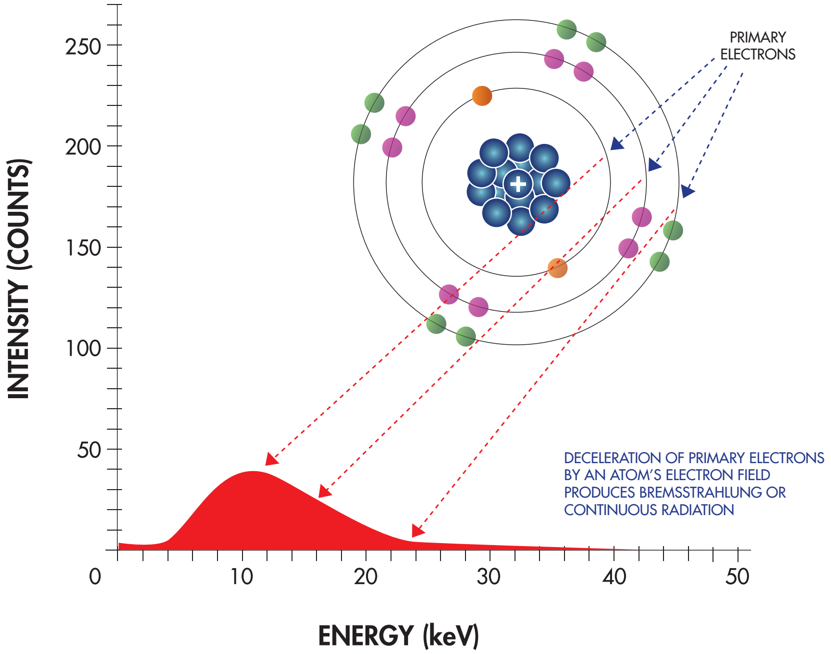


FIGURE 2.9. Diagram illustrating the process by which continuum, or bremsstrahlung, radiation is generated in an X-ray tube. Note the typical "humped" shape of the continuum, which covers an energy range up to the equivalent energy of the excitation potential applied to the tube (here, 40 keV).

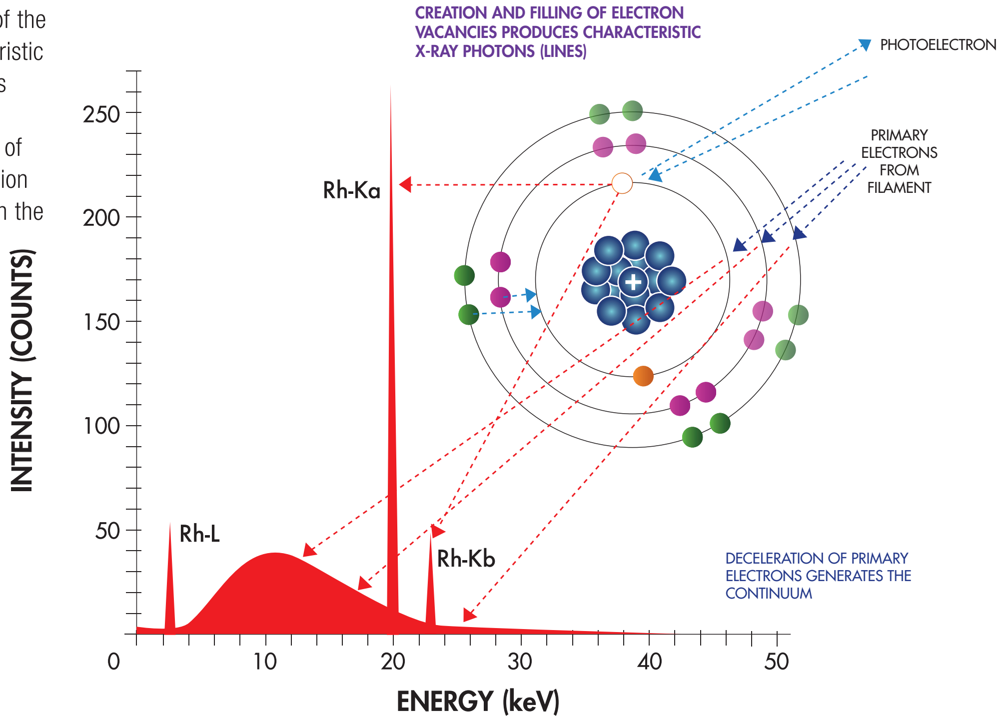


FIGURE 2.10. Diagram of the process by which characteristic fluorescence emission lines are generated by the X-ray tube. Note the appearance of sharp, characteristic emission tube lines superimposed on the continuum.

Bremsstrahlung **(German for “braking radiation”) is the radiation produced when electrons are decelerated by the electric field near the nuclei in the target. Because this process does not involve atomic transitions, it is a continuum: X-rays of smoothly varying intensity are produced across a range of energies, from zero up to a maximum equivalent to the excitation potential (see fig. 2.9).**

Fluorescence **is produced when an electron has enough energy to overcome the binding energy in the atoms of the target material and can knock an electron out of the inner shell to create a vacancy that is subsequently filled by higher orbital electrons. The only difference between this and the photoelectric effect/electron cascading process described in the section “The Generation and Naming of Characteristic Lines” is that, in this case, it was initiated by an electron rather than a high-energy X-ray. The net result is the same: the production of characteristic radiation at discrete energies corresponding to the transition of electrons between shells to fill the vacancies created in the target (anode) atoms. These characteristic X-rays appear as sharp lines superimposed on the continuum background (see fig. 2.10).**

As mentioned above, excitation of the sample for X-ray fluorescence can be induced by the anode characteristic lines as well as the continuum. X-ray tubes can be made with almost any solid material as the anode, but in practice the most commonly encountered are rhodium (Rh), silver (Ag), and tungsten (W). The anode characteristic lines appear at different energies for each anode and, in some cases, can interfere with the detection of elements in the sample occurring at the same or nearby energies. Since changing the anode usually is not possible, strategies are needed for shaping the output of the X-ray beam to reduce such potential interferences, which is discussed in the next section.

Controlling the Tube Output: Voltage

An electron volt (eV) is a unit of energy equal to the amount of energy gained (or lost) by a single electron moving across a potential difference of one volt. In an X-ray tube, the amount of energy produced (in keV) by the electrons moving from the cathode (filament wire) to the anode (target material) is equivalent to the potential between them (in kV); for example, a potential of 50 kV produces X-rays with energies up to 50 keV.

The voltage of the tube directly determines the maximum energy of the continuum, but to excite the characteristic lines of the anode, the electrons must have sufficient energy to remove a core electron from the anode material; that is, their energy must be greater than the absorption edge for the anode element. The tube voltage necessary to supply this energy (in keV) is called the excitation potential (in kV).

Excitation potentials are designated by the symbol V_x, where x corresponds to the electron orbital being excited (e.g., $x = K$, L_I, L_{II}, L_{III}, or M_I, M_{II}, M_{III}, M_{IV}, M_V). Excitation potentials for common anode materials are given in table 2.2. Note that for any given element, the largest excitation potential is always that required to remove electrons from the innermost, or K, shell. Subsequently less energy is required to remove electrons from the L and M shells, respectively.

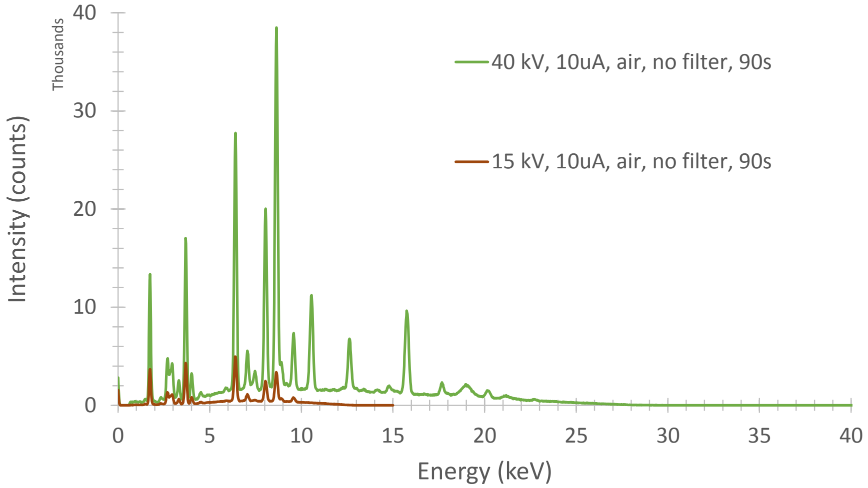
TABLE 2.2. Excitation potentials (kV) for common anode materials.

Element (Z)	K (kV)	L_{III} (kV)	M_V (kV)
Cu (29)	9.0	0.9	
Rh (45)	23.2	3.0	0.3
Ag (47)	25.5	3.4	0.4
W (74)	69.5	10.2	1.8

For example, in an X-ray tube with a tungsten (W) anode, an excitation potential of 69.5 kV is required to excite electrons in the K shell. Because most handheld XRF spectrometers have a maximum voltage of 40–50 kV, these instruments cannot excite the K-shell electrons of W, but they can excite the L- and M-shell electrons with excitation potentials of 10.2 kV and 1.8 kV, respectively. By contrast, instruments with a rhodium (Rh) anode can excite the Rh K-shell electrons, and thus these lines will appear quite prominently in the tube output spectrum.

Figure 2.11 illustrates the effect of changing the tube voltage on the X-rays produced. Here, the anode is rhodium (Rh), which has a K-shell excitation potential of $V_K = 23.2$ kV. When the instrument is operated at a voltage of 15 kV, only the continuum is produced. At 40 kV, the Rh characteristic K lines are excited. The intensity of these lines increases with higher applied voltage (e.g., 50 kV compared to 40 kV) because the intensity is dependent on the total number of electrons produced with energies just above the absorption edge (excitation potential) for the K shell of Rh, and higher voltages produce more electrons at all energies up to the maximum, E_{max}.

FIGURE 2.11. XRF spectra collected at voltage settings of 40 kV and 15 kV, at a current setting of 10 μA. Note that the higher tube voltage facilitates the excitation of fluorescent X-rays at higher energies.



Controlling the Tube Output: Current

The quantity of electrons flowing through the filament wire—the current—also affects the intensity of X-rays and the continuum. Figure 2.12 shows the output of a tube, at a fixed applied voltage, for different currents. Note that the distribution of energies generated does not change, only the intensity.

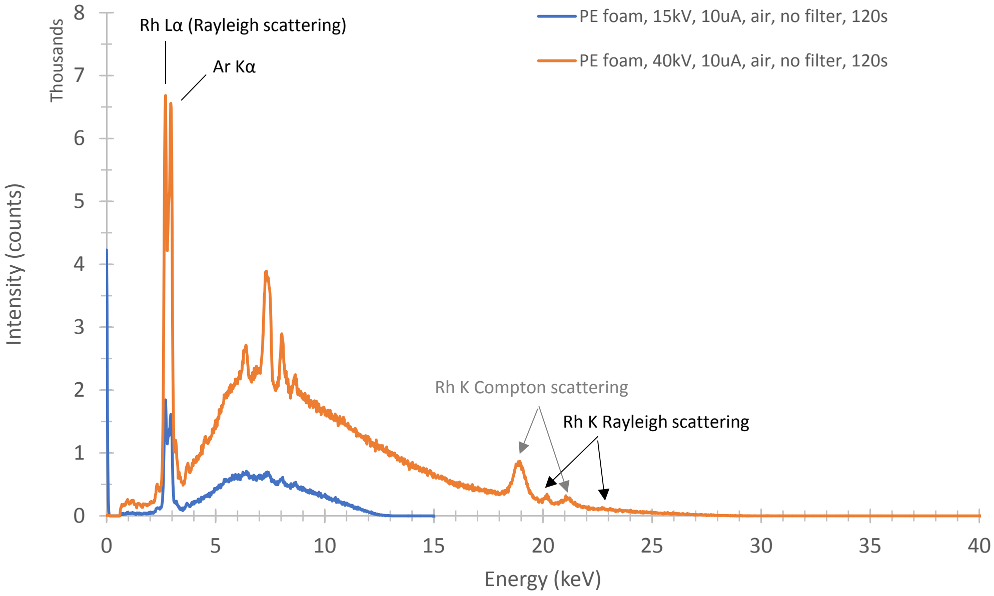


FIGURE 2.12a. Excitation spectra using polyethylene foam cube, obtained at different voltage settings without beam filters in exercise 2.3a. Data collected using a Bruker Tracer III-SD, Rh tube.

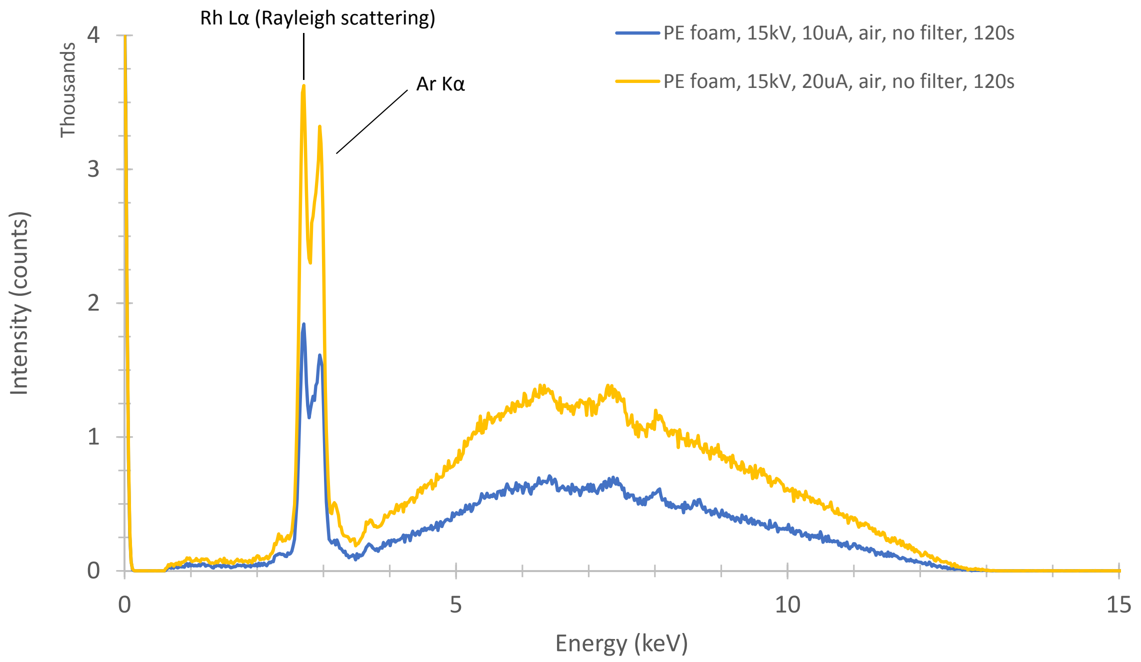


FIGURE 2.12b. XRF spectra collected at current settings of 20 μA and 10 μA, with the tube voltage fixed at 15 kV. Note that the intensity of the fluorescence emission increases with increasing current, but the energy range over which the excitation occurs remains the same.

Voltage-Current Effects

The output of the X-ray tube is a combination of the continuum and characteristic lines and, as such, is controlled by both the voltage and the current. The applied voltage determines the range of energies produced and whether characteristic lines of the anode are excited. The total integrated intensity of the continuum is proportional to the square of the tube-operating voltage (V) and directly proportional to the applied current (A):

$$I_{continuum} \propto \mathrm{V}^2$$

$$I_{continuum} \propto \mathrm{A}$$

Understanding the shape of the tube output is important for determining which elements in the sample may be excited. For most applications, the continuum provides excitation of a broad range of elements: for each element, only the portion of the continuum *above* the absorption edge can contribute to the excitation of that element. The characteristic anode lines can provide additional excitation of those elements with absorption edges just below the energy of the characteristic lines. In exercise 2.3a, you will investigate the effect of voltage and current on the tube output for your particular instrument.

In general, the ideal excitation conditions for the detection of light(er) elements are low kV and high μA. By contrast, for optimum detection of heavier elements with higher excitation potentials, high kV and high μA are used. Note, however, that the total power (kV × μA) needs to stay below the max rating of the instrument. For example, 40 kV × 11 μA = (40 × 10^3 V) × (11 × 10^{-6} A) = 44 × 10^{-2} W = 0.44 W. The maximum rating of the tube, which may vary depending on the instrument, is typically around 4 W, with maximum operating voltages between 6 and 50 kV.

Reducing Unwanted Signals: Filters

The output from the X-ray tube can be further modified through the use of filters. In most portable XRF spectrometers, these are typically transmission filters, which filter the X-rays coming from the tube as well as the X-rays generated at the sample on their way to the detector. Filters work on the principle of absorption. They are usually thin (a few to several hundred microns thick) sheets of metal, which will attenuate but not completely block the X-rays passing through them. As discussed in the section “Mass Attenuation Coefficients, Absorption Edges, and Enhancement,” absorption by an element increases sharply at the absorption edges and gradually decreases with increasing energy. Therefore, the material of the filter is selected such that its absorption edge is just *below* the lowest energy to be suppressed. The use of filters is explored in exercise 2.3b. Filters can be specifically tailored to reduce interference in a particular range of energies (fig. 2.13 and table 2.3). However, in most cases where a wide range of elements are of interest, the filters typically supplied by the manufacturer are sufficient. When selecting a filter, keep in mind that any filter will reduce the total number of X-rays reaching the sample and hence reduce the signal generated. In practice, it is a good idea to collect a spectrum without any filters to determine whether filters are necessary, and if so, which ones would provide the best result.

TABLE 2.3. Filters commonly used in portable XRF units.

Filter	Energy Range Most Impacted by Filter
None	Does not apply
1 mil Ti	5–8 keV
1 mil Ti / 12 mil Al	0–11 keV
1 mil Cu / 1 mil Ti / 12 mil Al	0–15 keV
6 mil Cu / 1 mil Ti / 12 mil Al	0–22 keV

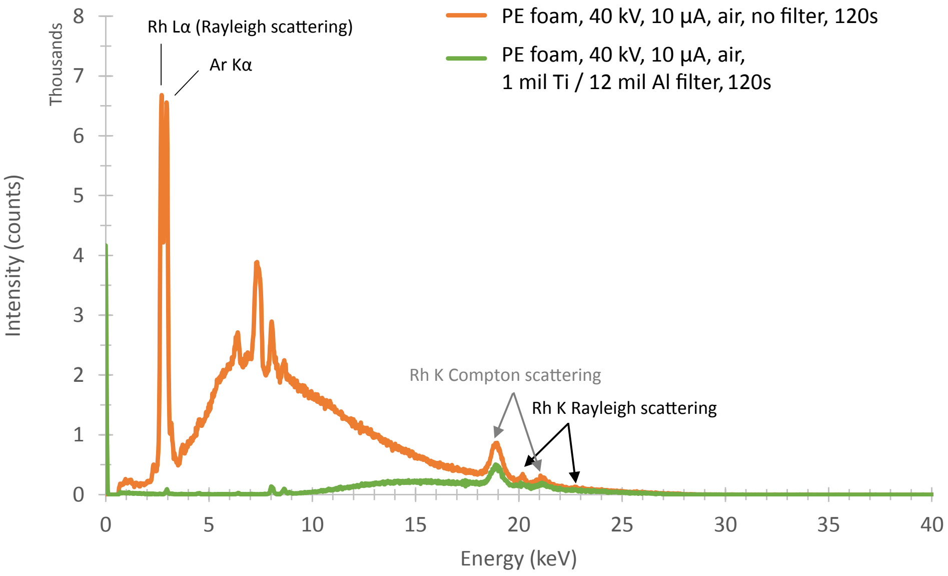


FIGURE 2.13. Spectra collected from a polyethylene foam sample with and without a filter. Note that the filter dramatically reduces the scatter and tube emission at lower energies.

Use of filters to suppress a portion of the excitation spectrum

As discussed in the section “Controlling the Tube Output: Voltage,” the excitation of atoms in a sample is most efficient if the incoming X-rays have energies just above the absorption edge of that element. While the number of X-rays with the appropriate energy can be increased by increasing the voltage or current of the tube, this also increases the number of X-rays being produced at other energies, which sometimes may result in saturation of the detector. Filters may be used to reduce those parts of the tube spectrum that are not necessary for excitation of the elements of interest. For example, when trying to detect low quantities of pesticides (or pigments) that may contain As, Hg, Pb, or Br, suppression of the background in the 9–13 keV energy range can be achieved using a composite filter such as 12 mil Al / 1 mil Ti / 1 mil Cu. Note that filter thickness is in units of mil, in which 1 mil = 0.0254 mm.

Use of filters to reduce unwanted background scattering

Scattering from the X-ray tube—both the continuum and characteristic lines—can obscure fluorescence coming from the sample. This is especially true if the signal coming from the sample is weak. Filters can be used to selectively reduce background scatter in the region of interest, helping enhance the detection of weak fluorescence signals. For example, the detection of silver using a Rh anode X-ray tube can be difficult since the Rh Kβ Compton scatter appears at the same energy as the Ag Kα characteristic line. To reduce the Rh characteristic lines, which appear at 20.2 and 22.7 keV, a filter material with an absorption edge of < 20 keV (e.g., Mo, Nb, or Zr) could be used.

Several manufacturers offer handheld XRF spectrometers with voltage, current, and filter settings that cannot be independently changed, but rather have different programs (modes) for certain applications (see appendices 1.2 and 1.3) and/or software with the ability to eliminate spectral artifacts (e.g., escape and sum peaks; see "Spectral Artifacts: Escape Peaks and Sum Peaks"). By understanding how instrument parameters affect the excitation beam, users of mode-based instruments can better leverage the capabilities of the different programs available to them. Instead of focusing on the name of the program (such as "soil" or "alloy" mode), users can tailor their choices to the analytical task based on which elements they would like to excite and detect.

Measuring X-rays: Detectors

Fundamentally, a detector is a silicon-based device that converts X-ray photons into electronic pulses. Composed of a nonconducting or semiconducting material sandwiched between two charged electrodes, an incoming X-ray photon ionizes the detector material, creating electron-hole pairs and causing the material to become momentarily conductive. The number of electron-hole pairs produced is proportional to the energy of the X-ray photon. The newly freed electrons are accelerated toward the detector anode by a potential difference applied across the electrodes. When they hit the anode, they generate a voltage pulse, which is also proportional to the energy of the photon. This voltage pulse is then passed through a digital pulse processor (DPP), or multichannel analyzer (MCA), which determines the X-ray energy.

All handheld XRF spectrometers utilize this sort of detection scheme, typically referred to as energy-dispersive, to reflect the fact that all X-ray photons are collected simultaneously and separated according to their energy by the processors. As this process is repeated for all X-ray photons coming from the samples, the MCA counts how many times X-ray photons of each energy hit the detector. As illustrated in figure 2.14, different photon energies are recorded in different "bins" by the MCA, building up a spectrum. The width of each bin is related to the resolution of the detector: the narrower the bin, the higher—that is, better—the spectral resolution.

Another important parameter for detectors is the maximum count rate, or the maximum number of photons per second (counts per second, or cps), that can be recorded. If the rate of X-ray photons hitting the detector exceeds the maximum count rate, the detector is "saturated" and no longer able to collect reliable spectra. To avoid saturating the detector, it may be necessary to reduce the X-ray flux by lowering the current. By contrast, if signals are very weak and the instrument is already running at maximum output, it may be necessary to collect for longer times to build up enough counts in each channel to produce a spectrum with an adequate signal-to-noise ratio. Similarly, when attempting to confirm low intensities of a signal,

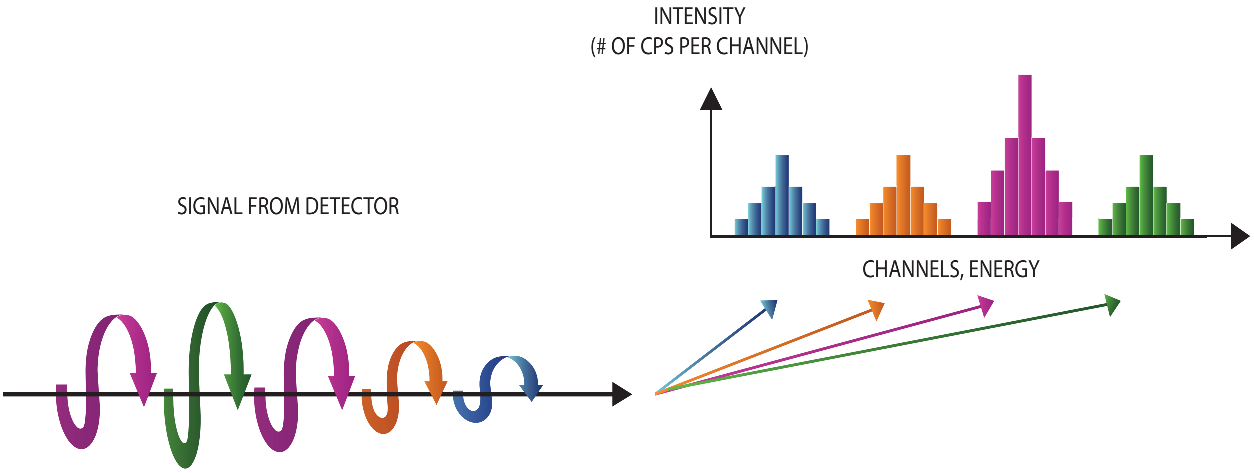


FIGURE 2.14. Diagram of the process by which an MCA records photon energies in different bins to build up a spectrum.

it may be useful to collect multiple spectra from different regions and apply statistics to the composite dataset.

One of the primary reasons that portable XRF has become possible and so powerful is the development of improved detector technologies. Most significantly, the change from lithium-drifted silicon detectors that necessitated liquid nitrogen for cooling, to silicon PIN diode (SiPIN) and silicon drift detectors (SDDs) that are Peltier (electronically) cooled, enabled their use in portable equipment. SDDs can even run at room temperature. A comparison of the spectral resolution and effective count rate ranges for SiPIN detectors and SDDs is presented in table 2.4. By convention, the spectral resolution of a detector is specified as full width at half maximum (FWHM) of the Mn Kα line.

Sometimes the spectral resolution of a detector is not adequate for effective separation of two peaks. In these cases, the software can assist in resolving such spectral-line overlaps by a process of mathematical deconvolution, where the relative intensities of Kα/Kβ or Lα/Lβ peaks, together with the theoretical peak shape, are used. To help manage expectations of what a particular detector is capable of differentiating, it is useful to test the instrument on samples containing elemental pairs that are difficult to separate. For example, pure titanium and pure barium, measured separately and followed by looking at different ratio mixtures (in which multiple peaks overlap), are a common pair (see exercise 3.2f).

TABLE 2.4. Comparison of spectral resolution and effective count rate ranges for SiPIN detectors and SDDs.

Detector	Effective Count Rate Range (cps)	Resolution
SiPIN	3,000–20,000	149–240 eV at Mn Kα
SDD	10,000–300,000	140–180 eV at Mn Kα

Spectral Artifacts: Escape Peaks and Sum Peaks

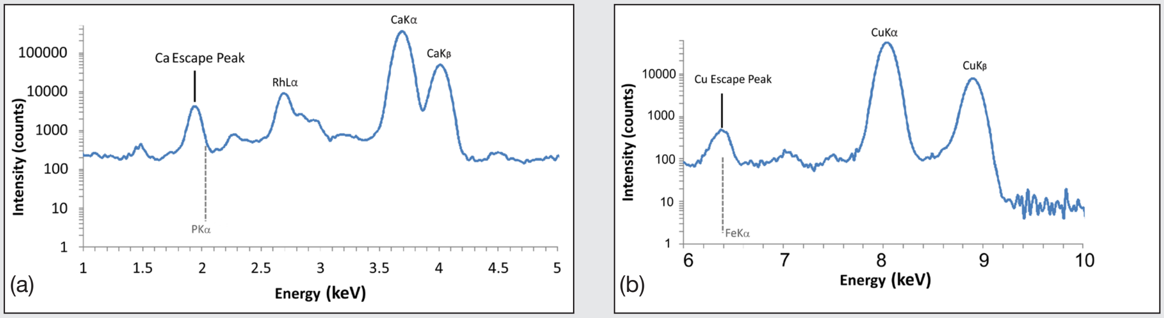
Because of the way energy-dispersive detectors are constructed and operated, spectral artifacts—additional peaks generated that do not correspond to the elemental makeup of the sample—may be generated. The most important spectral artifacts for cultural heritage materials are escape peaks and sum peaks.

Escape peaks

When fluorescent X-rays from a sample hit the Si atoms in the detector, a Si Kα fluorescence photon is generated if the X-rays have an energy greater than the excitation potential of Si (1.84 keV). Usually, the Si Kα photon is reabsorbed by the detector. Occasionally, it “escapes.” When this happens, the energy of the incoming X-ray photon as recorded by the detector is reduced by the amount of energy lost to the escaped

Si Kα photon (1.74 keV). Hence, it is referred to as an escape peak. Escape peaks are generally observable only for very large spectral lines, that is, those with very high count rates. Many XRF spectra software programs automatically correct for escape peaks, but it is always good practice to check for their presence, as they may be misinterpreted as fluorescence from an element in the sample (see sidebar).

A Ca Kα (3.69 keV) line would have an escape peak at 3.69–1.74 = 1.95 keV. This could easily be mistaken for the P Kα line, which appears at 2.01 keV. Knowing whether P is associated with Ca would be important, for example, in determining the presence of bone black (fig. 2.15a). Similarly, Cu Kα (8.05 keV) would have an escape peak at 8.05–1.74 = 6.31 keV, which could be mistaken for the Fe Kα peak (6.40 keV) (fig. 2.15b).



FIGURES 2.15a, 2.15b. Examples of escape peaks in energy-dispersive XRF spectra: (a) Ca escape peak, which can be misidentified as a P Kα peak; (b) Cu escape peak, which appears at an energy very close to the Fe Kα peak. Note that the intensity of both spectra are displayed on a log scale.

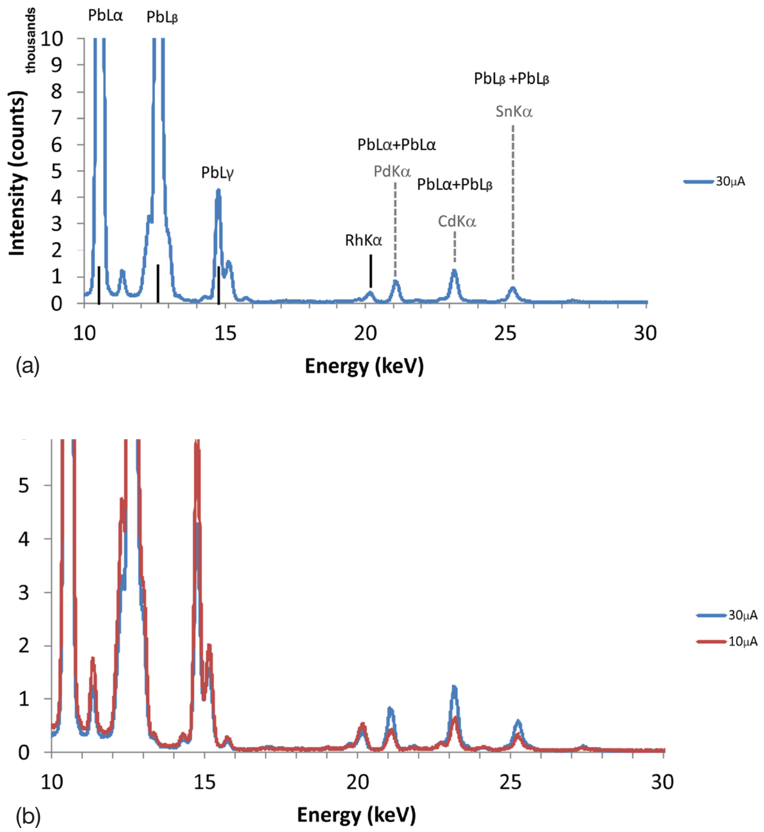
Sum peaks

The second of the detector artifact peaks are sum peaks, also referred to as pile-up peaks. Sum peaks can occur at very high count rates when multiple photons reach the detector closer together in time than can be separated by the processing electronics. For example, if two photons with the same energy hit the detector simultaneously, the detector cannot distinguish between the two and thus puts out a voltage pulse proportional to the sum of the energy from both photons. This appears as a peak in the XRF spectrum at twice the energy of the XRF emission line. Sum peaks can be created from the combination of *any* multiple photons. Statistically, they are most likely to occur from the most intense peaks (i.e., those with the highest count rates), and so the most commonly encountered are combinations of α and β lines within a K or L series (table 2.5). Sum peaks are commonly seen in instruments with SiPIN detectors but less often with SDD detectors due to their higher count rate capacity.

Identification of sum peaks can be relatively straightforward, especially if they appear in the XRF spectrum at energies that do not correspond to the known characteristic emission lines from elements. In some cases, however, sum peaks may be mistaken for element emission lines. The most commonly encountered are those associated with sum peaks from the L-series lines from Pb. The sum peaks from combinations of Lα and Lβ lines of Pb appear at the same energies as Kα lines from Pd, Cd, and Sn (figs. 2.16a, 2.16b; see table 2.5). If peaks at these energies are observed in an XRF spectrum, one should

TABLE 2.5. Commonly encountered peak overlaps with Pb L sum peaks.

Element	Sum Peaks	Energy (keV)	Coincidence Peak (keV)	
Pb L lines	Pb Lα + Pb Lα	21.10	Pd Kα	21.19
	Pb Lα + Pb Lβ	23.16	Cd Kα	23.16
	Pb Lβ + Pb Lβ	25.27	Sn Kα	26.25



FIGURES 2.16a, 2.16b. XRF spectra showing Pb sum peaks, which have potential overlaps with Pd Kα, Cd Kα, and Sn Kα peaks: (a) spectrum acquired at a current setting of 30 μA, displaying prominent Pb sum peaks; (b) comparison of spectra acquired at current settings of 30 μA and 10 μA, showing a decrease in Pb sum peaks with decreasing current.

consider the possibility of sum peaks if the Pb signal is strong. When considering whether something is a sum peak, remember that element emission lines will always have all the peaks in a series: if Kα is present, then Kβ must be as well. Sum peaks will not meet these criteria. Another way to identify a sum peak is to decrease the current; sum peaks should either disappear or reduce in relative intensity. To counterbalance the decrease in current to circumvent sum peaks, collection time can be increased to collect enough photons for measurement. A filter can also be used to reduce the Pb signal in this instance.

In addition to the tube characteristic peaks and bremsstrahlung, other peaks or spectral artifacts (i.e., those not generated by the K, L, or M fluorescence emission lines from the elements in the sample) may appear in the XRF spectrum:

Interactions in the detector:
- Sum peaks: detection of two or more pulses as one
- Escape peaks: partial loss of energy due to fluorescence in Si detector
- Spectral line overlap due to limited detector resolution

Interactions in the analysis system:
- X-ray tube target characteristic lines
- Detector housing lines: for example, Fe, Ni, Cu trace peaks
- Window lines: possible Ca trace peaks
- Collimator and instrument housing: possible Al trace peaks
- Environment interference peaks: Ar from air (vacuum or He flush can be used to prevent this)

(continued)

Phenomena in the sample:

- **Rayleigh scatter (scattered X-ray tube radiation with no loss of energy)**
- **Compton scatter (scattered X-ray tube radiation with partial loss of energy)**
- **Matrix effects: a fluorescence photon excited in the sample can be absorbed by the atom of another element, preventing the photon from reaching the detector.**
- **Diffraction peaks are encountered on rare occasions when the sample has a high degree of crystallinity.**

2.3 Exercises: Understanding the Effects of Instrument Parameters on Excitation and Spectral Interpretation

A question frequently asked by users new to XRF instruments is: "What settings should I use?" Indeed, while most instruments are touted as "just point and shoot," users quickly realize that decisions need to be made about instrument settings before collecting a spectrum.

The exercises that follow explore parameters that you, as the user, can select or adjust and their impact on the excitation spectrum: the energy range of X-rays interacting with the object/sample, as well as the relative and absolute intensities of X-ray photons generated within this range. Some instruments offer a fixed array of preset "modes," or "programs" (these may be called *mining*, *metals*, *alloy*, *soil*, *plastic*, etc.): these types of instruments are called HH Mode in this workbook. Other types of instruments allow you to define operating parameters more flexibly and are called HH Flex in this workbook. Other XRF instruments that are stationary or portable (but not handheld) and have flexibly adjustable parameters are described as Flex in this workbook. Table 2.6 lists examples in each category, although the list is not exhaustive.

TABLE 2.6. Description of HH Flex, HH Mode, and Flex instrument types based on adjustability of acquisition parameters and X-ray tube power.

Category	Instrument Description	Examples
HH Flex	Handheld, low-power X-ray tube, parameters are flexibly adjustable. Vacuum and/or helium atmosphere typically possible.	Bruker Tracer, ELIO, and CRONO
HH Mode	Handheld, low-power X-ray tube, parameter sets available as "modes." Vacuum and/or helium atmosphere typically possible.	Olympus Vanta, Thermo Niton, SciAps X series, Hitachi/Oxford X-Met
Flex	Stationary or portable, higher-power X-ray tube, parameters are flexibly adjustable. Helium atmosphere typically possible.	Bruker Artax, custom-built instruments

Note: **After you have completed the exercises, compare your results with the findings in the Expected Outcomes section that follows.**

Understanding the characteristics of the excitation creating X-ray fluorescence from the sample is critical for correct interpretation of XRF spectra, for the following reasons:

- The excitation of characteristic X-ray lines in the sample will occur only if the X-ray output of the instrument has components with sufficiently high energy to exceed the excitation potential for the X-ray line of interest (see "Mass Attenuation Coefficients, Absorption Edges, and Enhancement"). For example, if the operator chooses to use a 15 kV accelerating potential (also referred to as voltage) to analyze a ceramic or glass object, that is not sufficient to excite the K lines of strontium ($V_{K(\mathrm{Sr})}$ = 16.11 kV). If strontium is present in trace amounts, as it may be in ceramic or glass that contains calcium, then you likely would not observe the weak Sr Lα_1 line at 1.806 keV because of the presence of a more intense Si K$\alpha_{1,2}$ line at 1.740 keV (fig. 2.17).

- In addition to characteristic X-ray lines from elements present in the sample, each spectrum may contain peaks from elements present in the instrument components that interact with the X-ray beam before and/or after its interaction with the sample. Some of the elements in instrument components may also be present in the sample, so you need to be aware of the identity and intensity of X-ray lines related to instrument components to be able to decide whether an X-ray line represents a sample contribution or is simply an “instrumental background.”

Each instrument has its own unique set of characteristics depending on the anode, operating conditions, and other components. Therefore, it is recommended that the following exercises be carried out on any new instrument before collecting spectra.

Note: Though every effort has been made to include instruments used frequently for the analysis of cultural heritage, it is beyond the scope of this workbook to include every possible model and configuration. The Expected Outcomes section provides models for interpreting spectra in the context of instrument parameter choices. Please consult the manufacturer of your instrument if your outcomes are very different and you need specific information about your instrument’s modes or settings and their relation to operating parameters and excitation spectra.

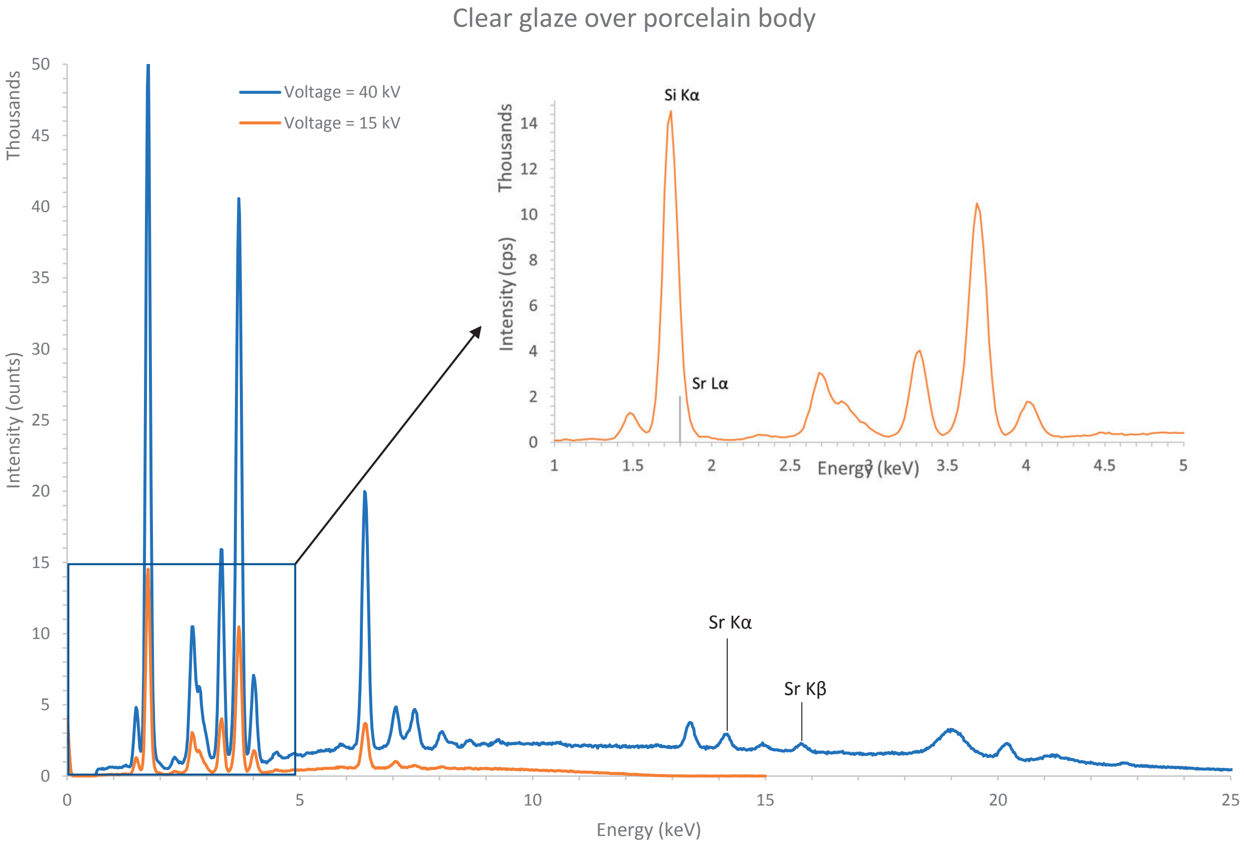


FIGURE 2.17. XRF spectra of clear glaze over porcelain obtained with 40 kV and 15 kV accelerating potentials. Note that the Sr K lines are excited at 40 kV but not at 15 kV. The low-energy Sr Lα peak overlaps with the Si Kα line. The presence of Sr likely would go unnoticed if analysis of the porcelain was conducted with only 15 kV accelerating potential. Spectra were collected using a Bruker Tracer III-SD XRF unit.

A note about programs/modes:
For some instruments, such as those available from Thermo Scientific and Olympus, selection of a specific program/mode results in automatic collection of multiple spectra, each with a different set of parameters (see appendix 1). The spectra may be presented separately or superimposed on one another to produce a "composite" spectrum. Such preset parameters typically are combinations of accelerating potential and beam filters selected to optimize the excitation and detection of characteristic X-ray lines from the sample in different energy regions. The beam current is usually adjusted by the instrument software to the highest value possible based on the power rating of the X-ray tube, unless the measurement dead time exceeds a predetermined value, in which case the current is automatically lowered to keep dead time under this threshold. Information on composition and thickness of the beam filters may be proprietary and not be disclosed to consumers.

Spectrum Acquisition Parameters for Exercises

The availability of a wide variety of XRF instrumentation and continuously evolving technology means you, as the user, need to play an active role in selecting the appropriate acquisition parameters. To begin, you must determine whether your instrument offers a fixed array of preset "modes," or "programs," or whether you can set parameters flexibly. First, use table 2.6 to choose the instrument category with which you are working. Then, consider whether your instrument has a low-power X-ray tube (such as in handheld or HH instruments) or whether you are working with a somewhat larger instrument that has a higher-power X-ray tube (denoted as Flex; see table 2.6). At the time of this writing, voltage and current can be up to 50 kV and 600 mA, respectively, in these instruments.

Appendix 1 has detailed information on Bruker, Thermo Scientific, and Olympus instruments; refer to the section specific to your instrument to guide you in determining the recommended settings. Before proceeding with the exercises below, consult table 2.7 to see how the parameters used for spectra in the exercises may relate to spectra collected with the parameters you can select for your instrument. Table 2.8 provides examples for how you may complete table 2.9 for various types of instruments (HH Flex, HH Mode, and Flex). For the exercises below, use table 2.9 to record the recommended settings for your category.

Note: Make informed choices by consulting the user manual to learn as much as possible about the meaning of different preset modes/programs. For flexibly adjustable instruments, make sure you are aware of the X-ray tube power and possible current settings for low- and high-voltage values. In the newest handheld XRF units, the use of large area SDDs set very close to the instrument's nose has increased sensitivity to light (low Z) elements to a great degree. This has eliminated the use of vacuum pumps in some models, though small helium tanks may still be offered to further increase sensitivity to light elements. Depending on your specific instrument, you may not be able to explore the effect of vacuum or helium atmosphere on the detection of light elements.

TABLE 2.7. User-adjustable instrument parameters, including filters.

Spectrum	Voltage (V)	Current (I)*,**	Vacuum	Filter***	Acquisition Time
A	High (40–50 kV)	Low	None (air)	None	120 s
B	Same as A	Same as A	None (air)	Ti/Al or similar	120 s
C	Low (15–20 kV)	Same as A	None (air)	None	120 s
D	Same as C	Double the current used for C	None (air)	None	120 s
E	High (40–50 kV)	High	None (air)	None	120 s
F	High (40–50 kV)	High	None (air)	Filter #1	120 s
G	High (40–50 kV)	High	None (air)	Filter #2	120 s
H	High (40–50 kV)	High	None (air)	Filter #3	120 s
I	High (40–50 kV)	High	None (air)	Filter #4	120 s

* The current setting will depend on the maximum power rating of the instrument and the voltage equipped with X-ray tubes that can output a maximum of 4 W power. Larger instruments have 30–40 W sources. Before deciding on specific parameters, consult your user manual for the maximum power rating and the voltage and current range of your instrument. Please refer to Appendix 1, tables A1.1, A1.2, or A1.3 depending on your instrument type.

** For mode- or program-based instruments (HH Mode), the current is typically not selectable by the user as the optimum current will be adjusted by the instrument. Current settings for each spectrum obtained by HH Mode instruments are logged with spectra and users can see values when examining the spectrum files.

*** For HH Mode instruments, high voltage conditions are accompanied by the use of filter. In this case, note the presence of the filter and possibly also its material.

TABLE 2.8. Example of completed spectrum log for each instrument category (HH Flex, HH Mode, Flex).

HH Flex Instrument (Bruker Tracer III-SD)							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
A	PE Foam High V, low I, air, no filter, 90s	N/A	40 kV	10 µA	Air	None	120 s
	Spectrum name:	polyethylene_foam_ 40kV_10uA_air_nofilter_120s					
B	PE Foam High V, high I, air, Ti/Al, 90s	N/A	40 kV	10 µA	Air	Al/Ti or other filter	120 s
	Spectrum name:	polyethylene_foam_ 40kV_10uA_air_TiAl_120s					
HH Mode Instrument (Olympus Vanta)							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
A	PE Foam High V, low I, air, no filter, 60s	Geochem High	40 kV	Preset	Air	Preset	60 s
	Spectrum name:	polyethylene_foam_Geochem_ High_Air_60s					
D	PE Foam Low V, high I, air, no filter, 60s	Geochem Low	10 kV	Preset	Air	None	60 s
	Spectrum name:	polyethylene_foam_ Geochem_Low_High_Air_60s					
Flex Instrument (Bruker Artax)							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
A	PE Foam High V, low I, air, no filter, 120s	N/A	50 kV	200 µA	Air	None	120 s
	Spectrum name:	polyethylene_foam_50kV_200uA_air_nofilter_120s					
B	PE Foam High V, low I, air, Ti/Al filter,120s	N/A	50 kV	200 µA	Air	Al/Ti or other filter	120 s
	Spectrum name:	polyethylene_foam_ 50kV_200uA_air_TiAl_120s					

TABLE 2.9. Template for sample, experimental conditions, and file name.

Instrument:							
	Sample/Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
A	Polyethylene foam or PMMA tile						120 s
	High V, low I, air, no filter						
	Spectrum name:						
B	Polyethylene foam or PMMA tile						120 s
	High V, low I, air, Ti/Al or other filter						
	Spectrum name:						
C	Polyethylene foam or PMMA tile						120 s
	Low V, low I, air, no filter						
	Spectrum name:						
D	Polyethylene foam or PMMA tile						120 s
	Low V, high I, air, no filter						
	Spectrum name:						
Optional spectra to collect with flexibly adjustable instruments: explore all available beam filters.							
E	Polyethylene foam or PMMA tile						120 s
	High V, high I, air, no filter						
	Spectrum name:						
F	Polyethylene foam or PMMA tile						120 s
	High V, high I, air, filter #1						
	Spectrum name:						
G	Polyethylene foam or PMMA tile						120 s
	High V, high I, air, filter #2						
	Spectrum name:						
H	Polyethylene foam or PMMA tile						120 s
	High V, high I, air, filter #3						
	Spectrum name:						
I	Polyethylene foam or PMMA tile						120 s
	High V, high I, air, filter #4						
	Spectrum name:						

EXERCISE 2.3a:

Visualizing the Excitation Spectrum

The accurate characterization of the excitation spectrum generated by an instrument requires the use of a calibrated X-ray detector, a specialized piece of equipment not typically found in most museum laboratories. However, we can exploit the X-ray scattering properties of materials with low average atomic numbers to obtain a reasonable approximation of the tube output by collecting a spectrum from a material containing only elements (i.e., C, H, and O) that cannot be detected with air-path XRF units (in fact, hydrogen does not even emit X-rays). Rayleigh (elastic) scattering of the impinging X-rays by these materials will redirect some of them to the detector, allowing you to visualize the following:

- The range and relative intensities of X-rays emitted by the tube
- Characteristic X-ray lines of the anode material
- X-ray lines contributed by the instrument due to the beam's interaction with the materials of the collimators, lens components, aperture materials, window material, and so forth.

SUGGESTED SAMPLE

A small cube (about 2 × 2 × 2 cm) of clean, white, archival polyethylene foam (e.g., Ethafoam) or a small tile of clear polymethyl methacrylate (PMMA or Plexiglas) is recommended (fig. 2.18a). If your instrument has a small cap for the aperture (see chap. 1, fig. 1.6), choose a sample that will both fit underneath the cap and fully cover the aperture (fig. 2.18b).

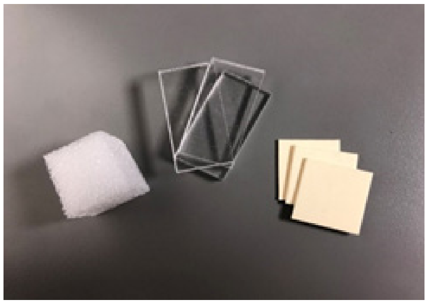


FIGURE 2.18a. Suggested samples to be used in chapter 2 exercises. From left: polyethylene foam cube, PMMA tiles, and matboard squares.

FIGURE 2.18b. Polyethylene foam cube sample sized to fit underneath the cap and fully cover the aperture.

MEASUREMENT

Place the polyethylene foam cube or PMMA tile over the instrument's aperture, and cover with a small sample cap (if available). Acquire spectra using each of the conditions (A–I) listed in table 2.7:

- If you are using a flexible handheld (HH Flex) model or a model with a higher-power X-ray tube (Flex), acquire spectra based on the parameters in table 2.7 and on your instrument's maximum power output (see appendix 1). In completing the spectrum log, file names should be as detailed as possible to facilitate comparisons, for example: polyethylene_foam_40kV_10uA_air_nofilter_120s (table 2.9).
- If you are using a mode-based handheld instrument (HH Mode), collect a spectrum in programs or modes that most closely match the conditions listed in table 2.7 (see appendix 1 for information on Thermo Scientific and Olympus Vanta models and modes). Again, in completing the spectrum log, file names should be as detailed as possible to facilitate comparisons, for example: polyethylene_foam_modename_beamparameter_air_120s (table 2.9).

Note as many specifics about the acquisition parameters as possible in table 2.9.

General observations about excitation spectra

Use the questions below to help interpret your results. Examine each of the spectra you collected and address the following:

1. At what energy does the continuum end?
2. Does the continuum have a "humped" shape similar to that shown in figures 2.9 and 2.10? If not, why?
3. Can you identify the X-ray tube anode material based on peaks present in the spectra? For each spectrum, which family of X-ray lines is present for the anode material (K or L)?
4. Are any other peaks present in the spectra? To what elements do these peaks relate?

Effect of voltage (V) on excitation spectra

Compare spectra obtained at the same current but different voltage settings (accelerating potentials) without filters: spectra A and C (see table 2.7). (This comparison cannot be done for Thermo Scientific and Olympus handheld units because a filter is used with high-voltage settings.)

5. What is the impact on the overall shape and intensity of the spectrum?
6. What is the impact of decreasing the acceleration potential on the energy (keV) at which the maximum intensity of the continuum spectrum appears?

Effect of current (I) on excitation spectra

Compare spectra obtained at the same voltage setting (accelerating potential) but with different current settings, without filters: spectra C and D (see table 2.7). (This comparison cannot be done for Thermo and Olympus handheld units because a filter is used with high-voltage settings.)

7. What is the impact of increasing the current without changing the accelerating potential?

EXERCISE 2.3b:

Evaluating the Effects of Filters on the Excitation Spectrum

As discussed in the section “Reducing Unwanted Signals: Filters,” the insertion of filters into the X-ray beam path can help modify the tube output to suppress a specific portion of the excitation or to reduce unwanted background signal. Most XRF instruments have multiple beam filters that can be placed between the X-ray source and the sample, but the way in which beam filters are selected and positioned varies with the instrument:

- Manual placement: user selects and places filters in the beam path using a filter holder.
- Semiautomated placement: filters are located on internal filter wheel, but user determines selection of filter.
- Automated placement: filters are located on internal filter wheel and are automatically selected and rotated into position based on analysis mode/program selected and beam parameter set within that program.

SUGGESTED SAMPLE

See exercise 2.3a.

MEASUREMENT

Acquire spectra using the different beam conditions (A–I) outlined in table 2.7 with all available beam filters for your particular instrument. In completing the spectrum log (table 2.9), include the filter condition in the file name (see exercise 2.3a).

General observations about the effect of filters on the excitation spectrum

Use the questions below to help interpret your results.

Compare spectra obtained with the same voltage settings but with and without beam filters (spectra A and B in table 2.7 or with different beam filters; wide energy range and high energy range beam conditions for modes available for Thermo Scientific, Olympus, and other instruments; see appendix 1).

1. What differences are observed between the spectra?
2. Looking only at the continuum portion of each spectrum (i.e., ignoring the sharp peaks), at what energy (keV) does the maximum intensity occur? What energy range of the spectrum do the filters most impact?

EXERCISE 2.3c:

Distinguishing Elements in the Sample from Instrument and Substrate Contributions

Even though manufacturers go to great lengths to minimize contributions to the signal from the XRF instrument itself, inevitably some X-ray peaks in the spectra may be related to materials in the instrument. Since these elements may also be present in the sample or object being analyzed, one must be able to distinguish between the two. The first step in determining whether a peak relates to an element in the sample or in the instrument is to examine spectra of polyethylene or PMMA (see the spectra collected in exercise 2.3a) and identify any low-intensity elemental lines coming from the instrument. Next, examine the same peaks detected in the sample, using this as a reference.

Peaks arising from instrument components generally are very low in intensity. It would be hard to confuse the high-intensity iron lines in the spectrum of a steel sword with the low-intensity iron peaks contributed by a spectrometer. However, it might be difficult to determine whether a low-intensity iron peak in a spectrum collected, for example, from paper or parchment is an instrument contribution or an indicator of trace levels of iron in the sample. Paper and parchment contain trace amounts of commonly encountered metals, and in the following exercise, the detected trace elements in matboard and blotter/filter paper are compared to those arising from the instrument as a way to practice distinguishing elements in the sample from instrument contributions.

SUGGESTED SAMPLE

- A small cube (about 2 × 2 × 2 cm) of clean, white, archival polyethylene foam. If your instrument has a small cap for the aperture (see chap. 1, fig. 1.6), choose a sample that will both fit underneath the cap and fully cover the aperture (see fig. 2.18b).
- Small (about 2 × 2 cm, 1.5 to 3 mm thick) piece of clean white or beige matboard (see fig. 2.18a).
- Small (about 2 × 2 cm) pieces of blotter paper or filter paper. Stack several pieces to about 3 mm in thickness, and place a PMMA tile on top to weigh the stack down and eliminate air gaps.

EXPERIMENT

Using the parameters in table 2.10, collect spectra on the polyethylene foam (spectrum A), matboard (spectrum B), and blotter or filter paper (spectrum C). Use the same parameters for all three samples.

- If you are using a flexible handheld (HH Flex) or a model with a higher-power X-ray tube (Flex), acquire spectra using the conditions in table 2.10 and based on your instrument's maximum power output (see appendix 1). File names should be as detailed as possible to facilitate comparisons, for example: matboard_40kV_10uA_air_nofilter_120s.
- If you are using a mode-based handheld instrument (HH Mode), collect spectra in programs or modes that most closely match the conditions in table 2.10. File names should be as detailed as possible to facilitate comparisons, for example: polyethylene_foam_modename_beamparameter_air_120s.

Distinguishing elements in the sample from instrument contributions

Use the questions below to help interpret your results.

Using the spectrum from the polyethylene foam as a reference for the peaks contributed by the instrument, examine each of the spectra you collected from the matboard and blotter/filter paper. Address the following:

1. How do the peaks in the spectra from the matboard or blotter/filter paper compare to those observed in the spectrum from the polyethylene foam sample? What elements do these represent?
2. Which low-intensity peaks (and elements) in the spectra from the matboard and blotter/filter paper are present in the sample, and which are due to instrument contributions or other spectral components? ***Hint:*** If possible, normalize the two spectra you are comparing to a point in the background on either side of the low-intensity peak you are examining.

TABLE 2.10. Spectra to acquire for investigating instrument and substrate background contributions.

	Instrument:						
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
A	Polyethylene foam						120 s
	High V, low I, air, no filter						
	Spectrum name:						
B	Matboard						120 s
	High V, low I, air, no filter						
	Spectrum name:						
C	Blotter or filter paper (~3 mm thick stack)						120 s
	High V, low I, air, no filter						
	Spectrum name:						

2.4 Expected Outcomes

EXERCISE 2.3a:

Visualizing the Excitation Spectrum

EXPECTED OUTCOMES TO EXERCISE QUESTIONS

General observations about excitation spectra (Bruker Tracer III-SD)

Spectra used in addressing the following questions from exercise 2.3a are shown in figure 2.19.

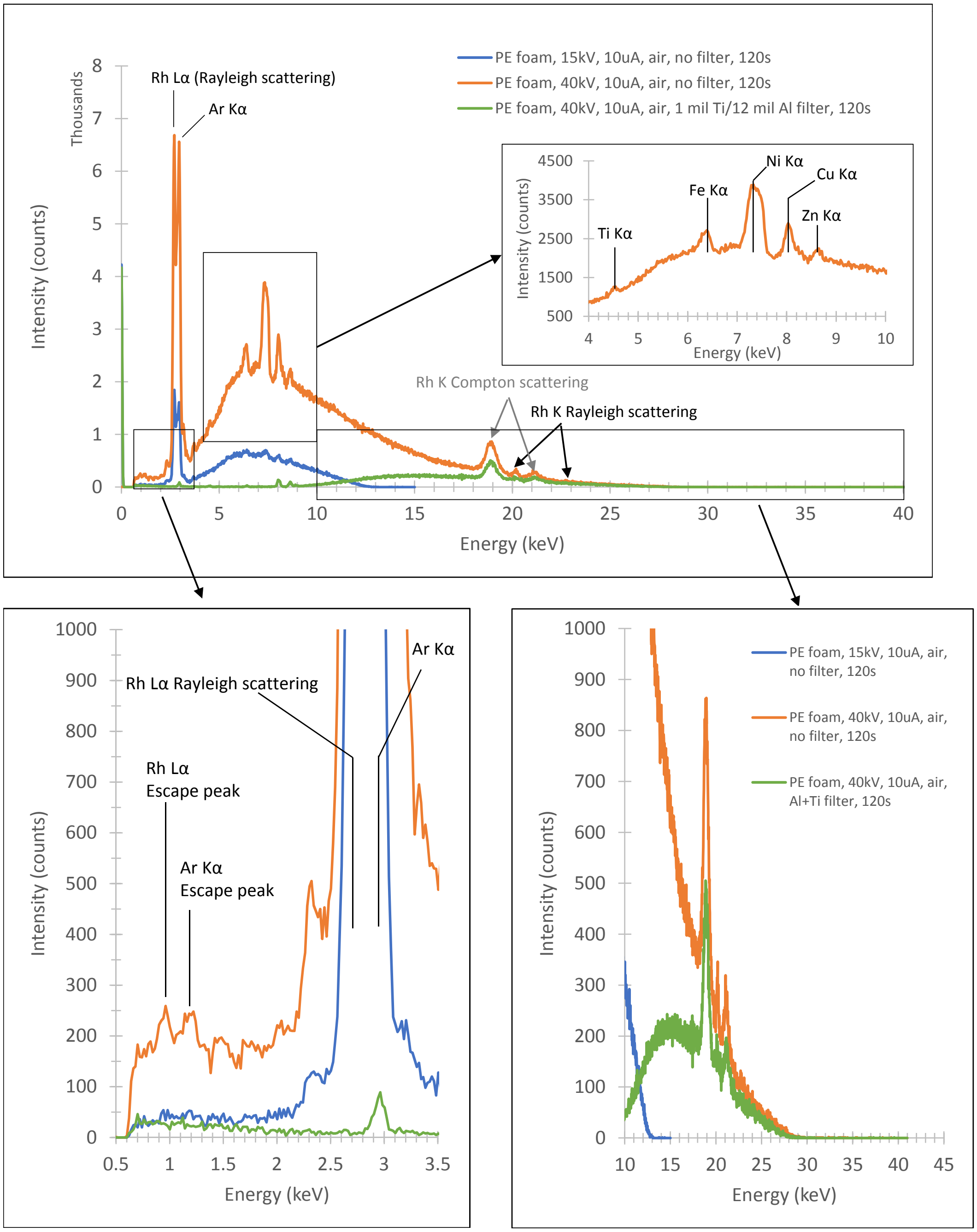


FIGURE 2.19. Excitation spectra using polyethylene foam cube in exercise 2.3a. Data collected using a Bruker Tracer III-SD, Rh tube.

1: At what energy does the continuum end?

- For each spectrum, the continuum ends at the X-ray energy (keV) equivalent of the accelerating potential, or voltage. For example, if the instrument voltage is 40 kV, the continuum ends at 40 keV. Further, if the instrument voltage is 15 kV, the continuum ends at 15 keV. You may need to zoom in at the high-energy end of your spectrum to observe this.

2: Does the continuum have a “humped” shape similar to that shown in figures 2.9 and 2.10? If not, why?

- The typical “humped” continuum can be observed when there is no beam filter in the X-ray path. If you observe regions in the spectrum that appear “flat” or “smooth,” this indicates that a beam filter is present (see exercise 2.3b for further discussion on filters).

3: Can you identify the X-ray tube anode material based on peaks present in the spectra? For each spectrum, which family of X-ray lines is present for the anode material (K or L)?

- The Bruker Tracer III-SD used to collect these spectra has a Rh tube. Unless filters in the beam path completely absorb their characteristic X-ray peaks, you should observe Rh K and/or L lines due to Rayleigh scattering in spectra of polyethylene foam or PMMA tile.
- At the 40 kV voltage setting, both the K and L lines of the Rh anode are excited. The presence of a 1 mil Ti / 12 mil Al beam filter eliminates the L lines from the excitation spectrum.
- At the 15 kV voltage setting, only the Rh L lines are excited and the Rh K lines are absent from the excitation spectrum. Since there is no filter present, the Rh L lines can be observed.

4: Are any other peaks present in the spectra? To what elements do these peaks relate?

- The Bruker Tracer III-SD spectra exhibit the presence of argon (Ar), a component of the atmosphere. Unless removed with a vacuum pump or displaced by helium, Ar peaks may be observed in spectra.
- Peaks for Ti, Fe, Ni, Cu, and Zn can also be detected. These elements are present in instrument components, and X-ray lines are excited either by the beam on its way to the sample or by X-rays traveling from the sample toward the detector. Note that the broad hump on the low-energy side of the Ni Kα peak is the Ni Kα Compton scattering peak. From the presence of the latter peak, we can conclude that Ni fluorescence is generated by the beam on its way to the sample and the polyethylene foam is scattering these X-rays to the detector: both Rayleigh and Compton scattering peaks are present in the spectrum.
- At the low energy end of spectra collected without a beam filter in air, one may observe escape peaks for the Rh Lα and Ar Kα lines at 0.95 keV and 1.22 keV, respectively.
- The escape peak for an intense X-ray line appears 1.74 keV lower than its energy due to the energy loss associated with the generation of a Si Kα fluorescent X-ray photon in the detector’s material. As long as the energy of the incident X-ray is greater than the excitation potential of Si K lines (1.84 keV), the likelihood of generating escape peaks will be higher for intense peaks with energies that are close to the excitation potential. The energies of Rh Lα and Ar Kα lines are 2.70 and 2.96 keV, respectively, so these X-ray photons will be efficient generators of escape peaks.

General observations about excitation spectra (Olympus Vanta)

Spectra used in addressing the following questions from exercise 2.3a are shown in figure 2.20.

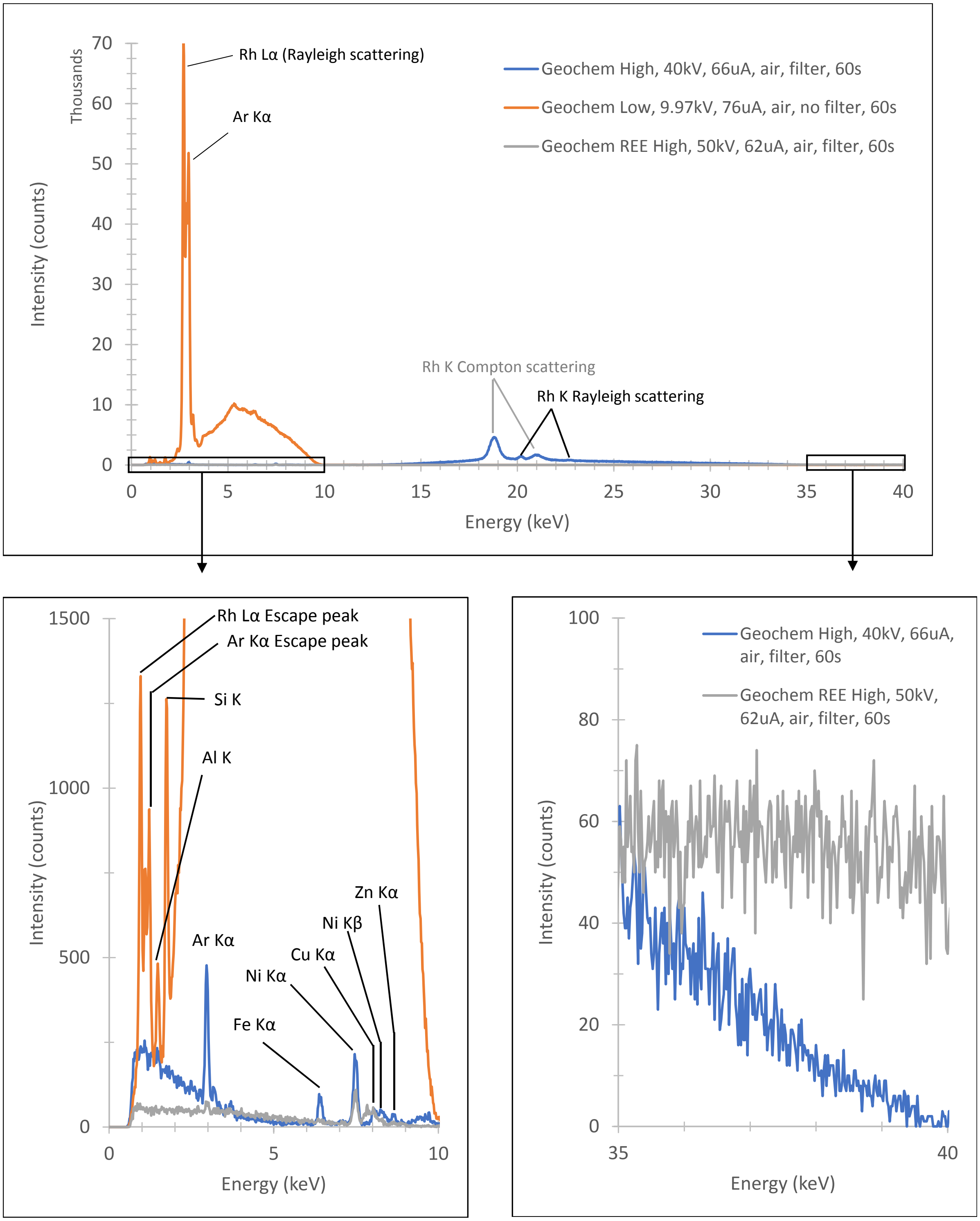


FIGURE 2.20. Excitation spectra using polyethylene foam cube in exercise 2.3a. Data collected using an Olympus Vanta.

1: At what energy does the continuum end?

- For each spectrum, the continuum ends at the X-ray energy (keV) equivalent of the accelerating potential, or voltage.
- At 40 kV voltage setting, the continuum ends at 40 keV.
- At 9.97 kV voltage setting, the continuum ends at 9.97 keV.
- At 50 kV voltage setting, the continuum ends at 50 keV. However, the instrument is set up to display X-ray energies only up to around 41 keV. This means that the continuum portion of the spectrum in this mode will have a non-zero value around 41 keV.

2: Does the continuum have a “humped” shape similar to that shown in figures 2.9 and 2.10? If not, why?

- The typical “humped” continuum can be observed when there is no beam filter in the X-ray path. For the Olympus Vanta, the only modes in which there is no beam filter in the X-ray path are the Geochem Low and the Geochem REE Low.
- The Geochem High and Geochem REE High modes involve beam filters in the X-ray path. Regions in the spectrum are observed that appear “flat” or “smooth,” and correspond to energies of the excitation spectrum absorbed strongly by the filter components.

3: Can you identify the X-ray tube anode material based on peaks present in the spectra? For each spectrum, which family of X-ray lines is present for the anode material (K or L)?

- The Olympus Vanta used to collect these spectra has a Rh tube. Unless filters in the beam path completely absorb their characteristic X-ray peaks, you should observe K or L lines due to Rayleigh scattering in spectra of polyethylene foam or PMMA tile.
- The spectrum obtained in the 9.97 kV Geochem Low mode contains only Rh L peaks because the Rh K peaks are not excited at this accelerating potential.
- The spectrum obtained in the 40 kV Geochem High mode contains only Rh K peaks because the beam filter eliminates the Rh L peaks.
- The spectrum obtained in the 50 kV Geochem REE High mode does not contain either Rh L or Rh K peaks because the beam filter material eliminates both sets.

4: Are any other peaks present in the spectra? To what elements do these peaks relate?

- The Olympus Vanta spectra exhibit the presence of Ar because of the presence of air during the measurement.
- In Geochem Low mode in air, one may observe escape peaks for the Rh Lα and Ar Kα lines at 0.95 keV and 1.22 keV, respectively.
- The spectrum collected in the Geochem Low mode exhibits Al and Si peaks, which are likely instrument contributions.
- The 40 kV Geochem and 50 kV Geochem REE modes have very low intensity peaks for Fe, Ni, Cu, and Zn, which are likely also due to instrument contributions.

Effect of voltage on excitation spectra (Bruker Tracer III-SD)

Spectra used in addressing the following questions from exercise 2.3a are shown in figure 2.21.

Comparison of spectra obtained at different voltage settings without beam filters is not possible for most HH Mode type instruments (e.g., Olympus Vanta, Thermo Scientific Niton) because higher-voltage modes of these units involve the use of beam filters. Therefore, the sample spectra discussed here were all collected with a Bruker Tracer III-SD instrument.

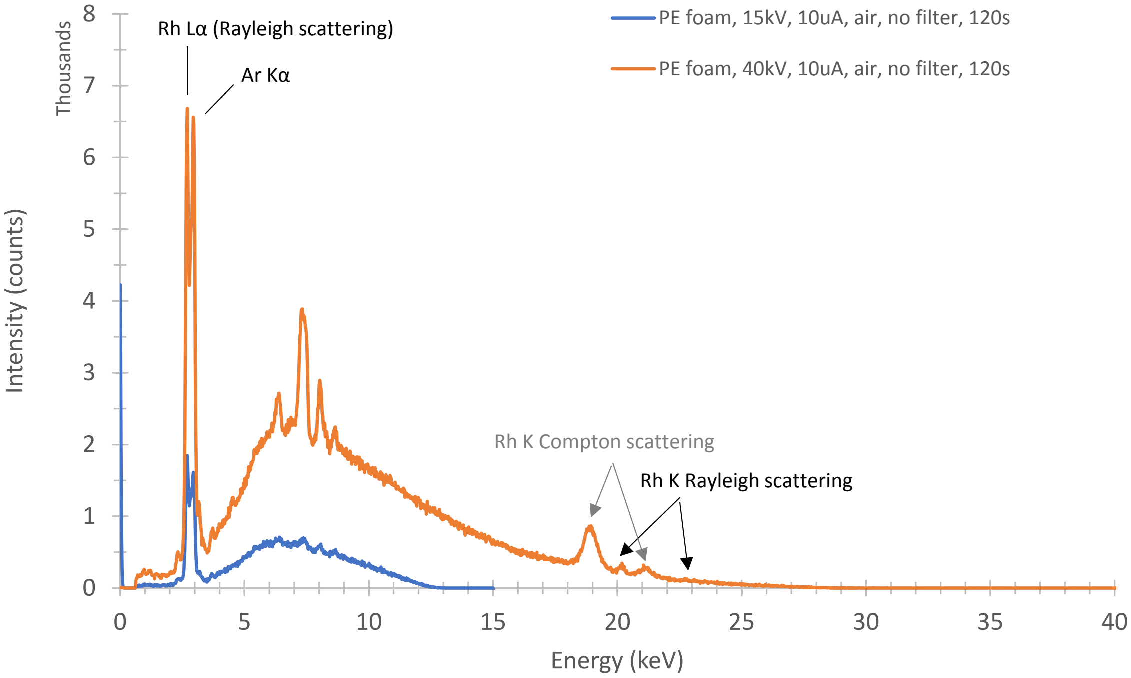


FIGURE 2.21. Excitation spectra using polyethylene foam cube, obtained at different voltage settings without beam filters in exercise 2.3a. Data collected using a Bruker Tracer III-SD, Rh tube.

5: What is the impact on the overall shape and intensity of the spectrum?

- Higher accelerating potential settings (voltage) result in an increase in the energy range of the X-ray photons available for exciting the sample and an overall increase in the intensity of the excitation spectrum.

6: What is the impact of decreasing the acceleration potential on the energy (keV) at which the maximum intensity of the continuum spectrum appears?

- Higher accelerating potential settings (kV) cause an increase in the energy (keV) at which the maximum intensity of the continuum spectrum appears.

Effect of current on excitation spectra (Bruker Tracer III-SD)

Spectra used in addressing the following questions from exercise 2.3a are shown in figure 2.22.

Comparison of spectra obtained at the same voltage but at different current settings is not possible for most HH Mode type instruments (e.g., Olympus Vanta, Thermo Scientific Niton) because the instruments optimize current settings automatically. Therefore, example spectra discussed here were all collected with a Bruker Tracer III-SD instrument.

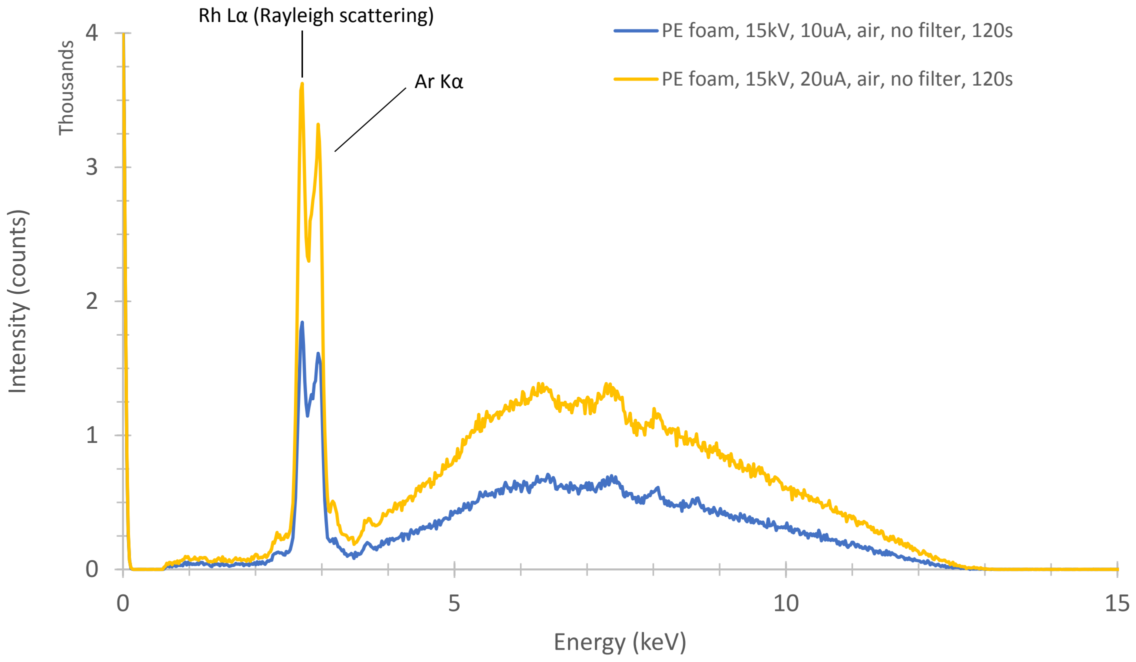


FIGURE 2.22. Excitation spectra using polyethylene foam cube, obtained at different current settings in exercise 2.3a. Data collected using a Bruker Tracer III-SD, Rh tube.

7: What is the impact of increasing the current without changing the accelerating potential?

- Increasing the current without changing the accelerating potential results in an increase in the intensity of the excitation spectrum without a shift in its energy distribution.

EXERCISE 2.3b:

Evaluating the Effects of Filters on the Excitation Spectrum

EXPECTED OUTCOMES TO EXERCISE QUESTIONS

Effect of filters on excitation spectra (Bruker Tracer III-SD)

Spectra used in addressing the following questions from exercise 2.3b are shown in figures 2.23 and 2.24.

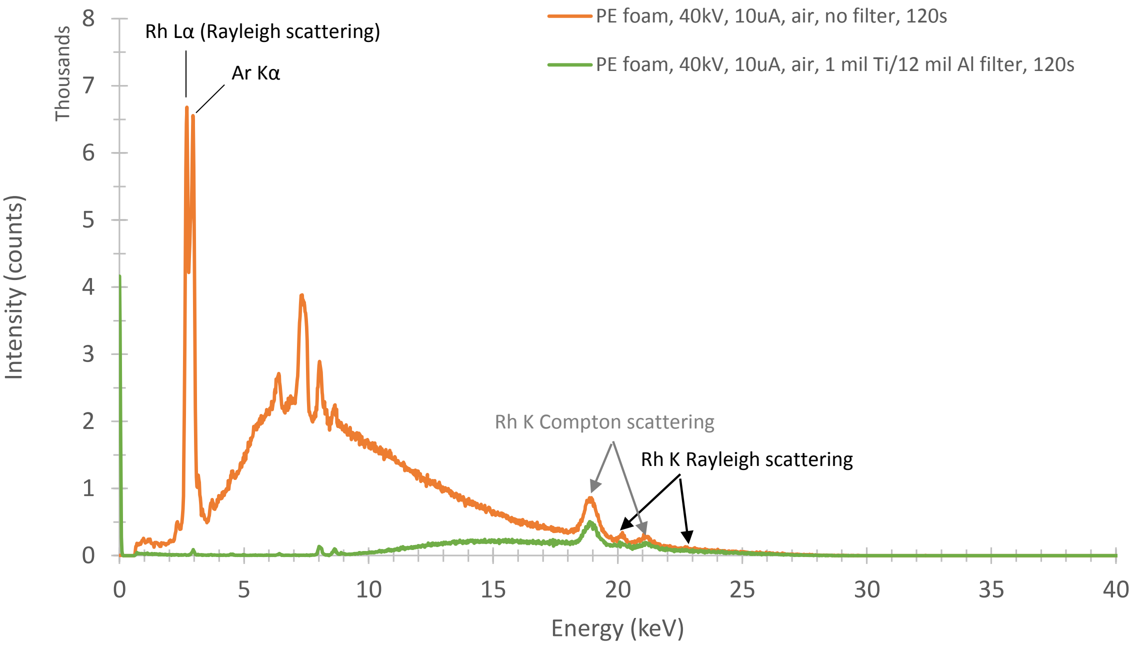


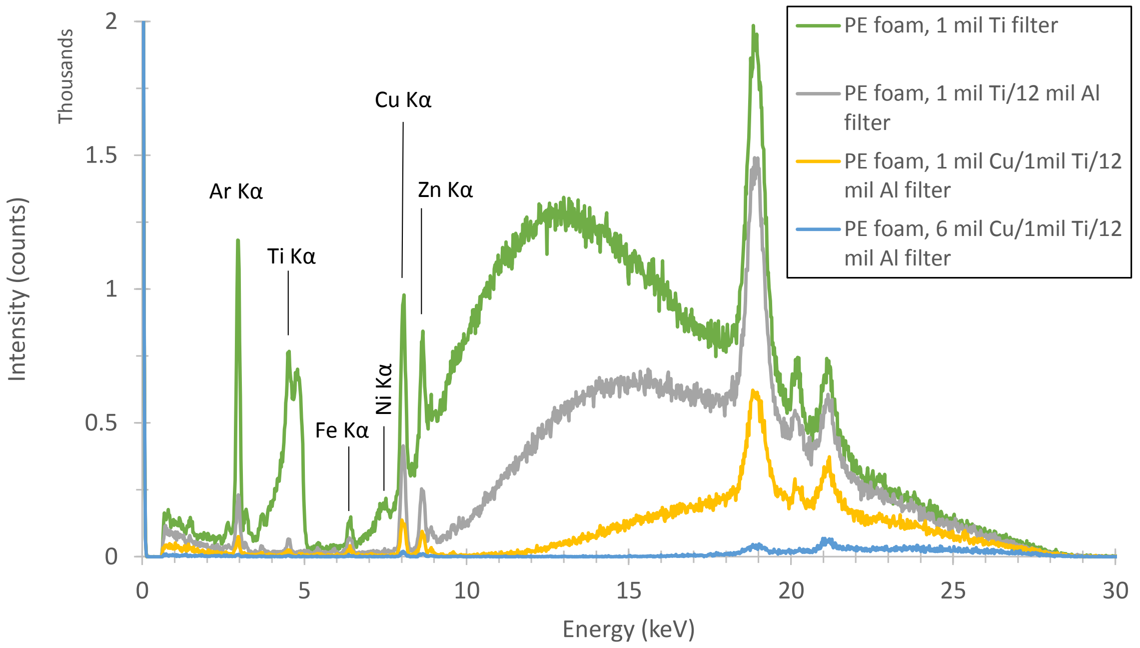
FIGURE 2.23. Excitation spectra using polyethylene foam cube, obtained without and with a filter in exercise 2.3b. Data collected using a Bruker Tracer III-SD, Rh tube.

1: What differences are observed between the spectra?

- Figure 2.23 compares spectra obtained without a filter and with a filter. The filter is composed of two stacked metals: aluminum (Al) foil with a thickness of 12 mil (305 μm) and titanium (Ti) foil with a thickness of 1 mil (25.4 μm). The titanium layer faces the X-ray tube of a Bruker Tracer III-SD spectrometer.
- The presence of a filter in the beam path lowers the overall intensity of the excitation spectrum. The characteristic Rh L lines of the anode are eliminated by the Al / Ti filter. The Ar K line and the peaks (Ti, Fe, Ni, Cu, Zn) contributed by instrument components are much lower in intensity. The filter's use produces a low, flat background up to around 11 keV, at which point the scattered continuum starts to increase slightly.

2: Looking only at the continuum portion of each spectrum (i.e., ignoring the sharp peaks), at what energy (keV) does the maximum intensity occur? What energy range of the spectrum do the filters most impact?

- Figure 2.24 compares spectra obtained with all four filters supplied with a Bruker Tracer III-SD instrument at an accelerating potential of 40 kV and a current of 30 μA.



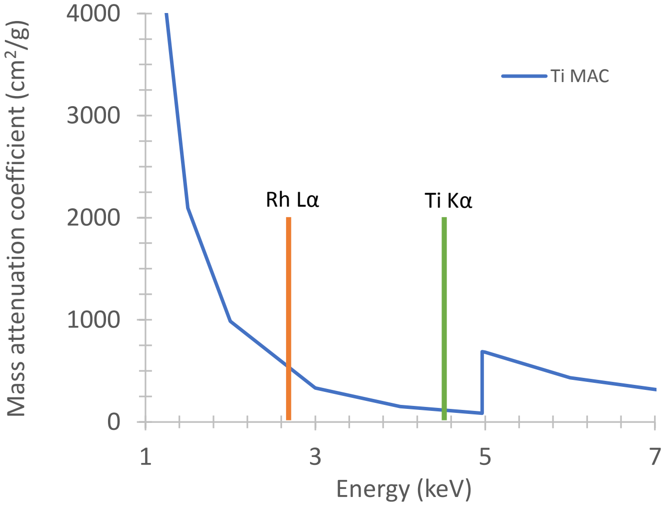


FIGURE 2.24. Excitation spectra using polyethylene foam cube, obtained with all four filters in exercise 2.3b. Data collected using a Bruker Tracer III-SD, Rh tube (40 kV, 30 uA, air, 120s). In the graph at bottom, the mass attenuation coefficient (MAC) of titanium (Ti) indicates the ability of a Ti filter to absorb X-rays of different energies.

- In all cases, the Rh L lines from the X-ray tube are eliminated by the filter, and the overall intensity of the excitation spectrum is lowered. The intensity of Ar K lines and the peaks contributed by instrument components (Ti, Fe, Ni, Cu, Zn) are much lower in intensity as well.
- The spectrum obtained with a 1 mil (25.4 µm) Ti filter exhibits a Ti Kα peak on top of a gradual increase in the continuum intensity from around 3.5 keV to the excitation potential of Ti K lines: 4.96 keV. The intensity of the excitation spectrum abruptly decreases above this energy due to the strong absorption of photons from the incident X-ray beam by the Ti filter. As the photons increase in energy, the Ti filter becomes increasingly transparent and the excitation spectrum gradually increases in intensity starting at around 6 keV.
- The Ti filter eliminates the Rh L lines from the X-ray tube and the Ti K lines generated by the filter material can enhance the excitation of Ar, Cl, and S in the beam path and the sample.
- Filters composed of multiple films from elements with increasing atomic numbers result in the absorption of broader regions of the excitation spectrum (see table 2.3).

The MAC of Ti indicates the ability of a Ti filter to absorb X-rays of different energies (see fig. 2.24):

- **The high MAC of Ti at low energies means that the Ti filter will absorb low-energy X-rays generated by the X-ray tube. This includes the strong absorption of the Rh L lines.**
- **Argon (Ar) is present in the atmosphere inside and outside of the instrument (unless vacuum or helium is used).**
- **The steep drop in the intensity of the excitation spectrum, starting at 4.96 keV, is due to the strong absorption of X-rays by Ti at its excitation potential.**

EXPLANATION OF OBSERVATIONS

Beam filters absorb portions of the excitation spectrum, partially or entirely, depending on the filter materials and the filter thickness. The specific energy ranges absorbed depend on the filter material. The relation between an element's ability to absorb incident X-rays and the energy of those X-rays is described by the X-ray linear attenuation (μ) or MAC (μ/ρ) (see the section "Mass Attenuation Coefficients, Absorption Edges, and Enhancement"). A good rule of thumb is that filters absorb strongly right above the energy equivalent of the excitation potential for the filter material.

EXERCISE 2.3c:

Distinguishing Elements in the Sample from Instrument and Substrate Contributions

EXPECTED OUTCOMES TO EXERCISE QUESTIONS

Distinguishing elements in the sample from instrument contributions (Bruker Tracer III-SD)

Spectra used in addressing the following questions from exercise 2.3c are shown in figure 2.25.

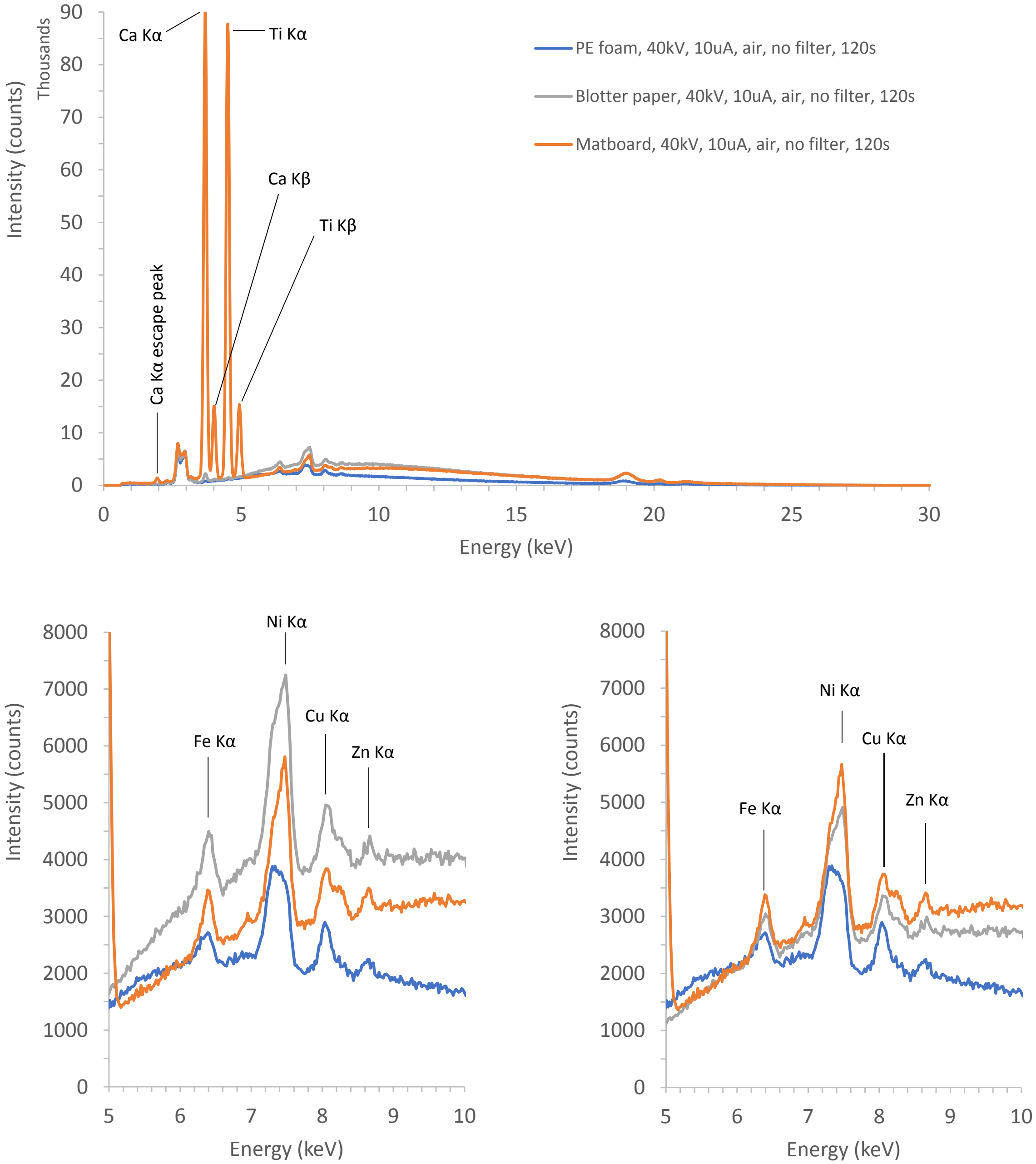


FIGURE 2.25. Excitation spectra for analysis of matboard and blotter/filter paper to distinguish between elements in the sample and elements from instrument contributions in exercise 2.3c. Bottom left: detail of 5–10 keV range; bottom right: detail with spectra normalized at about 6 keV. Data collected using a Bruker Tracer III-SD.

1: How do the peaks in the spectra from the matboard or blotter/filter paper compare to those observed in the spectrum from the polyethylene foam sample? What elements do these represent?

- The matboard spectrum has Ca and Ti K emission lines. These likely relate to the presence of calcium carbonate used as an alkaline reserve in the matboard and the presence of titanium dioxide pigment.

2: Which low-intensity peaks (and elements) in the spectra from the matboard and blotter/filter paper are present in the sample, and which are due to instrument contributions or other spectral components?

- The spectrum of the matboard displays a small peak that corresponds to the energy of the Ca Kα line minus 1.74 keV (the energy of the Si Kα line): this is an escape peak.
- The spectrum of the blotter paper contains Ca K lines that are higher in intensity than the Ca K peaks in the spectrum of the polyethylene foam. Additionally, the matboard spectrum has low-intensity peaks for Fe, Ni, Cu, and Zn. The intensity of the Fe and Ni peaks appears greater than that of the Kα for these elements in the spectrum of the polyethylene foam, suggesting contributions from elements in the paper in addition to contributions from the instrument itself.
- By normalizing spectra to the intensity of the polyethylene spectrum at 6.0 keV, the peak heights (or areas) of the Fe Kα line can be compared more easily. The same approach can be used to compare the Ni Kα peak by normalizing the spectra to the intensity of the polyethylene spectrum around 7.8 keV, between the Ni and Cu Kα peaks.

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3. Practical Exercises on Mock-Ups

X-ray fluorescence spectroscopy is a powerful technique for characterizing the elemental composition of a wide variety of materials, but its effective use requires an understanding of (1) how to select the appropriate instrument parameters to collect spectra that will provide the desired information for the particular material under study, and (2) how to interpret the resulting spectra, both in terms of assigning the peaks to the appropriate elements and in terms of recognizing features in the spectra arising from instrumental artifacts or spectral anomalies.

The exercises in chapter 2 are designed to help you become more familiar with your instrument and, in particular, to learn how the voltage and current settings affect output of the X-ray tube and how to recognize instrumental artifacts unique to your specific instrument. If you haven't already carried out those exercises, please do so before moving on to the exercises in this chapter.

The exercises in chapter 3 will familiarize you with the various challenges most commonly encountered in the collection and interpretation of XRF spectra of cultural heritage materials. The suggested samples have been designed to mimic configurations of materials or mixtures of elements often encountered in the study of cultural heritage materials, and to introduce you to more complex situations that can produce spectra that may be misinterpreted by an untrained researcher.

How to Use This Chapter

Each of the four sections in this chapter addresses common issues relevant to the study of cultural heritage materials and objects. An introduction to each topic is given, followed by suggested mock-up sample(s) to be used in the exercises (for directions on how to make the samples, see appendix 2). The exercises in each section are followed by a series of questions designed to help you, as the user, see the connection between the obtained spectral results and the theoretical concepts.

If your instrument has a camera, it is a great tool for positioning the instrument nose to the sample. In the exercises that ask you to analyze the sample under different instrument parameters, it is important to analyze the same spot on the sample as consistently as possible to see the differences in spectral responses brought on by these parameter changes and not by the inhomogeneity of the sample or setup changes. Use the camera to be consistent in positioning.

All the exercises in this workbook require obtaining spectra for interpretation. For some mode-based instruments, the default output is numerical values of the elemental content. If you do not know how to access the spectra in your instrument software, contact your instrument manufacturer.

Table 3.1 lists suggested mock-up samples, cross-referenced according to the concept to be explored and the class of material. It is strongly suggested that you carry out at least one exercise under each concept, even if the suggested samples are not of a material that you regularly work with or anticipate encountering. (See appendix 2 for sample preparation instructions; see appendix 3 for a list of materials and instrument suppliers.)

TABLE 3.1. Suggested mock-up samples for use in the exercises, cross-referenced by concept to be explored and class of material.

	Detection of high vs. low Z elements	Detection of elements in different layers	Detection of elements in substrate	Detection of elements in fine mixtures (inhomogeneity on micro scale)	Detection of elements in rough/uneven surfaces	Detection of elements in coarse mixtures (inhomogeneity on macro scale)	Inference of presence of organic matter
Painted surfaces	UM Blue-CoBlue (3.1b)	Ti White-Lithopone layers (3.2c) Ti White-PG7 layers (3.2e)	UM Blue-CoBlue (3.1b) Bone Black (3.1c)	Ti White-Lithopone mixtures (3.2c) Prussian Blue serial dilutions (3.3a)	Accordion pleat (3.4a)	Cd Red lines (3.2a)	“Varnish” layer (3.1b) PMMA backing (3.3b, 3.3d)
	Bone Black (3.1c) Alizarin (3.1d)						
Manuscripts/ Drawings	UM Blue-CoBlue (3.1b)	Interleaving material (3.2d, 3.2e)	Drawing materials on paper (3.3d)	Ti White-Lithopone mixtures (3.2c) Prussian Blue serial dilutions (3.3a)	Accordion pleat (3.4a)	Cd Red lines (3.2a)	“Varnish” layer (3.1b) PMMA backing (3.3b, 3.3d)
Photographs	Bone Black (3.1c) Alizarin (3.1d)	B&W photograph (3.3b)	B&W photograph (3.3b)				
Metals	Copper alloy (3.1e)	“Corroded” surface (3.2b) Lead-tin solder with Al sheets (3.2d)	Copper alloy (3.1e) Lead-tin solder (3.1f)	Copper alloy (3.1e) Lead-tin solder (3.1f)	“Corroded” surface (3.2b)	Lead-tin solder (3.1f)	“Varnish” layer (3.1b) PMMA backing (3.3b, 3.3d)
	Lead-tin solder (3.1f)						
Ethnographic/ Archaeological		Ti White-Lithopone layers (3.2c) Ti White-PG7 layers (3.2e)	Drawing materials on paper (3.3d)	Ti White-Lithopone mixtures (3.2c) Prussian Blue serial dilutions (3.3a)	Accordion pleat (3.4a)	Cd Red lines (3.2a)	“Varnish” layer (3.1b) PMMA backing (3.3b, 3.3d)
						Lead-tin solder (3.1f)	
Ceramics/ Glass	Glass (3.1a)		Glass (3.1a)		Accordion pleat (3.4a)		

Each exercise involves the collection and comparison of a series of spectra with different sets of parameters. As the user, you should choose instrument modes or voltage/current settings based on the information in table 2.6 (see chap. 2) and appendix 1 and complete the spectrum log in as much detail as possible. Examples of completed spectrum logs for each instrument category are presented in table 3.2.

TABLE 3.2. Example of completed spectrum logs for each instrument category.

HH Flex Type Instrument (Bruker Tracer III-SD)							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
S1	Glass	N/A	40 kV	2 µA	Air	None	90 s
	High V, low I, air, no filter, 90s						
	Spectrum name:	S1_Glass_ 40kV_2uA_air_nofilter_90s					
S4	Glass	N/A	15 kV	20 µA	Vac	None	90 s
	Low V, high I, vac/He, no filter, 90s						
	Spectrum name:	S4_Glass_ 15kV_2uA_vac_nofilter_90s					
HH Mode Type Instrument (Olympus Vanta)							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
S1	Glass	Geochem High	40 kV	Preset	Air	Preset	90 s
	High V, low I, air, no filter, 90s						
	Spectrum name:	S1_Glass_ High_Air_90s					
S4	Glass	Geochem Low	10 kV	Preset	Vac	None	90 s
	Low V, high I, vac/He, no filter, 90s						
	Spectrum name:	S4_Glass_ Geochem_Low_Vac_90s					
Flex Type Instrument (Bruker Artax)							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
S1	Glass	N/A	50 kV	200 µA	Air	None	90 s
	High V, low I, air, no filter, 90s						
	Spectrum name:	S1_Glass_ 50kV_200uA_air_nofilter_90s					
S4	Glass	N/A	20 kV	400 µA	He	None	90 s
	Low V, high I, vac/He, no filter, 90s						
	Spectrum name:	S4_Glass_ 20kV_400uA_He_nofilter_90s					

- If instructed to use “vacuum,” use either vacuum or helium atmosphere for the enhancement of light elements. Some instruments may not offer either capability. Sample spectra are included with each exercise to demonstrate signal enhancement.
- While the use of “no filter” is specified for most spectra, it may not be possible to achieve this with HH Mode type instruments. These units typically use preset filter types in almost every mode, with the exception of modes geared toward the detection of the lightest elements. Please note if a preset filter is used by your instrument.

3.1 Detection of Low and High Z Elements

The exercises in this section explore how elements across the periodic table may be detected with different efficiencies. Although the exercises are separated according to low and high Z elements, it should be remembered that it is the energy at which the fluorescence occurs that determines its detection efficiency. The relationship between atomic number Z and energy of the possible fluorescent X-rays was shown earlier (see chap. 2, fig. 2.3). Note that whereas low Z elements can produce only low-energy fluorescence, higher Z elements can fluoresce at both high and lower energies (i.e., through K, L, and M emission lines) depending on the atomic structure of the element. A full list of emission energies of the elements appears in appendix 4.

Low Z Elements: Low-Energy Fluorescence

Here, low Z materials refer to those containing elements with atomic numbers lower than 20. These are not necessarily the only elements in these materials, however; higher Z elements may be present, but the majority are low Z elements. Low Z materials emit only K fluorescence lines, which occur at very low energies (~3 keV or under). In this energy range, absorption of the fluorescence by air can reduce the signal. Thus, eliminating as much of the air between the sample and the detector as feasible, through the use of either a vacuum or a He purge, will improve detection efficiency. One simple way to determine whether you have reduced the amount of air is to look at the peak for argon (at ~3 keV): if the vacuum/purge is working, the peak should decrease.

The lowest atomic number that may be detected depends on the particular detector (e.g., silicon drift detector [SDD] vs. silicon PIN diode [SiPIN]) and instrument setup (e.g., vacuum or He purge vs. air path). Elements commonly found in cultural heritage materials, such as chlorine and sodium (in corrosion products), sulfur and phosphorus (in pigments), silicon (in glasses), and aluminum and magnesium (in metals and pigments) may or may not be detectable by your instrument. If you suspect one of these elements is present, you should carry out an analysis on a known sample containing the element of interest to determine the efficiency of your instrument toward that element; if you cannot detect it in the known reference sample, you cannot say whether it is present or absent in the unknown.

Because most materials are mixtures of low and high Z elements, the low-energy region of the resulting XRF spectrum can become quite congested. In addition to K lines from low Z elements, other features that occur in this region of the spectrum include L and M lines from heavier elements. Therefore, when interpreting this region of the spectrum, care must be taken to recognize and identify those components that may be due to higher Z elements, paying attention to possible overlaps that may obscure the emission from a lower Z element (fig. 3.1).

Example: As shown in figure 3.2, the presence of P with Ca can be difficult to determine, due to the overlap of the Ca escape peak (3.69–1.74 = 1.95 keV, with the P Kα peak at 2.015 keV). Another example (not shown) is the Pb M lines (2.346 keV) overlapping the S K line (2.307 keV); if Pb is present, it can be difficult to determine whether S is also present.

Of course, the elements of which organic materials are comprised—carbon, nitrogen, and oxygen—are present in many of the materials studied, whether as binding media, varnishes, or corrosion products. Although these elements typically cannot be detected by XRF, always keep in mind their presence can affect the spectra collected. The effect of low Z elements (which may be detected only weakly or not at all) on the resulting XRF spectrum is explored in the exercises in this section.

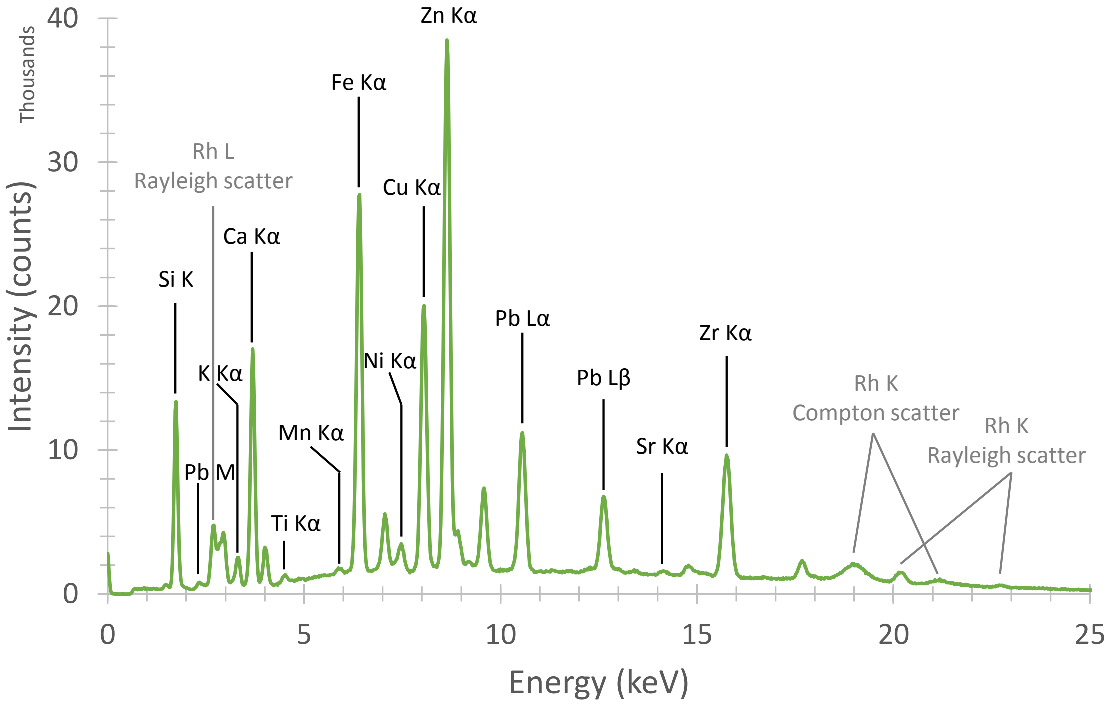


FIGURE 3.1. Typical spectrum for materials with high and low Z elements, showing congestion in the low-energy region due to K lines as well as L and M lines.

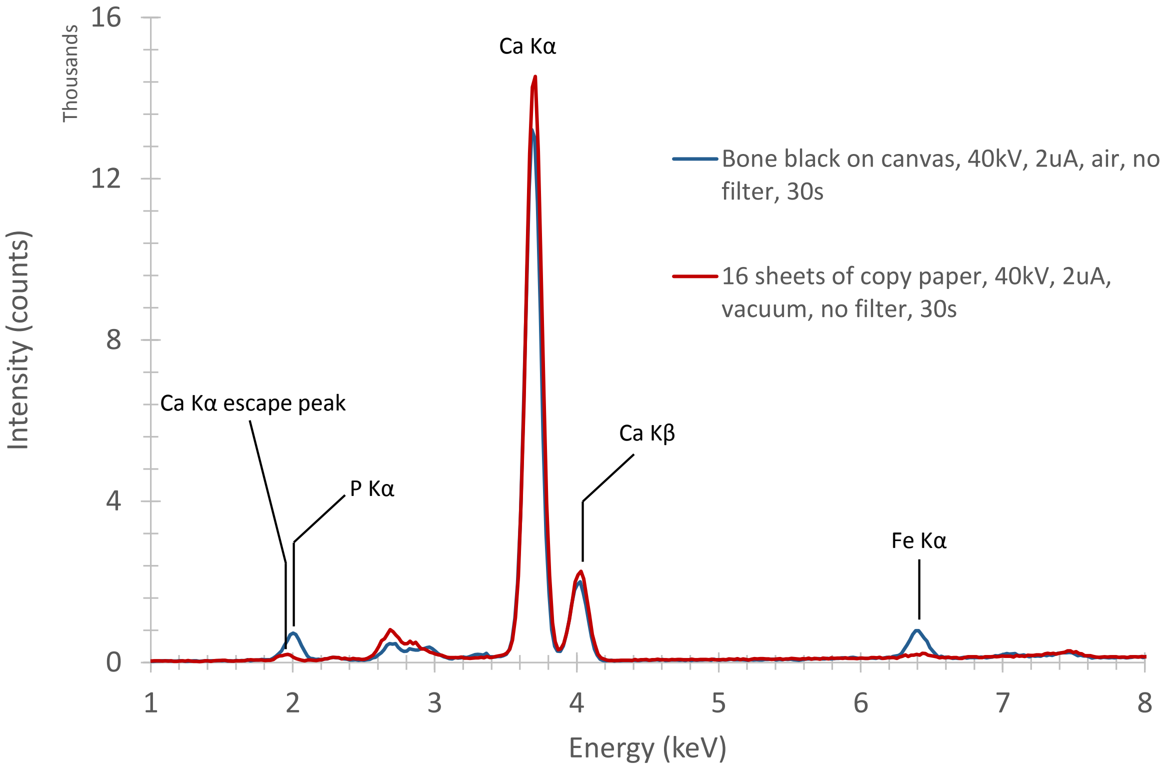


FIGURE 3.2. Spectra showing overlap of P Kα peak and Ca Kα escape peak.

Note: **After you have completed the exercises, compare your results with the findings in the Expected Outcomes section that follows.**

EXERCISE 3.1a:

Glass: Detecting Full Spectral Energy Range

In this exercise, a glass sample containing both high and low Z elements is studied. As discussed above, X-ray fluorescence emission from elements commonly found in glass—notably silicon, sodium, and potassium—is low in energy and thus can be attenuated upon passing through air. Exercises are conducted both with and without a vacuum/He purge, and the results compared to understand how the presence of air between the sample and the detector affects detection efficiency of these elements. Additionally, the effect of optimizing the tube parameters to enhance the detection of elements with X-ray fluorescence emission at low- and high-energy ranges is explored.

FIGURE 3.3. Glass sample, showing one side.

SUGGESTED SAMPLE

A glass sample (multicolored glass mosaic tile squares work well) with smooth surface (see fig. 3.3).

EXPERIMENT

Comparing voltage-current settings and air-vacuum impact on spectra

Collect spectra from the glass sample using conditions A–D (table 3.3). If the two sides of the sample have different roughnesses, place the smoother side facing the X-ray source and detector (fig. 3.4). If the sample is small enough, use the safety cap if available (see chap. 1, fig. 1.6).

TABLE 3.3. Conditions A–D for comparison of voltage-current settings and air-vacuum impact on spectra for exercise 3.1a.

Instrument:							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
A	Glass						
	High V, mid I, air, no filter, 90s						
	Spectrum name:						
B	Glass						
	Low V, mid I, air, no filter, 90s						
	Spectrum name:						
C	Glass						
	Low V, high I, air, no filter, 90s						
	Spectrum name:						
D	Glass						
	Low V, high I, vac, no filter, 90s						
	Spectrum name:						

Effect of accelerating potential (voltage)

Use the questions below to help interpret your results. Compare spectra for conditions A and B:

1. How does the spectrum acquired at 40 kV compare with its 15 kV counterpart?
2. If you did not know the conditions, how could you deduce what voltage was used from the spectrum?

Effect of current

Compare spectra for conditions B and C.

3. What are the elements identified using the 15 kV, 10 µA (low V, mid I) conditions, and how does this compare to results obtained with a higher current? Which condition yields a less noisy spectrum?
4. Did the higher current produce artifacts in this sample? If so, describe them.

Effect of vacuum

Compare spectra for conditions C and D.

5. How does the spectrum taken with vacuum compare to the one taken in air, especially at the lower-energy end of the spectrum (i.e., <5 keV)?

FIGURE 3.4. Photo showing the glass sample, smooth side facing the XRF nose on the Bruker III-SD unit head. (See chap. 1, fig. 1.6 for use of the safety cap.)

EXERCISE 3.1b:

Ultramarine–Cobalt Blue Mixture on Canvas: Exploring Low and High Z Elements within the Same Sample; “Varnish” Mock-Up

This exercise explores similar concepts to exercise 3.1a, but on a painted sample containing two blue pigments: one with only low Z elements and another with a higher Z element. Here again, enhancing the detection efficiency of low Z elements through the use of a vacuum pump or He purge, combined with the optimization of instrument parameters for the detection of lower-energy fluorescence, is explored.

SUGGESTED SAMPLE

A paint-out mock-up of a mixture of ultramarine and cobalt blue paints applied to unprimed canvas; see appendix 2 for instructions.

EXPERIMENT

Analyze the sample using instrument conditions A–E (table 3.4). Position the nose of the XRF unit so that it is facing toward the painted surface side of the sample. If using a stand, place the painted surface of the sample down, toward the XRF nose. Make sure the sample lies flat so there is no air gap. If needed, use weighted ropes to flatten the canvas’s edges, but do not place the ropes in the direct beam path of the X-rays (fig. 3.5). For the “varnish” layer, use a Mylar film that is approximately 1 mil (25.4 mm) thick. Place the Mylar film between the painted surface and the nose of the XRF instrument.

Substrate and instrument contributions

Use the questions below to help interpret your results. Compare spectra for conditions A and C.

1. What are the elements contributing to the background (canvas substrate and instrument)?
2. What is the elemental composition of the paint mock-up?

Effect of vacuum

Compare spectra for conditions A–D.

3. What is the effect of the vacuum on the spectra for canvas substrate (A, B)?
4. For spectra C and D, how do you maximize for the low Z (atomic number) elements (here, Al, Si, S, K, Ca)? How do you maximize for the high Z elements (here, Co)?

Effect of mock varnish on analysis

Compare spectra for conditions D and E.

5. What is the effect of the Mylar film? Which elements are most affected by the addition of the Mylar film?

FIGURE 3.5. Photo showing position of the sample on the XRF head, with weights to ensure the canvas lies flat. Painted surface is directly facing the XRF aperture.

TABLE 3.4. Conditions A–E for exploring low and high Z elements within the same sample (mixture of ultramarine blue and cobalt blue paints) for exercise 3.1b.

Instrument:							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
A	Canvas substrate						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
B	Canvas substrate						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						
C	Canvas/Ultramarine–Cobalt blue mixture painted area						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
D	Canvas/Ultramarine–Cobalt blue mixture painted area						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						
E	Canvas/Ultramarine–Cobalt blue mixture painted area with one ca. 1 mil thick film on top to mimic “varnish” layer						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						

EXERCISE 3.1c:

Bone Black on Canvas: Exploring Low Z Elements and Possible Spectral Interferences

Here, further exploration of the peaks produced in the low-energy region of the spectrum, with emphasis on identification of overlaps and other possible interferences, is carried out on a painted sample containing the pigment bone black.

SUGGESTED SAMPLES

A paint-out mock-up of bone black applied to bare canvas; see appendix 2 for instructions. Note the reserved bare canvas area; it is important to analyze the substrate to understand its contributions to the spectral response. In addition, 16 small squares of copy paper, stacked.

EXPERIMENT

Collect spectra from the sample using conditions A–F (table 3.5). Position the sample (or instrument) so that the painted surface is in front of the XRF nose. The sample must lie flat, with no air gap. If needed, place weights at the edge of the canvas but not in the direct beam path of the X-rays.

TABLE 3.5. Conditions A–F for exploring low Z and possible spectral interferences (bone black on canvas) for exercise 3.1c.

Instrument:							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
A	Canvas substrate						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
B	Canvas substrate						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						
C	Bone black painted area						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
D	Bone black painted area						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						
E	16 copy paper sheets						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						
F	Bone black painted area						
	Low V, high I, vac, no filter, 30s						
	Spectrum name:						

Elemental composition of the paint layer

Use the questions below to help interpret your results. Compare spectra for conditions A and C.

1. What are the elements contributing to the background (canvas substrate and instrument)?
2. What is the elemental composition of the bone black paint?

Effect of vacuum

Compare spectra for conditions B and D.

3. What is the effect of vacuum on the spectral response?

Distinguishing real and artifact peaks: P Kα peak and Ca Kα escape peak

Compare spectra for conditions C, D and E.

4. What type of artifact peak of calcium (Ca) is coincident with the phosphorus (P) peak? ***Hint:*** Analysis of the 16 sheets of copy paper (spectrum E), which typically has a calcium-based filler or buffer compound, will help you visualize an artifact peak of calcium (unless your spectrometer is set to eliminate spectral artifacts automatically).
5. How can you determine whether phosphorus (P) is part of the paint composition or an artifact peak of calcium (Ca) is present?

Effect of accelerating potential

Compare spectra for conditions D and F.

6. Which accelerating potential (voltage) setting is better for low Z elements: 15 kV or 40 kV? Why?

EXERCISE 3.1d:

Alizarin Crimson on Canvas: Exploring Low Z Elements and Possible Spectral Interferences

This exercise investigates the peaks produced in the low-energy region of the spectrum for an organic pigment bound to a laking substrate, with emphasis on identification of overlaps and other possible interferences.

SUGGESTED SAMPLE

A paint-out mock-up of Winsor & Newton Designers Gouache alizarin crimson applied to bare canvas; see appendix 2 for instructions.

EXPERIMENT

Collect spectra from the sample using conditions A–D (table 3.6). Position the sample (or instrument) so that the painted surface is in front of the XRF nose. The sample must lie flat, with no air gap. If needed, place weights at the edge of the canvas but not in the direct beam path of the X-rays.

TABLE 3.6. Conditions A–D for exploring low Z elements and possible spectral interferences (alizarin crimson on canvas) for exercise 3.1d.

Instrument:							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
A	Canvas substrate						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
B	Alizarin crimson painted area						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
C	Alizarin crimson painted area						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						
D	Alizarin crimson painted area						
	Low V, high I, vac, no filter, 30s						
	Spectrum name:						

Elemental composition of the paint layer

Use the questions below to help interpret your results. Compare spectra for conditions A and B.

1. What are the elements contributing to the background (canvas background and instrument)?
2. What is the elemental composition of the alizarin crimson paint?

Effect of vacuum

Compare spectra for conditions B and C.

3. How does the vacuum affect the spectral response?

Effect of accelerating potential

For conditions C and D, compare the spectra you collected for the alizarin crimson painted area with different accelerating potential and current.

4. Which are the better conditions (voltage, current) for this paint mock-up, given its elemental makeup?

High Z Elements: Multiple Fluorescence Lines

In contrast to the detection of low Z elements explored in the previous exercises, which can fluoresce only through the emission of low-energy K lines, elements with higher atomic numbers can produce fluorescence at multiple energies (i.e., through K, L, and M emission lines). Detection is dependent both on the efficiency with which the lines are excited and on the efficiency with which they can be detected. Figure 2.3 (see chap. 2) provides a guide for determining which lines may be detected as a function of atomic number. A general rule of thumb is that the excitation voltage should be approximately 1.5 times greater than the absorption edge of the element of interest to efficiently produce fluorescence. For XRF spectrometers operating at excitation voltages of 50 kV, the upper limit for the excitation of K lines is reached at about barium (Z=56, absorption edge 37.44 keV). The detection of barium—both K and L lines—is explored later in this chapter, in exercises 3.2c (layers) and 3.2f (mixtures).

In practice, because the efficiency of the detectors commonly found in handheld XRF spectrometers starts to drop off at higher energies, for elements with atomic numbers above about 50 (Sn), the L lines become increasingly important to ensure accurate identification. For higher Z elements commonly encountered in cultural heritage materials—e.g., platinum, gold, mercury, and lead—the K lines are not excited by a tube operating at 50 kV; thus, the L lines, which appear between roughly 9 and 11 keV, are the primary means of identification.

One issue often encountered with higher Z elements, particularly those present in large quantities such as in a metal sculpture or a lead-ground painting, is that the production of fluorescent X-rays is so efficient it can saturate the detector and lead to instrumental artifacts such as sum peaks and escape peaks. These effects are more commonly encountered in instruments with a SiPIN detector than with the SDDs being put into the newer instruments, which can handle much higher count rates. Thus, it is important to know what kind of detector your instrument uses.

The exercises in this section explore the detection of materials containing high Z elements, focusing on the concepts of excitation of K, L, and M lines and the recognition of spectral artifacts such as sum peaks and escape peaks.

EXERCISE 3.1e:

Copper Alloy (Brass) Coupon: Spectral Artifacts Created by High Count Rates

In this exercise, a copper alloy coupon/plate, consisting mainly of copper (Cu), is studied to investigate how different current settings affect signal level and, in some cases, create spectral artifacts that can be misidentified. Metal samples typically give strong signals (high count rates), which can induce spectral artifacts such as sum peaks, escape peaks and saturation. To avoid saturation and spectral artifacts, optimizing the tube parameters for this situation is paramount.

SUGGESTED SAMPLE

A flat copper brass plate.

EXPERIMENT

Analyze the copper brass plate using conditions A and B (table 3.7).

TABLE 3.7. Conditions A and B for investigation of spectral artifacts created by high current for exercise 3.1e.

Instrument:							
	Sample / Condition	**Mode**	**Voltage**	**Current**	**Atm.**	**Filter**	**Time**
A	Copper brass plate						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
B	Copper brass plate						
	High V, medium I, air, no filter, 30s						
	Spectrum name:						

Effect of current

Use the questions below to help interpret your results. Compare spectra for conditions A and B.

1. How do the identified elements compare to the expected composition of the copper alloy?
2. How would you determine whether peaks are coming from the instrument or from the sample?
3. Are there spectral artifacts? If so, what is the origin of these artifacts? How can you determine whether these are real or artifact peaks?
4. How would you determine the optimal conditions (voltage, current, filter, acquisition time, vacuum/He or no vacuum/He) to analyze the metal alloy?

EXERCISE 3.1f:

Lead-Tin Solder Disk: Detecting High and Low Z Elements and Determining Spectral Artifacts

A sample of commercial solder containing both lead (Pb) and tin (Sn) is used to further explore how to collect meaningful spectra over a wide energy range. Furthermore, this exercise builds on the concepts learned in the previous section; specifically, how judicious selection of excitation parameters and vacuum/purge conditions can enhance the detection of lower-energy X-ray fluorescence lines (such as the Sn L lines).

As in exercise 3.1e, spectral artifacts are easily created in this type of sample. Importantly, one of the main objectives of exercise 3.1f is to learn to recognize the sum lines of lead (Pb), which are easily misidentified due to the coincidence of the lead (Pb) sum peaks with palladium (Pd Kα line, 21.19 keV), cadmium (Cd Kα line, 23.16 keV), and tin (Sn Kα line, 25.26 keV).

SUGGESTED SAMPLE

Lead-tin solder, flattened with a rubber or plastic mallet. Use the side that is smoother (fig. 3.6).

FIGURE 3.6. Flattened lead-tin solder. Use of a rubber mallet has created lines on the side of impact. The other side is smoother, with no lines; that side should be used in exercise 3.1f.

EXPERIMENT

Collect spectra from the lead-tin solder sample using conditions A–C (table 3.8).

TABLE 3.8. Conditions A–C for detecting Z elements and determining spectral artifacts of the lead-tin solder for exercise 3.1f.

Instrument:							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
A	Lead-tin solder						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
B	Lead-tin solder						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						
C	Lead-tin solder						
	High V, high I, air, no filter, 30s						
	Spectrum name:						

Effect of vacuum

Use the questions below to help interpret your results. Compare spectra for conditions A and B.

1. What are the elements identified for the lead-tin solder? What are the elements identified from the instrument?
2. What is the effect of vacuum?

Effect of current

Compare spectra for conditions A and C.

3. Comparing the low- and high-current conditions, are there spectral artifacts in these spectra? If so, what is the origin of these artifacts? How can you check whether a peak is real or an artifact?
4. How would you determine the optimal conditions (voltage, current, filter, acquisition time, vacuum, or air) to analyze the metal alloy?

3.2 Heterogeneous Materials: Spot Size, Layers, and Mixtures

Most cultural heritage objects are made up of a complex heterogeneous mixture of materials. If the scale of the heterogeneity is sufficiently large, it may be possible to isolate individual components or materials for XRF analysis. But if the heterogeneity is on a scale that is smaller than the spot size of the instrument or is present in the form of layers or mixtures, then the collected spectra will reflect *all* the materials present. The exercises in this section explore how XRF spectra are affected when the object of study is heterogeneous, in terms of either scale, layering, or mixtures of materials, and how careful analysis of the spectra can yield important information about the location of elements within a complex stratigraphy.

Spot Size

Most handheld XRF spectrometers have an aperture on the order of 3–8 mm; make sure that you know the aperture size for your particular instrument. While a relatively large aperture size may be appropriate for the examination of large-scale, relatively homogeneous materials such as modern metals, photographs, or large color fields in paintings, there are many cases where the scale of the feature of interest is smaller than the aperture of the instrument. This is most frequently encountered in the study of illuminated manuscripts, which typically consist of finely painted features. In these cases, the resulting XRF spectrum will have contributions from all the different individual components within the aperture area. ***Tip:*** It may be helpful to use a card or sheet of Mylar with an aperture cut to the same size as your instrument's spot size to visualize the different (surface) components that may be probed.

EXERCISE 3.2a:

Cadmium Red Lines on Titanium White Ground with Various Line Widths

In this exercise, you will study the effect of the spot size of the instrument relative to the scale of the feature under examination. XRF spectra are collected from a sample on which lines of cadmium red paint of different widths are painted over a titanium white ground, and the degree to which the spot size of the instrument allows for the individual elements to be isolated is explored. This exercise exemplifies the situation of analyzing fine details, such as might be found in a manuscript or drawing.

SUGGESTED SAMPLE

Titanium white applied to bare, unprimed canvas. Lines of cadmium red of different widths (1 mm, 3 mm, and 7 mm) are subsequently painted on top of the titanium white ground (fig. 3.7). See appendix 2 for instructions.

EXPERIMENT

Collect spectra from the sample using conditions A–D (table 3.9). Position the sample (or instrument) so that the painted surface is in front of the XRF nose. The sample must lie flat, with no air gap. If needed, place weights at the edge of the canvas but not in the direct beam path of the X-rays.

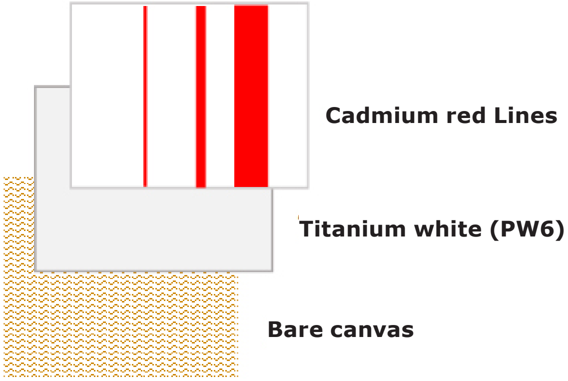


FIGURE 3.7. Diagram showing layers of sample used to study effect of spot size. Titanium white is applied to bare canvas, followed by lines of cadmium red of different widths.

TABLE 3.9. Conditions A–D for effect of spot size on cadmium red (CR) lines on titanium white ground with various line widths for exercise 3.2a.

Instrument:							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
A	Titanium white on canvas						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
B	Thin CR line (1 mm width)						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
C	Medium CR line (3 mm width)						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
D	Thick CR line (7 mm width)						
	High V, low I, air, no filter, 30s						
	Spectrum name:						

Effect of line width

Use the questions below to help interpret your results. Compare spectra for conditions A–D.

1. How are the spectra affected by the line widths? Which line width completely covers the spot size?
2. In each of the three line widths, is the titanium detected in the spectra due to the underlying paint or from the exposed sides?
3. The Ti K lines overlap with the Ba L lines. How do you approach understanding the peak positions in this region with the presence of both Ti and Ba in this mock-up?

Layers

Along with considering heterogeneity on the x-y plane, because X-rays are penetrating radiation, one also needs to consider heterogeneity in the z-direction. This is especially important in the case of layered materials. Many cultural heritage materials have a layered construction; for example, coatings, overlapping paint layers, or images present on both the recto and verso of a leaf from an illuminated manuscript. In cases such as these, where the layers cannot be physically separated, the collected XRF spectra will contain contributions from each layer. In some cases, careful examination of the XRF spectra can provide clues as to the composition and relative positioning of different layers.

In a layered structure, fluorescence emission from elements in the lower layers is reduced by two factors: (1) attenuation of the excitation beam by the upper layers, and (2) attenuation of the subsequently produced fluorescent X-rays as they pass through the upper layers on their way to the detector. In general, because lower-energy fluorescence is absorbed more readily than higher-energy fluorescence, this can create a recognizable change in the XRF lines produced from elements present in subsurface layers. This attenuation effect is most easily seen in the Pb L series of emission lines (fig. 3.8).

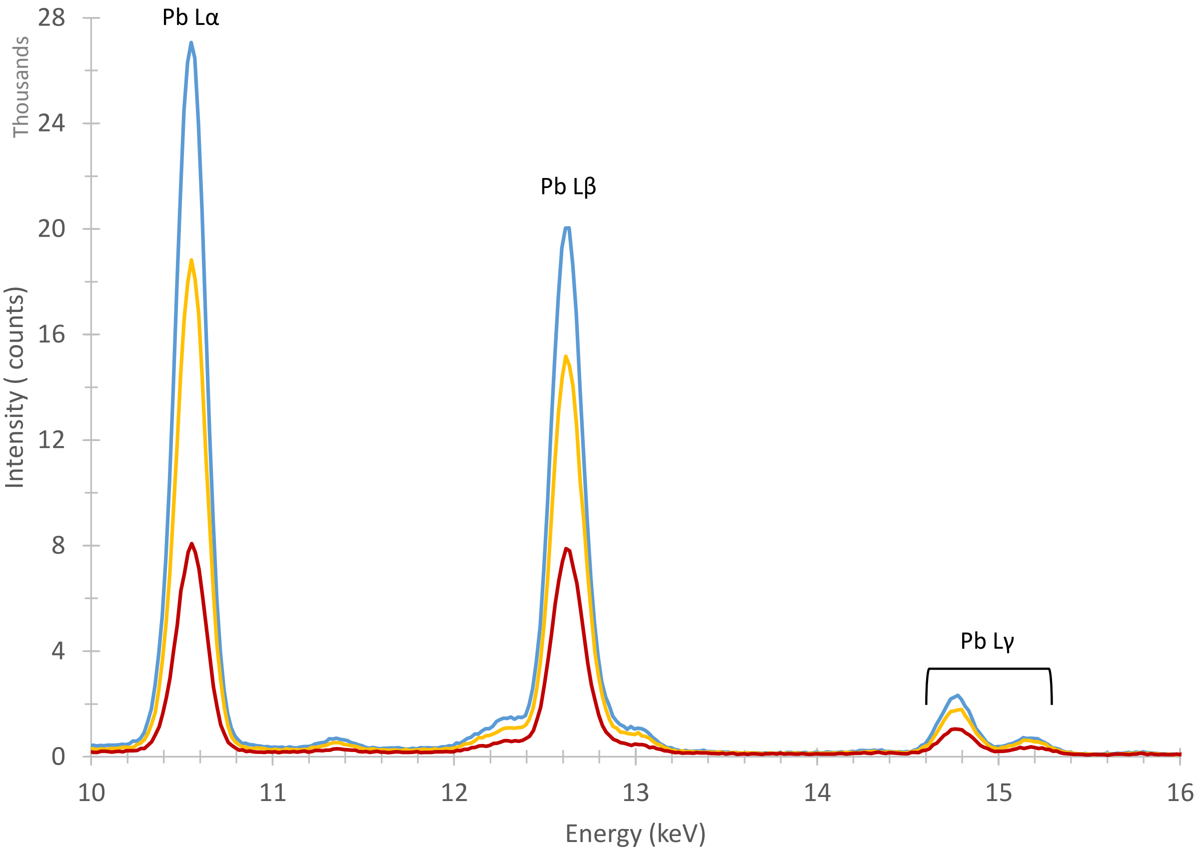


FIGURE 3.8. Spectra showing attenuation of Pb L lines, with Pb L lines on surface (blue trace) and in underlayer (medium depth, yellow trace, lower depth, red trace) with Lα/Lβ ratio inversion.

While this effect is more easily recognized in the L series lines, it can also occur between the Kα and Kβ lines in the K series, although for most elements these lines are sufficiently close in energy that the difference in attenuation may not be noticeable. It can also occur between different series produced by a single element: for example, elements for which both K and L emission lines are readily detectable, such as Sn and Ba, or M and L lines, such as Pb and Hg. In these cases, the lower-energy series lines will be attenuated to a much greater degree than the higher-energy lines. For example, in a sample in which Ba is present in a subsurface layer, the L series lines (at ~4.7 keV) will be strongly attenuated by material on the surface, while attenuation of the high-energy K series lines (at ~32 keV) will be minimal. In fact, attenuation of these low-energy lines can be so great that they may not be detectable at all. If the K lines of Ba are detected but no L lines are evident, this could be another indication of a layered structure.

This concept of the selective attenuation of lower-energy lines compared to higher-energy lines in stratified samples is explored in exercises 3.2b and 3.2c, in which mock-up samples mimick metals with corrosion layers and paintings consisting of multiple layers of paint, respectively.

Example: If lead is present on the surface of a layered paint sample, the Lα line will generally be larger than the Lβ line (see fig. 3.8). By contrast, if the lead is present in a subsurface layer (with the surface layer consisting of lower Z elements), each Pb L emission line will be attenuated differently according to its energy: the lower-energy Lα line will be attenuated the most, with the higher-energy Lβ line being attenuated to a lesser extent. The result of this is a change in the relative intensity of the Pb L lines. If the attenuation by the upper layer is sufficiently large, the ratio of the Lα/Lβ lines can even be inverted so that the Lβ line is the most intense in the series. This so-called inversion of the Lα/Lβ ratio is a good indication that the Pb is not *all* at the surface. Likewise, however, it should not immediately be assumed that the Pb is all in a sub-surface layer. As explored in the exercises in this section, such effects can be created by other factors, notably the presence of mixtures, as well as layered structures.

EXERCISE 3.2b:

Lead-Tin Solder with Malachite Paint Layers: Effects of "Corrosion" Layers

In this exercise, XRF spectra are collected from samples of lead-tin solder over which different thicknesses of the copper-containing pigment malachite have been painted to mimic surface corrosion in order to explore how surface layers affect spectra from the underlying substrate.

SUGGESTED SAMPLE

Three pieces of lead-tin solder wire, flattened with a rubber or plastic mallet. One piece remains bare; the second piece is covered with a layer of malachite paint; the third piece is covered with four layers of malachite paint. See appendix 2 for instructions.

EXPERIMENT

Collect spectra from the sample using conditions A–C (table 3.10). The painted side of the latter two samples should face the nose of the instrument.

TABLE 3.10. Conditions A–C for studying effect of surface layers on spectra from underlying substrates of lead-tin solder for exercise 3.2b.

Instrument:							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
A	Bare solder						
	High V, low I, vac, no filter, 90s						
	Spectrum name:						
B	1 layer of malachite paint						
	High V, low I, vac, no filter, 90s						
	Spectrum name:						
C	4 layers of malachite paint						
	High V, low I, vac, no filter, 90s						
	Spectrum name:						

Effect of corrosion thickness

Use the questions below to help interpret your results. Compare spectra for conditions A–C.

1. What is the composition of the bare solder?
2. How are the spectra affected by the thin and thick layers of malachite, that is, "corrosion"?
3. How are different parts of the energy spectrum affected by the corrosion layer? Why?
4. What is the nominal $L\alpha/L\beta$ ratio for the Pb L lines? How does the corrosion layer(s) affect this ratio? What conclusions can be drawn about the layering based on the Pb $L\alpha/L\beta$ ratio?

EXERCISE 3.2c:

Titanium White and Lithopone Painted Layers on Canvas: Paint Layers

This exercise examines a layered paint sample in which titanium white is present as the base layer and lithopone as the upper layer. This layered sample will also be used to compare different titanium white–lithopone mixtures in exercise 3.2f.

SUGGESTED SAMPLES

Sample 1: Unprimed bare canvas/titanium white (PW6) / lithopone (PW5). In addition, prepare two unprimed canvas samples, each painted with unmixed tubes of titanium white (sample 2) and lithopone (sample 3). See appendix 2 for instructions.

EXPERIMENT

Collect spectra from the samples using conditions A–E (table 3.11). Position the sample (or instrument) so that the painted surface is in front of the XRF nose. The sample must lie flat, with no air gap. If needed, place weights at the edge of the canvas but not in the direct beam path of the X-rays.

TABLE 3.11. Conditions A–E for examining titanium white and lithopone painted layers on bare canvas for exercise 3.2c.

Instrument:							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
A	Bare unprimed canvas						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
B	Titanium white (PW6) on canvas (unmixed tube paint)						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
C	Lithopone (PW5) on canvas (unmixed tube paint)						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
D	Canvas/PW6/PW5: Painted area, front side (facing detector)						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
E	Canvas/PW6/PW5: Painted area, back side (canvas facing detector)						
	High V, low I, air, no filter, 30s						
	Spectrum name:						

Analysis of unmixed paints on canvas

Use the questions below to help interpret your results. Compare spectra for conditions A–C.

1. What is the purpose of measuring the bare canvas, the titanium white only on canvas, and the lithopone paint only on canvas?

Analysis of layered mock-up: Canvas / titanium white / lithopone

Compare spectra for conditions D and E.

2. How do the spectra from the front and back sides differ?
3. The Ti K lines overlap the Ba L lines. How do you approach understanding the peak positions in this region with the presence of both Ti and Ba in this mock-up?

Interleaving Materials

The exercises above explore how careful interpretation of XRF spectra can yield clues as to whether a detected element is at the surface or in an underlying layer. This can be of importance in cases where there is a layer of material between the layer of interest and the instrument (e.g., a corrosion, dirt, or varnish layer). However, the same concepts can be applied to the selection of an interleaving material to reduce unwanted fluorescence from underlying materials (e.g., from supports or underlying folios in a bound manuscript). In this section, we explore how the thickness and composition of different materials affect the resulting spectra from underlying materials, with specific attention to the selection of interleaving materials.

An interleaving material must not contain any elements that themselves would create fluorescence. Thus, interleaving materials typically contain only very low Z elements, such as C, H, N, O, F, and Al. Common interleaving materials are Teflon (PTFE), Plexiglas (polymethyl methacrylate, or PMMA), cellulose (paper), or aluminum. Aluminum is generally preferable because it not only is more efficient at blocking unwanted X-ray fluorescence but also does not produce as strong a scattering background as do purely organic materials such as PMMA (see chap. 2, sec. 2.3, for a discussion and exercises on how scattering from a low Z support can affect the spectrum). Air can also be used as an interleaving material but, due to its low density, requires much greater thicknesses to be effective.

EXERCISE 3.2d:

Lead-Tin Solder Disk with Aluminum Sheets

In this exercise, the use of aluminum sheets as an interleaving material is explored by measuring the attenuation of Pb emission lines as the number of sheets of aluminum foil placed between the Pb and the detector is gradually increased.

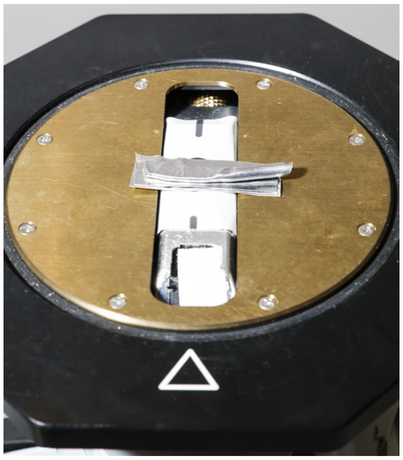


FIGURE 3.9. Photo showing position of lead-tin solder sample, with aluminum sheets between the sample and the XRF aperture.

SUGGESTED SAMPLE

Lead-tin solder wire, flattened to a disk with a rubber or plastic mallet; aluminum sheets, cut into smaller pieces that will cover the XRF aperture.

EXPERIMENT

Collect spectra from the sample using conditions A–D (table 3.12). Place aluminum sheets between the bare disk/wire and the XRF aperture (fig. 3.9).

Attenuation of spectral components

Use the questions below to help interpret your results. Compare spectra for conditions A–D.

1. What is the Pb Lα/Lβ line ratio in the bare solder disk?
2. How did the Al sheets affect the spectra of the lead-tin solder? How many sheets were needed to see the attenuation effect on the Pb Lα and Pb Lβ lines? On the Sn K lines? On the Sn L lines?
3. What general conclusions can you draw about how the different parts of the energy spectrum are affected by attenuation; that is, are the lower Z elements more sensitive to attenuation compared to the higher Z elements?

TABLE 3.12. Conditions A–D for measuring attenuation of Pb emission lines on layering of aluminum sheets for exercise 3.2d.

Instrument:							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
A	Bare lead-tin solder						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						
B	Lead-tin solder disk with (1) Al sheet						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						
C	Lead-tin solder disk with (2) Al sheets						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						
D	Lead-tin solder disk with (4) Al sheets						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						

EXERCISE 3.2e:

Layered Titanium White and Phthalocyanine Green 7 (PG7) with Sheets of Copy Paper for Attenuation of the Copper (Cu) Peak

Here, attenuation of lower-energy Cu K emission lines is monitored as the number of sheets of copy paper (not as high density as Al sheets) between the sample and the detector is increased. This may exemplify the situation encountered when analyzing pages in a bound manuscript in which there may be contributions from inks or pigments on the verso or from other pages behind the one being examined.

SUGGESTED SAMPLE

Paint the following layered mock-up: unprimed bare canvas / titanium white (PW6) / PG7; see appendix 2 for instructions.

EXPERIMENT

Collect spectra from the sample using conditions A–D (table 3.13). Position the sample (or instrument) so that the painted surface is in front of the XRF nose. Insert the indicated number of sheets of copy paper (8 sheets, approximately 1.5 mm thickness total; 16 sheets, approximately 3 mm thickness total) between the surface of the painted canvas and the XRF nose.

TABLE 3.13. Conditions A–D for monitoring attenuation of emission lines based on layering of sheets of copy paper for exercise 3.2e.

Instrument:							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
A	Painted canvas, no paper sheets						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						
B	Painted canvas, (1) paper sheet						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						
C	Painted canvas, (8) paper sheets						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						
D	Painted canvas, (16) paper sheets						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						

Attenuation of spectral components

Use the questions below to help interpret your results. Compare spectra for conditions A–D.

1. What is the elemental composition of the painted surface?
2. How did the sheets of paper affect the paint spectrum? Which elements were most impacted?
3. Why did it require more paper sheets to see the attenuation effect compared to the aluminum sheets in exercise 3.2d using the lead-tin solder?

Mixtures

Of course, not all heterogeneity is present in the form of different layers. Many, if not most, materials are intimate mixtures of different elements, creating heterogeneity on multiple scales. For example, copper alloys, paint mixtures, or natural stones are heterogeneous mixtures but on different length scales. However, for all these cases, since the scale of the heterogeneity is smaller than the spot size of the XRF instrument, all the elements will be simultaneously excited, and the resulting fluorescence emission from one element may be absorbed by other elements present in the surrounding matrix. The effect is similar to that observed in the layered structures explored in the above exercises, where absorption can noticeably affect the resulting XRF spectrum.

Learning to distinguish when elements are present as mixtures, as opposed to layers, is explored here: the analysis of samples containing titanium white and lithopone as separate layers is compared to results obtained when these materials are mixed together in a single layer. The ability to discriminate between these two states is complicated by the fact that the two main elements, Ti and Ba, produce emission lines that overlap. However, as discussed above, absorption—whether by an overlying layer or material in a surrounding matrix—will preferentially attenuate the lower-energy lines of an element (e.g., Ba L lines compared to Ba K lines), which may help determine the relative position of Ba within the samples' structure.

EXERCISE 3.2f:

Varying Ratio of Titanium White and Lithopone Mixtures

Here, we explore how to determine the presence of an element when there is coincidence of the elemental peaks—in this case, titanium (Ti K lines) and barium (Ba L lines)—in a paint mixture. The three samples prepared for this exercise will be compared with the layered paint sample used in exercise 3.2c.

SUGGESTED SAMPLE

Three pieces of painted canvas. Prepare mixtures of titanium white and lithopone in ratios of 1:1, 10:1, and 1:10. Paint a single layer on a piece of unprimed bare canvas for each of these mixtures. See appendix 2 for instructions.

EXPERIMENT

Collect spectra from the samples using conditions A–D (table 3.14). Position each sample (or instrument) so that the painted surface is in front of the XRF nose. The sample must lie flat, with no air gap. If needed, place weights at the edge of the canvas but not in the direct beam path of the X-rays.

TABLE 3.14. Conditions A–D for monitoring effect of varying paint ratios on spectra for exercise 3.2f.

Instrument:							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
A	Bare unprimed canvas						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
B	1:1 titanium white: lithopone mixture						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
C	1:10 titanium white: lithopone mixture						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
D	10:1 titanium white: lithopone mixture						
	High V, low I, air, no filter, 30s						
	Spectrum name:						

Resolution of overlapping Ti and Ba peaks

Use the question below to help interpret your results. Compare spectra for conditions A–D.

1. How do the different ratios of titanium white and lithopone affect the spectra?

Mixtures vs. layers of titanium white and lithopone on canvas

Compare spectra for conditions B and C with those from exercise 3.2c (D, front; E, back).

2. In comparing the Ti/Ba layers (see exercise 3.2c; D, front; E, back) and mixtures spectra, can you distinguish which are mixtures and layers? Explain.

3.3 Sensitivity and Detection of Minor/Trace Elements

The detection of elements present in minor or trace quantities requires the analyst to have a good understanding of not only how the instrument responds to low signal levels but also which signals originate from the sample and which originate from the instrument itself. The latter was explored in chapter 2, exercises 2.3a and 2.3c. It is important to remember that the instrument can produce fluorescence emission from elements present in the instrument, along with a broad spectral background (bremsstrahlung). Therefore, if trace or minor elements are of interest, it is always a good idea to collect a fresh spectrum of the instrument profile for comparison, using the same conditions as the spectrum of the sample.

Sometimes elements may be present, but below the limit of detection for the instrument. This concept is explored in exercise 3.3a in which a series of paint-outs containing decreasing amounts of the pigment Prussian blue is analyzed. Prussian blue is an iron-based pigment—ferric ferrocyanide ($Fe_4[Fe(CN)_6]_3$)—that has a very high tinting strength. Thus, although it may be visibly present, the amount of Fe K fluorescence may be below the detection limit or indistinguishable from the instrument background. In cases such as this, it may be helpful to collect spectra over a longer period than might be used for evaluation of more abundant elements to improve the signal-to-noise ratio.

The limits of detection and presence of trace/minor components are also important in the study of photographs. In exercises 3.3b and 3.3c, spectra from areas of maximum and minimum density on a photograph are compared to determine which elements are related to image forming or toning materials and which may be arising from elements present in the paper substrate (or other mounting materials). In addition, spectra are collected with the photograph mounted both with and without a Plexiglas backing sheet to assess the influence of scattering on the ability to detect elements present in small quantities (for more discussion on positioning of the XRF unit, see chap. 4).

Although not addressed here, advanced users can better assess trace detection by collecting multiple spectra, exporting raw data (when possible), and performing statistics on averaged results for specific elements.

The scattering of X-rays is inversely proportional to the average atomic number of the sample: X-rays are scattered more strongly from low Z materials than from high Z materials. If the elements of interest are present only in minor or trace quantities, an increase in background due to scattering may mask their presence. For thick low Z materials, such as the glass tile used in exercise 3.1a, the contribution to the background due to scattering generally cannot be avoided. However, for very thin materials such as drawings or photographs, where X-rays easily penetrate to the supporting material, contributions from scattering may be mitigated by judicious choice of a mounting strategy. A common example is a photograph mounted on a Plexiglas sheet, which can mask small peaks due to the large scattering background, compared to a photograph mounted such that only air is behind it during analysis; this will be explored in exercises 3.3b and 3.3c, and later in exercise 3.3d for drawing materials on paper.

EXERCISE 3.3a:

Prussian Blue Serial Dilution with Titanium White

A series of paint-outs containing serial dilutions of the pigment Prussian blue is analyzed to compare the sensitivity of detecting the Fe K fluorescence relative to detecting the color visually.

SUGGESTED SAMPLE

Paint-outs on unprimed bare canvas, prepared using mixtures A–E of Prussian blue and titanium white (figs. 3.10, 3.11). See appendix 2 for instructions.

Mixture A: 0.01 g Prussian blue with 12 g titanium white

Mixture B: 1:1 mixture A: titanium white

Mixture C: 1:1 mixture B: titanium white

Mixture D: 1:1 mixture C: titanium white

Mixture E: 1:1 mixture D: titanium white

A final mixture, mixture F, is titanium white paint only and will be used as the background measurement. For each mixture sample, cut the canvas to a size that will fit underneath the safety cap.

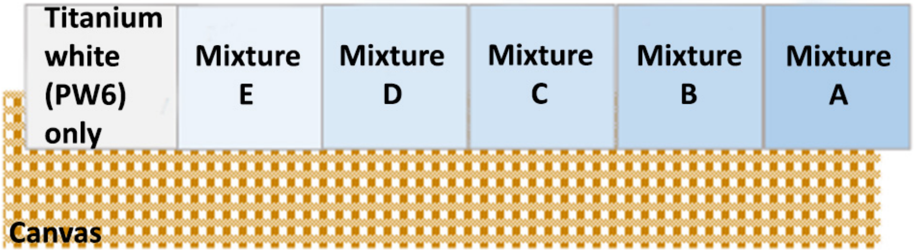


FIGURE 3.10. Schematic showing serial dilution of Prussian blue for the mock-up.

FIGURE 3.11. Photo showing painted areas of Prussian blue on the canvas.

EXPERIMENT

Position the sample (or instrument) so that the painted surface is in front of the XRF nose. Collect spectra from each portion of the paint-out (mixtures A–E) and pure titanium white (mixture F) according to the conditions described in table 3.15.

TABLE 3.15. Conditions A–F for serial dilution of Prussian blue paint-outs with titanium white for exercise 3.3a.

Instrument:							
	Sample / Condition	**Mode**	**Voltage**	**Current**	**Atm.**	**Filter**	**Time**
A	Mixture A						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
B	Mixture B						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
C	Mixture C						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
D	Mixture D						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
E	Mixture E						
	High V, low I, air, no filter, 30s						
	Spectrum name:						
F	Titantium white only						
	High V, low I, air, no filter, 30s						
	Spectrum name:						

Limits of color perception vs. iron detection via XRF

Use the questions below to help interpret your results. Compare spectra for conditions A–F.

1. What is the elemental composition of the serial dilutions?
2. At what dilution is it difficult to determine the presence of Prussian blue?
3. Would a longer acquisition time help in determining the presence of the iron (Fe) peak? Why or why not?

EXERCISE 3.3b:

Black-and-White Photograph, with and without PMMA Backing

This exercise focuses on detection of trace elements in a photograph, with emphasis on learning to distinguish trace elements in image/toning materials from those in the substrate or the instrument itself. In addition, the effect of scattering from a low Z mounting material on the ability to detect low-intensity fluorescence signals is explored.

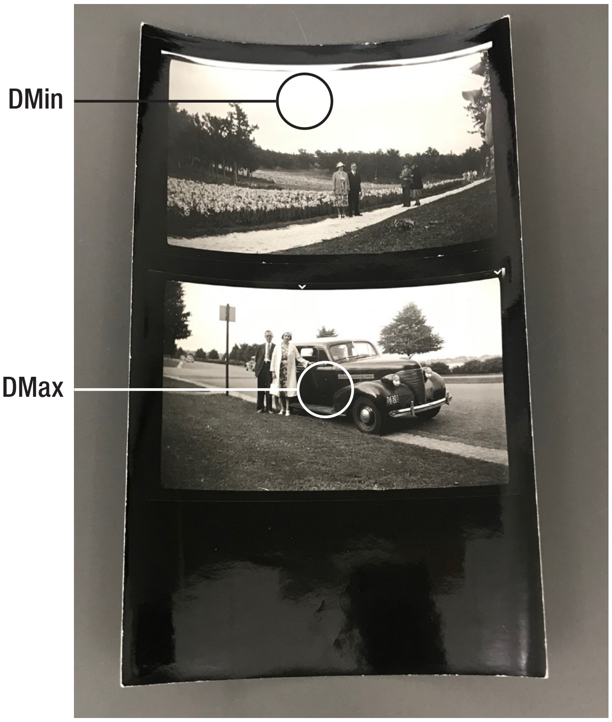


FIGURE 3.12. Indicated areas of DMax and DMin on a silver gelatin photograph. From the study collection of Paul Messier, head of the Lens Media Lab at Yale University's Institute for the Preservation of Cultural Heritage.

SUGGESTED SAMPLE

A black-and-white silver gelatin photograph that has sufficiently large dark (DMax), gray (DMedium), and light/white (DMin) areas to be analyzed by the XRF spectrometer (fig. 3.12). For the backing condition, use a relatively thick sheet of PMMA.

EXPERIMENT

Position the sample (or instrument) so that the photographic surface is in front of the XRF nose. Collect spectra from the photograph using conditions A–D (table 3.16).

Analysis of areas with increasing image density

Use the questions below to help interpret your results. Compare spectra for conditions A–C.

1. For silver gelatin prints, what are the elements of interest? What instrument conditions would you use to observe these elements?
2. What is the elemental composition of the DMin area? How does this inform us about the elemental composition of the photograph substrate?
3. What is the elemental composition of the DMedium and DMax areas?
4. Are any elements due to the instrument?

Effect of PMMA backing on spectra

Compare spectra for conditions C and D.

5. What is the effect of the PMMA backing? How does the PMMA backing affect interpretation of the spectral peaks? What could you do to counteract the effect of the mounting (here, PMMA backing) on the resulting spectra?

TABLE 3.16. Conditions A–D for detection of trace elements in a black-and-white photograph with and without PMMA backing for exercise 3.3b.

Instrument:							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
A	DMin area (low density, light/ white area)						
	High V, low I, vac, no filter, 120s						
	Spectrum name:						
B	DMedium area (medium density, gray area)						
	High V, low I, vac, no filter, 120s						
	Spectrum name:						
C	DMax area (high density, black area)						
	High V, low I, vac, no filter, 120s						
	Spectrum name:						
D	DMax area (high density, black area) w/ PMMA backing						
	High V, low I, vac, no filter, 120s						
	Spectrum name:						

EXERCISE 3.3c:

Albumen Photograph Print: Effect of Filter

This exercise builds on what was learned in exercise 3.3b to include using filters. It is intended to help in choosing appropriate instrument parameters to increase sensitivity in detecting elements that have a low signal-to-noise ratio.

SUGGESTED SAMPLE

An albumen photograph that has sufficiently large dark (DMax) and light/white (DMin) areas to be analyzed by the XRF spectrometer (fig. 3.13).

EXPERIMENT

Position the sample (or instrument) so that the photographic surface is in front of the XRF nose. Collect spectra from the photograph using conditions A–C (table 3.17).

Analysis of areas with increasing image density

Use the question below to help interpret your results. Compare spectra for conditions A–C.

1. How does the use of filters affect the analysis of photographs?

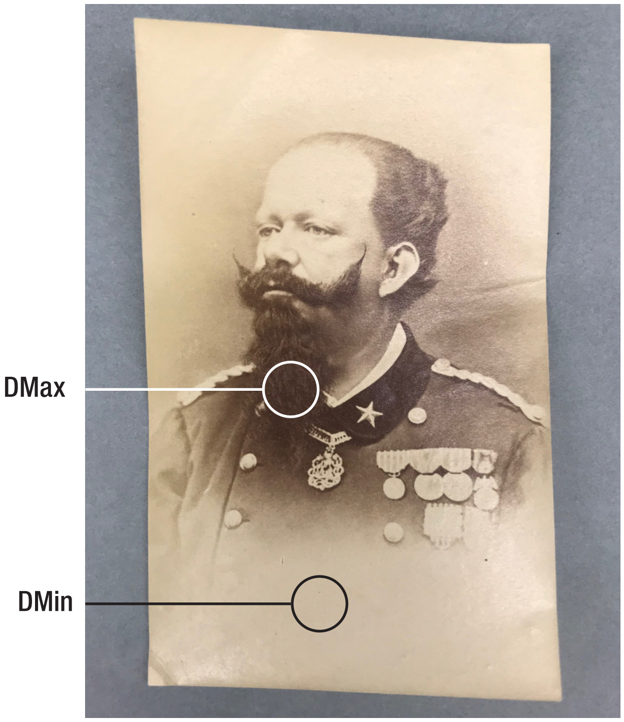


FIGURE 3.13. Indicated areas of DMax and DMin on an albumen photograph. From the study collection of Paul Messier, head of the Lens Media Lab at Yale University's Institute for the Preservation of Cultural Heritage.

TABLE 3.17. Conditions A–C for determining effect of filters on analysis of albumen photographs for exercise 3.3c.

Instrument:							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
A	DMax area (dark)						
	High V, high I, vac, no filter, 120s						
	Spectrum name:						
B	DMax area (dark)						
	High V, high I, vac, Cu/Ti/Al filter, 120s						
	Spectrum name:						
C	DMin area (light)						
	High V, high I, vac, Cu/Ti/Al filter, 120s						
	Spectrum name:						

EXERCISE 3.3d:

Drawing Materials on Paper: Sensitivity, with and without PMMA Backing

Here, three carbon-based black drawing media are studied. Since carbon cannot be detected via XRF, this exercise explores the challenge of whether elements present in trace or minor amounts can be distinguished from the instrumental background, and whether these trace elements may enable different black drawing media to be distinguished. As with the previous exercise, the influence of scattering from a Plexiglas mounting support on the ability to discern small peaks is explored.

SUGGESTED SAMPLE

Sheet of watercolor paper. On the paper, scribble a thick layer of each drawing media (graphite pencil, lithographic crayon, and black pastel) in the shape of a square that is larger than the instrument aperture. Make sure coverage is complete. ***Tip:*** Cut out the samples to a size that will fit underneath the safety cap, if using.

TABLE 3.18. Conditions A–H for detection of trace or minor elements in carbon-based drawing materials on paper, with and without backing, for exercise 3.3d.

Instrument:							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
A	Paper substrate						
	High V, low I, vac, no filter, 120s						
	Spectrum name:						
B	Graphite pencil on paper						
	High V, low I, vac, no filter, 120s						
	Spectrum name:						
C	Graphite pencil on paper with PMMA backing sheet						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						
D	Graphite pencil on paper						
	High V, low I, air, no filter, 120s						
	Spectrum name:						
E	Black pastel on paper						
	High V, low I, vac, no filter, 120s						
	Spectrum name:						
F	Black pastel on paper with PMMA backing sheet						
	High V, low I, vac, no filter, 120s						
	Spectrum name:						
G	Black pastel on paper						
	High V, low I, air, no filter, 120s						
	Spectrum name:						
H	Lithographic crayon on paper						
	High V, low I, vac, no filter, 120s						
	Spectrum name:						

EXPERIMENT

Position the sample (or instrument) so that the surface with the drawing media is in front of the XRF nose. Collect spectra from each of the three black drawing media using conditions A–H (table 3.18). For the backing condition, use a relatively thick sheet of PMMA.

Sensitivity to minor components

Use the questions below to help interpret your results. Compare spectra for conditions A, B, E, and H.

1. What is the elemental composition of the watercolor paper substrate? What is the elemental composition of each drawing material?

Impact of vacuum on spectra

Compare spectra for conditions B, D, E, and G.

2. What is the effect of vacuum?

Effect of PMMA backing sheet on spectra

Compare spectra for conditions B, C, E, and F.

3. How did the PMMA backing sheet affect the graphite pencil and black pastel spectra?

3.4 Distance/Topography

Distance from instrument to sample, and topography of the sample, can have an effect on the resulting XRF spectrum. Most handheld XRF spectrometers are designed to be operated with the nose in direct contact with the sample. However, this may not always be possible, either because the surface of the object may be marred by contact with the spectrometer or may not be flat enough to obtain sufficient contact. Increasing the distance from instrument to sample will have two effects, both of which will reduce the signal: (1) because the angle of the incident X-ray beam and detector are fixed, the detector will no longer be at the correct angle to efficiently collect fluorescence emission from the area excited by the incident beam, and (2) the increased volume of air through which the fluorescence emission must pass will preferentially attenuate lower-energy emission lines.

Exercise 3.4a explores the effect of distance and topography on the resulting XRF spectrum. To demonstrate this concept, the topography of the samples may be exaggerated compared to what may be normally encountered in the course of analysis, but it is important to note that even small distances may affect the signal.

EXERCISE 3.4a:

Phthalocyanine Green 7 (PG7) Painted on Pleated Filter Paper

This exercise explores the concepts of distance and topography by collecting spectra of paint that contains copper (Cu K at 8.05 keV) and chlorine (Cl K at 2.62 keV) applied to paper, then folded into pleats to create an exaggerated topography. By comparing spectra collected on the flat paper with spectra collected from the peaks, troughs, and sides of the folded paper, the effect of the air, both on the total signal loss, and preferential suppression of the lower energy Cl line compared to the higher energy Cu line, will be explored.

SUGGESTED SAMPLE

Two sheets of filter paper, painted with PG7. The first sheet will remain flat. The second sheet will be folded to make pleats (fig. 3.14). See appendix 2 for complete instructions. There should be several pleats on one sheet of filter paper so that the pleat trough, pleat apex, and pleat sides are accessible to the XRF head.

EXPERIMENT

Position the sample (or instrument) so that the painted surface is in front of the XRF nose. Several possible configurations are shown in figures 3.15a–d. Note that tape was applied to areas not in the vicinity of the XRF aperture. Collect spectra according to conditions A–D (table 3.19).

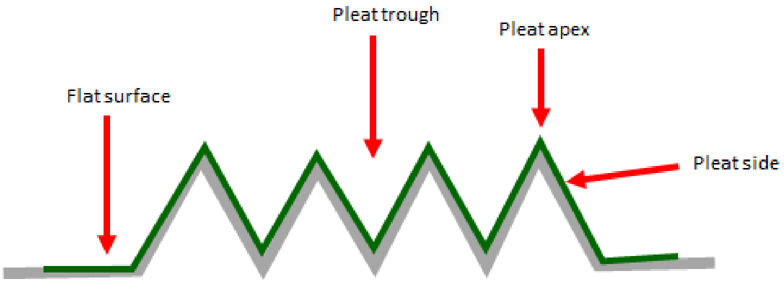


FIGURE 3.14. Schematic showing how to fold the painted filter paper, showing areas of flat surface, pleat trough, pleat apex, and pleat side.

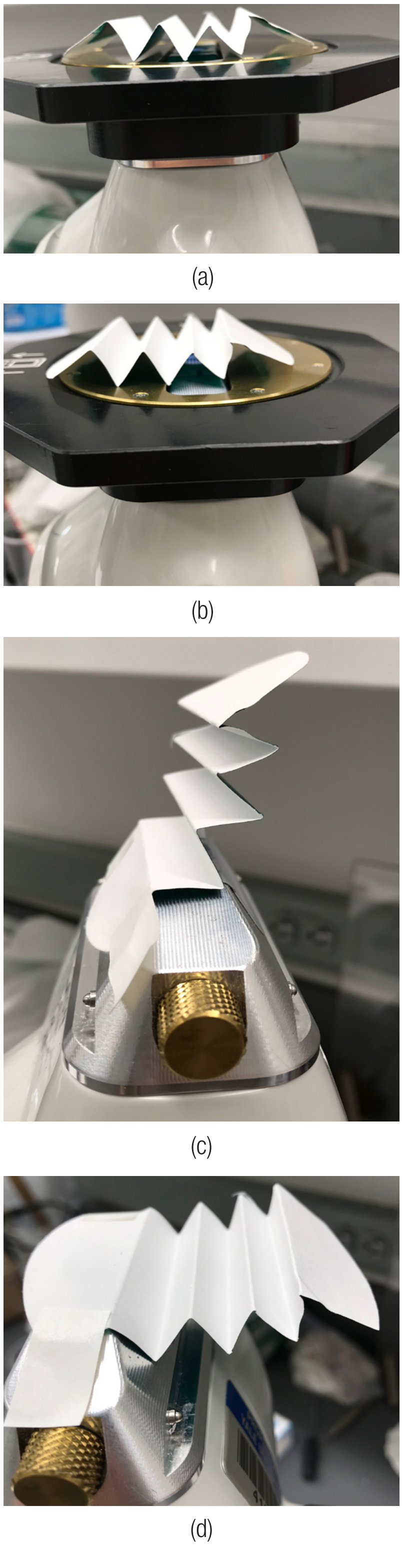

(a)
(b)
(c)
(d)

FIGURE 3.15a–d. Suggested configuration for analysis of (a) pleat apex area, (b) pleat trough, (c) pleat side, and (d) flat surface (as an alternative, you may use a separate painted, unfolded sheet for this configuration). For all configurations, make sure any tape does not overlap the aperture area.

TABLE 3.19. Conditions A–D for determining effect of distance/topography on pleated paper painted with phthalocyanine green (PG7) for exercise 3.4a.

Instrument:							
	Sample / Condition	**Mode**	**Voltage (V)**	**Current (I)**	**Atm.**	**Filter**	**Time**
A	Flat painted area						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						
B	Pleated painted area, apex						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						
C	Pleated painted area, side						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						
D	Pleated painted area, trough						
	High V, low I, vac, no filter, 30s						
	Spectrum name:						

Effect of flat and pleated areas

Use the questions below to help interpret your results. Compare spectra for conditions A–D.

1. Does the relative intensity of the peaks change in the different sections? Calculate the ratio between copper (Cu) and chlorine (Cl) peak intensities. Which peak (Cu or Cl) is more affected by the attenuation?
2. Do you trust your ability to be consistent in holding the unit for the pleat apex, side, and trough sections? Why is this important?

3.5 Expected Outcomes

EXERCISE 3.1a:

Glass: Detecting Full Spectral Energy Range

Effect of accelerating potential (voltage)

Spectra used in addressing the following questions from exercise 3.1a are shown in figure 3.16.

1: How does the spectrum acquired at 40 kV compare with its 15 kV counterpart?

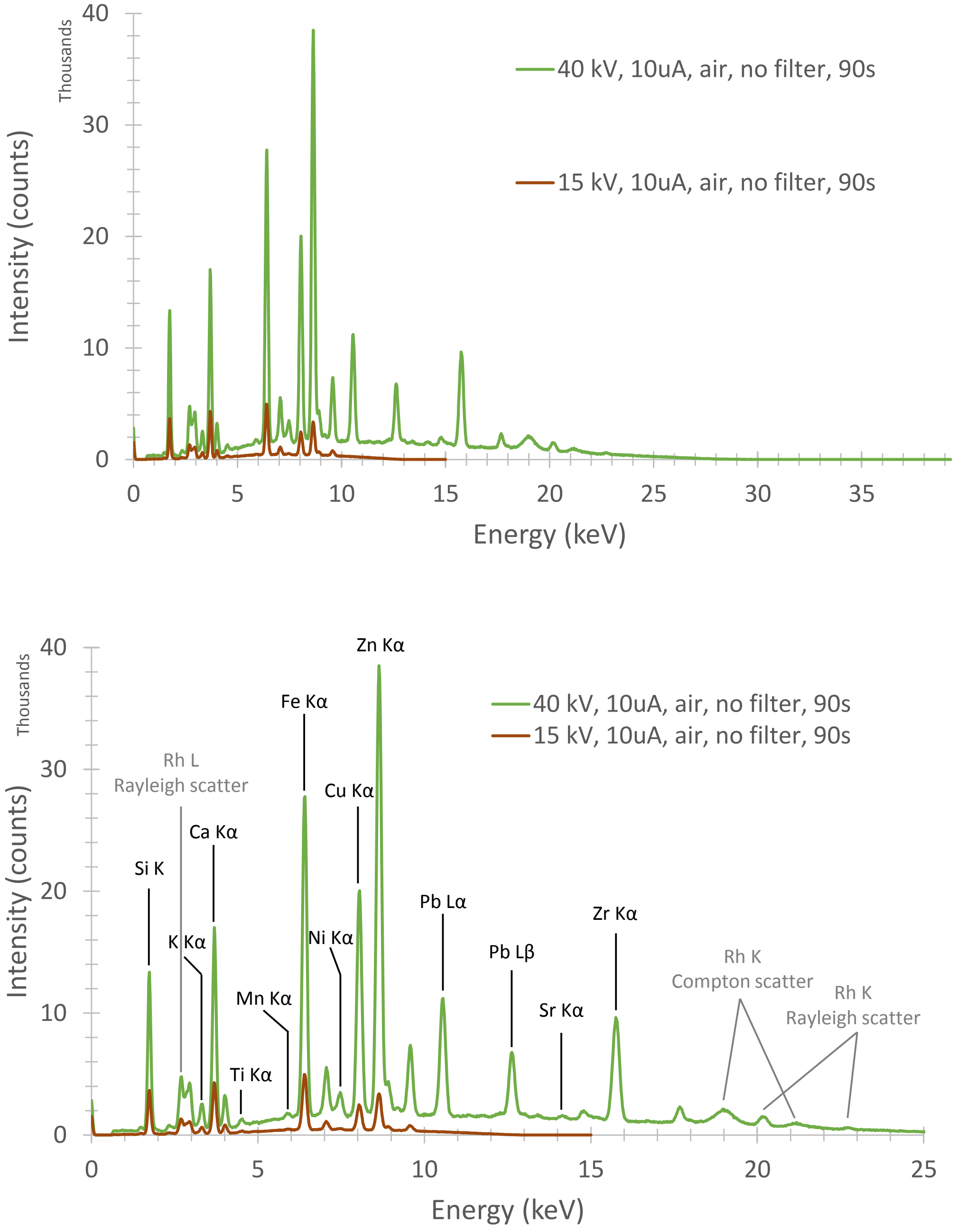


FIGURE 3.16. Spectra (with detail, bottom) for analysis of glass mosaic tile (effect of accelerating potential) in exercise 3.1a. Data collected using a Bruker Tracer III-SD, Rh tube.

- The higher accelerating potential (40 kV) is able to excite higher-energy X-ray lines (Pb L lines, Sr K lines, Zr K lines) that are not excited at the 15 kV setting. At the 40 kV setting, the Rh K lines of the X-ray source anode are excited and are visible due to Rayleigh (elastic) scattering and Compton (inelastic) scattering.
- The 15 kV accelerating potential is better suited to the excitation of light elements (Si, K, Ca) relative to the transition metal elements than the 40 kV setting. Relative to Mn, Fe, Ni, Cu, and Zn, the intensities of Si, K, and Ca lines are higher at 15 kV.

2: If you did not know the conditions, how can you deduce what voltage was used from the spectrum?

- Looking at the X-axis, which is the applied accelerating potential, the spectral curve will decrease to zero at the maximum applied potential (voltage).

EXPLANATION OF OBSERVATIONS

For a specific X-ray line in the sample to be excited, the accelerating potential (in kV) must be greater than the excitation potential of the X-ray line (in keV).

Effect of current

Spectra used in addressing the following questions from exercise 3.1a are shown in figure 3.17.

3: What are the elements identified using the 15 kV, 10 μA (low V, mid I) conditions, and how does this compare to results obtained with a higher current? Which condition yields a less noisy spectrum?

- The current cannot be controlled for every XRF spectrometer. In some instruments the current is automatically adjusted.
- A higher-current at the same accelerating potential increases the intensity of the excitation spectrum, and correspondingly increasing the signal intensity, allowing, in this example, the Al peak to be observed. There is also an increase in the intensity of the scattered and detected background, which consists of the continuum (bremsstrahlung radiation) and the characteristic lines of the X-ray anode (Rh L lines, in this case).
- The signal-to-noise ratio improves at higher-current settings.

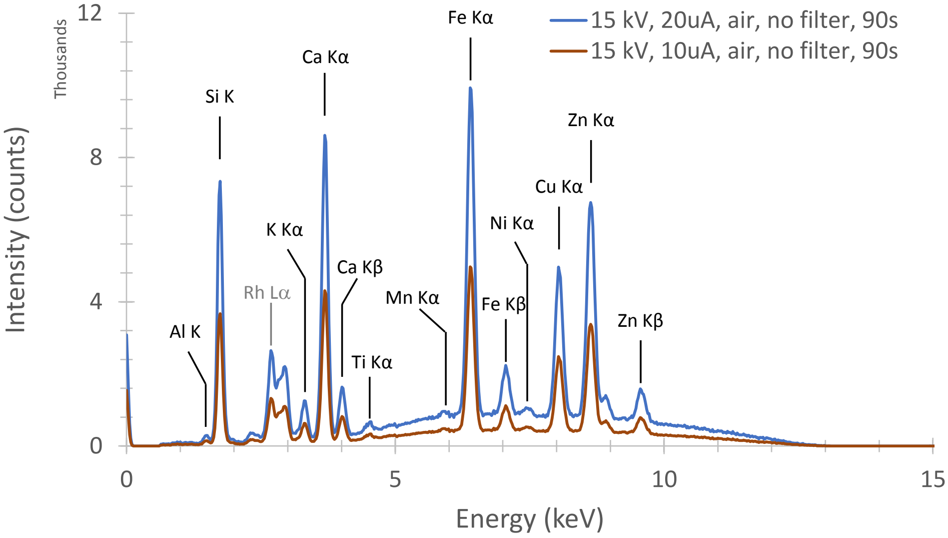


FIGURE 3.17. Spectra for analysis of glass mosaic tile (effect of current) in exercise 3.1a. Data collected using a Bruker Tracer III-SD, Rh tube.

4: Did the higher current produce artifacts in this sample? If so, describe them.

- In this sample, the higher current did not produce artifacts. If the intensity of the excited X-ray lines in the sample is too high, there is a chance of forming detector artifact peaks, such as escape peaks and sum peaks (or pulse pile-up peaks). If these artifact peaks interfere with the detection of an element in the sample, then it is best to lower the current and increase the collection time instead.

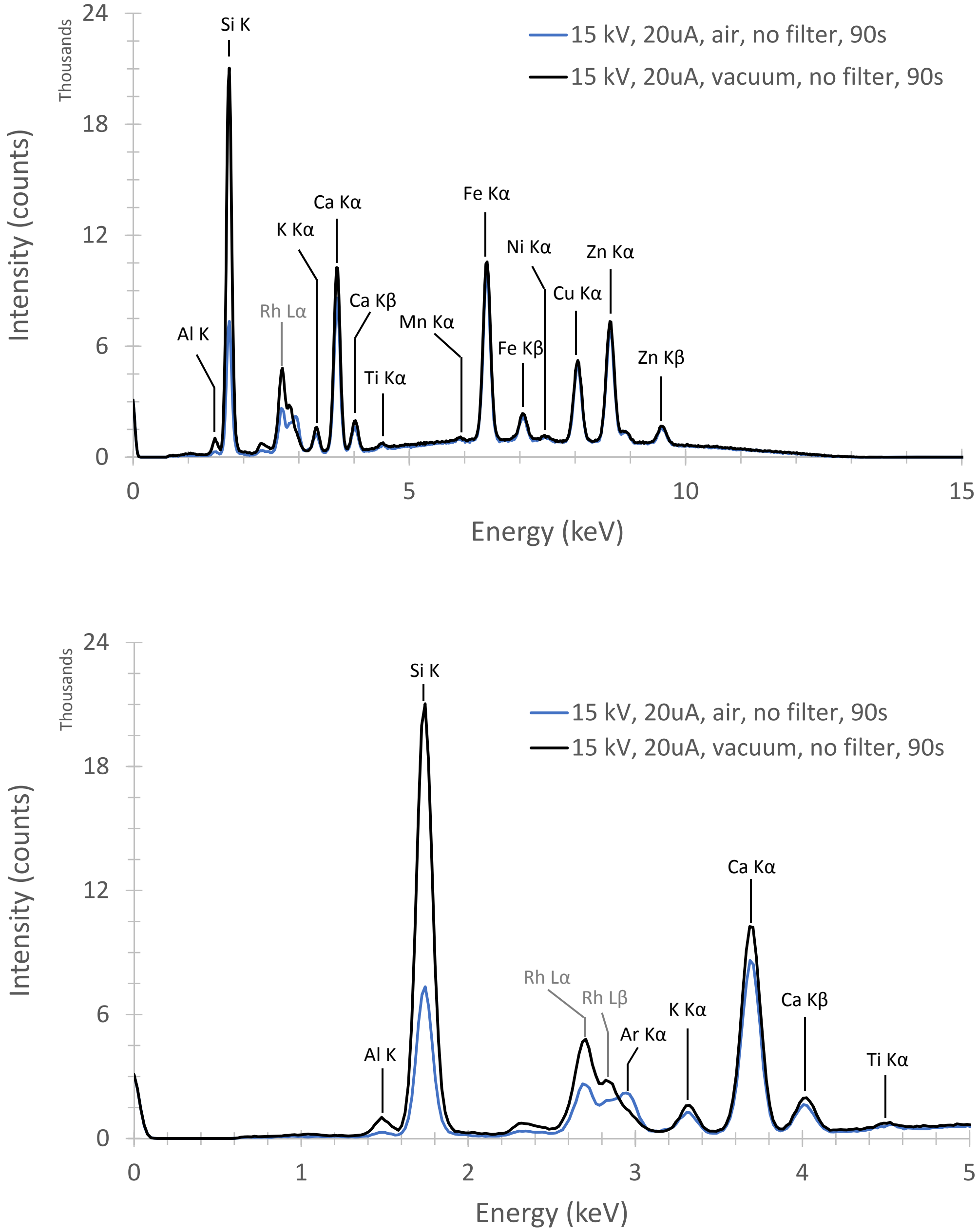


FIGURE 3.18. Spectra (with detail, bottom) for analysis of glass mosaic tile (effect of vacuum) in exercise 3.1a. Data collected using a Bruker Tracer III-SD, Rh tube.

Effect of vacuum

Spectra used in addressing the following questions from exercise 3.1a are shown in figure 3.18.

5: How does the spectrum taken with vacuum compare to the one taken in air, especially at the lower-energy end of the spectrum (i.e., <5 keV)?

- The effect of vacuum is most noticeable for glass components with low-energy peaks: Al, Si, K, Ca. These peaks appear more intense in spectra obtained with the vacuum pump. Some instruments may be capable of detecting Na and Mg as well.
- The intensity of the Ar peak (argon is 0.93% of the atmosphere) is lower in the spectrum obtained while using a vacuum pump to remove air from the interior of the instrument.
- Rh L peaks, which represent Rayleigh scattering of the excitation radiation by the sample, also appear more intense in spectra obtained with the vacuum pump.
- The effect of the vacuum pump on transition metals and elements with higher-energy X-ray peaks is moderate or minimal.

EXPLANATION OF OBSERVATIONS

The vacuum pump removes air from the path of the beam inside the instrument. Since nitrogen and argon in air can attenuate (absorb) low-energy X-rays, the use of a vacuum should help increase the intensity of low-energy peaks.

EXERCISE 3.1b:

Ultramarine–Cobalt Blue Mixture on Canvas: Exploring Low and High Z Elements within the Same Sample; "Varnish" Mock-Up

EXPECTED OUTCOMES TO EXERCISE QUESTIONS

Substrate and instrument contributions

Spectra used in addressing the following questions from exercise 3.1b are shown in figure 3.19.

1: What are the elements contributing to the background (canvas substrate and instrument)?

- Overlaying the spectrum of the canvas support with the spectrum of the mixture of the blue pigments on the canvas support helps visualize which elements in the spectrum of the blue pigment mixture may have contributions from the canvas.
- Detectable elements in the canvas support are K and Ca. Comparison of the canvas support spectrum to the spectrum of clean polyethylene foam or PMMA tile helps determine whether low-intensity peaks are instrument contributions or not.

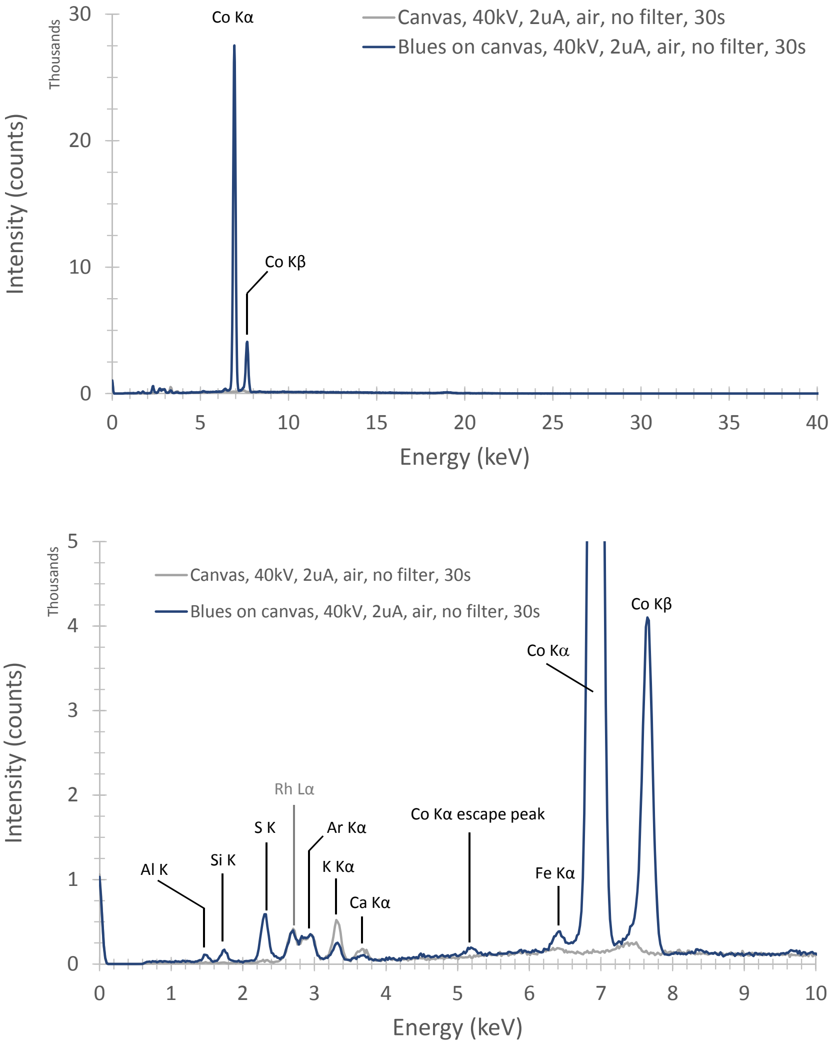


FIGURE 3.19. Spectra (with detail, bottom) for analysis of ultramarine blue–cobalt blue mixture on canvas (comparison of canvas with paint on canvas) in exercise 3.1b. Data collected using a Bruker Tracer III-SD, Rh tube.

2: What is the elemental composition of the paint mock-up?

- Elements unique to the blue paint mixture: Al, Si, S, Fe, Co.
- K and Ca may be present in the mixture of ultramarine blue and cobalt blue and in the canvas support.
- To determine if the ultramarine blue and the cobalt blue paints contain K or Ca, paint them out onto a thin polymer film circle used as a window material for XRF sample cups.
- The ultramarine blue used for this mock-up contains Al, Si, S, K, Ca, and Fe. Ultramarine blue also contains Na, but it is not detected with this instrument configuration.
- The cobalt blue used for this mock-up contains Al, Fe, and Co.
- The 5.19 keV peak is the escape peak for the high-intensity Co Kα peak (6.93 keV).

Effect of vacuum

Spectra used in addressing the following questions from exercise 3.1b are shown in figure 3.20.

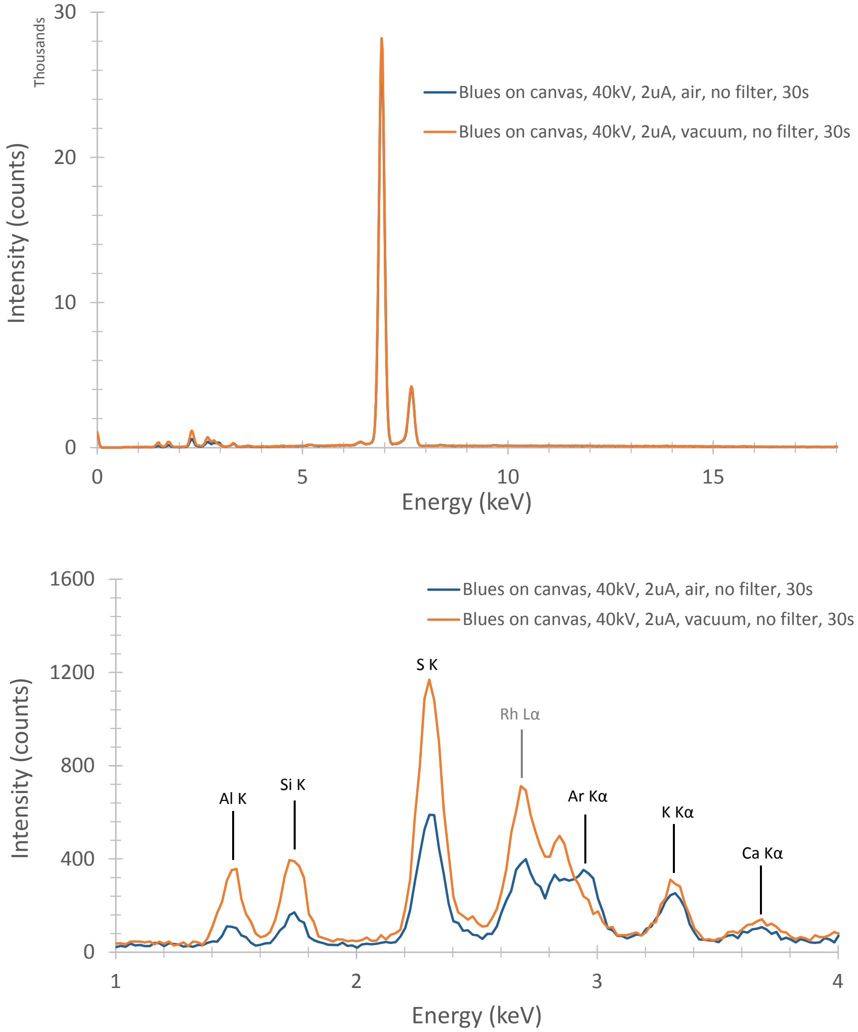


FIGURE 3.20. Spectra (with detail, bottom) for analysis of ultramarine blue–cobalt blue mixture on canvas (effect of vacuum) in exercise 3.1b. Data collected using a Bruker Tracer III-SD, Rh tube.

3: What is the effect of the vacuum on the spectra for the canvas substrate (A, B)?

- The effect of vacuum is most noticeable for paint and canvas components with low-energy peaks: Al, Si, S, K, Ca. These peaks (especially Al, Si, and S) appear more intense in spectra obtained with the vacuum pump.
- The intensity of the Ar peak (argon is 0.93% of the atmosphere) is lower in the spectrum obtained while using a vacuum pump to remove air from the interior of the instrument.
- Rh L peaks, which represent Rayleigh scattering of the excitation radiation by the sample, also appear more intense in spectra obtained with the vacuum pump.
- The effect of the vacuum pump on Co, which has higher-energy X-ray fluorescence emission peaks, is minimal.

4: For spectra C and D, how do you maximize for the low Z (atomic number) elements (here, Al, Si, S, K, Ca)? For the high Z elements (here, Co)?

- To optimize instrument parameters for the detection of low Z (atomic number) elements (Al, Si, S, K, Ca), use 15 kV or 20 kV accelerating potential, high current, and a vacuum pump or helium atmosphere.
- To optimize instrument parameters for the detection of Co, use 40 kV accelerating potential. Current should be adjusted to minimize escape and sum (pulse pile-up) peaks.

EXPLANATION OF OBSERVATIONS

The vacuum pump removes air from the path of the beam inside the instrument. Since nitrogen and argon in air can attenuate (absorb) low-energy X-rays, the use of a vacuum should help increase the intensity of low-energy peaks.

Effect of mock varnish on analysis

Spectra used in addressing the following questions from exercise 3.1b are shown in figure 3.21.

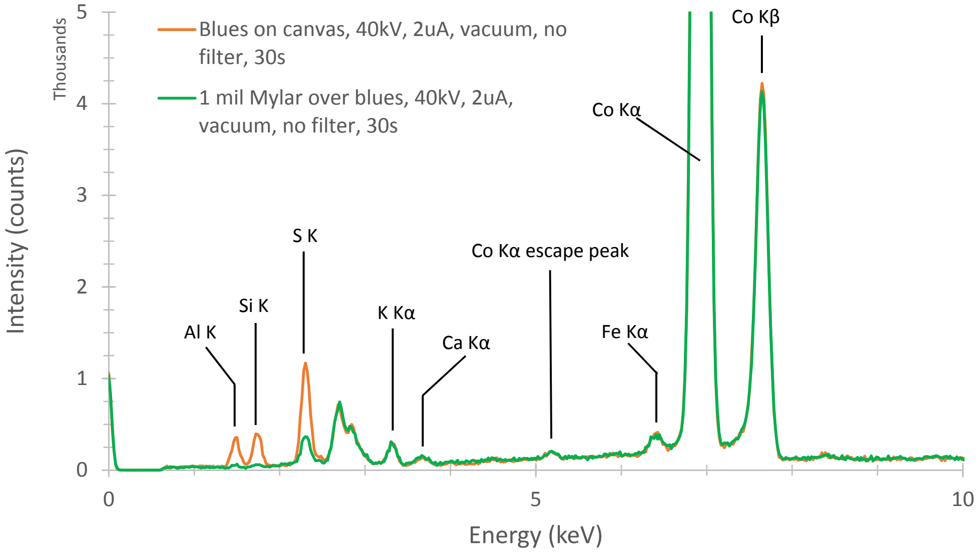


FIGURE 3.21. Spectra for analysis of ultramarine blue–cobalt blue mixture on canvas (effect of mock varnish on analysis) in exercise 3.1b. Data collected using a Bruker Tracer III-SD, Rh tube.

5: What is the effect of the Mylar film? Which elements are most affected by the addition of the Mylar film?

- The effect of the “varnish” layer is to attenuate (lower the intensity of) low-energy X-ray lines. The Al, Si, and S peaks are lowered significantly by the presence of the varnish layer.
- K and Ca peak intensities and those of heavier elements are not affected.

EXPLANATION OF OBSERVATIONS

- A 1 mil polyethylene terephthalate (PET) or Mylar film acts as a thick (25.4 µm) varnish layer. Natural and synthetic varnishes are composed of organic molecules with C, O, and H. The excitation potential of C is 0.28 kV; the excitation potential of O is 0.54 kV.
- Photons from the excitation source must pass through the “varnish” layer on their way to the blue paint mixture. A small fraction of the lowest-energy photons are absorbed before they have a chance to interact with the blue paint layer.
- Characteristic X-ray fluorescence photons from the blue paint layer (and canvas) must pass through the “varnish” layer on their way to the detector. The X-ray line energies of Al K (1.49 keV), Si K (1.74 keV), and S K (2.31 keV) are sufficiently close to the C and O excitation potentials; thus, some of the Al, Si, and S characteristic photons are absorbed by C and O in the “varnish” layer on their way to the detector. Note that for Al, Si, and S, their Kα and Kβ lines are so close that they are listed together as K lines here.

EXERCISE 3.1c:

Bone Black on Canvas: Exploring Low Z Elements and Possible Spectral Interferences

EXPECTED OUTCOMES TO EXERCISE QUESTIONS

Elemental composition of the paint layer

Spectra used in addressing the following questions from exercise 3.1c are shown in figure 3.22a.

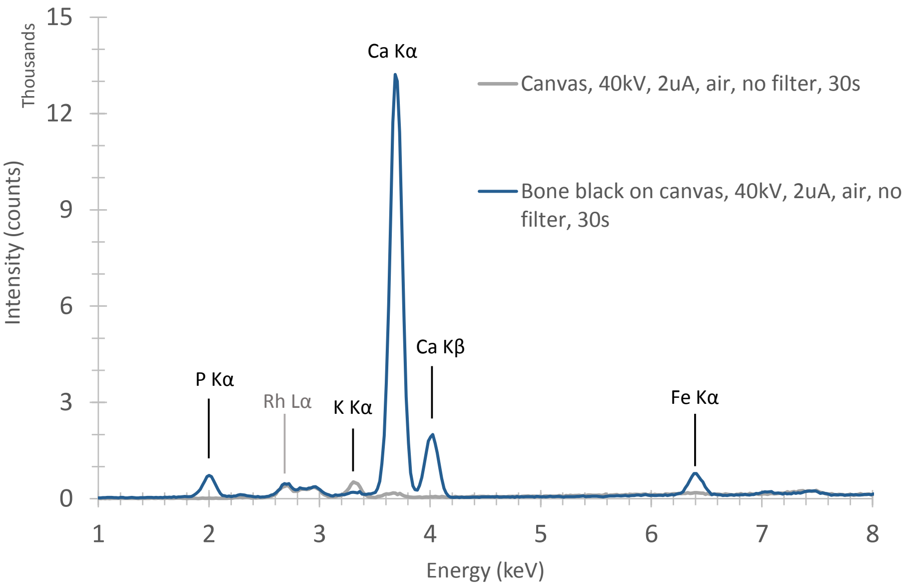


FIGURE 3.22a. Spectra for analysis of bone black on canvas and canvas substrate in exercise 3.1c. Data collected using a Bruker Tracer III-SD, Rh tube.

1: What are the elements contributing to the background (canvas substrate and instrument)?

- Overlaying the spectrum of the canvas support with the spectrum of bone black on the canvas support helps visualize which elements in the spectrum may have contributions from the canvas and which are from the pigment.
- Detectable elements in the canvas support are K and Ca.
- Comparison of the canvas support spectrum to the spectrum of clean polyethylene foam or PMMA tile helps determine whether low-intensity peaks are instrument contributions or not.

2: What is the elemental composition of the bone black paint?

- Elements unique to the bone black paint: P, Ca, Fe. Bone black mostly contains calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) as well as some carbon.

Effect of vacuum

Spectra used in addressing the following questions from exercise 3.1c are shown in figures 3.22b and 3.22c.

3: What is the effect of vacuum on the spectral response?

- The effect of vacuum is most noticeable for paint and canvas components with low-energy peaks: P and Ca. These peaks appear more intense in spectra obtained with the vacuum pump (compare figs. 3.22a and 3.22b, and overlay in fig. 3.22c).
- The intensity of the Ar peak (argon is 0.93% of the atmosphere) is lower in the spectrum obtained while using a vacuum pump to remove air from the interior of the instrument.

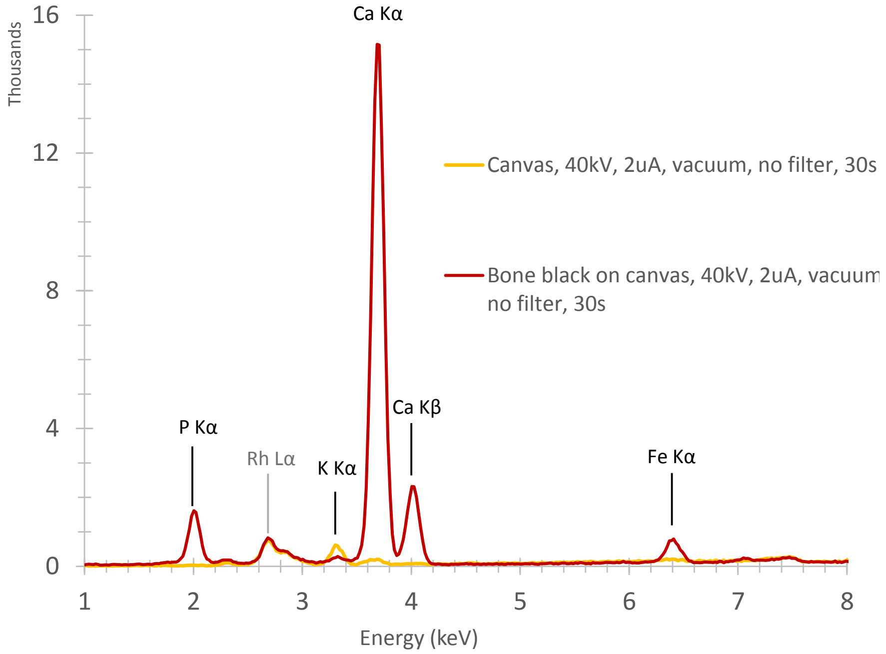


FIGURE 3.22b. Spectra for analysis of bone black on canvas and canvas substrate with vacuum in exercise 3.1c. Data collected using a Bruker Tracer III-SD, Rh tube.

- Rh L peaks, which represent Rayleigh scattering of the excitation radiation by the sample, also appear more intense in spectra obtained with the vacuum pump.
- The effect of the vacuum pump on Fe, which has higher-energy X-ray emission peaks, is minimal.

Distinguishing real and artifact peaks: P Kα peak and Ca Kα escape peak

Spectra used in addressing the following questions from exercise 3.1c are shown in figure 3.22c.

4: What type of artifact peak of calcium (Ca) is coincident with the phosphorus (P) peak?

- A high-intensity Ca Kα peak (3.69 keV) can give rise to an escape peak at 1.95 keV. The P K lines are at 2.01 keV (P Kα and Kβ appear at nearly the same energy) and thus the Ca Kα escape peak can interfere with their detection.

5: How can you determine whether phosphorus (P) is part of the paint composition or an artifact peak of calcium (Ca) is present?

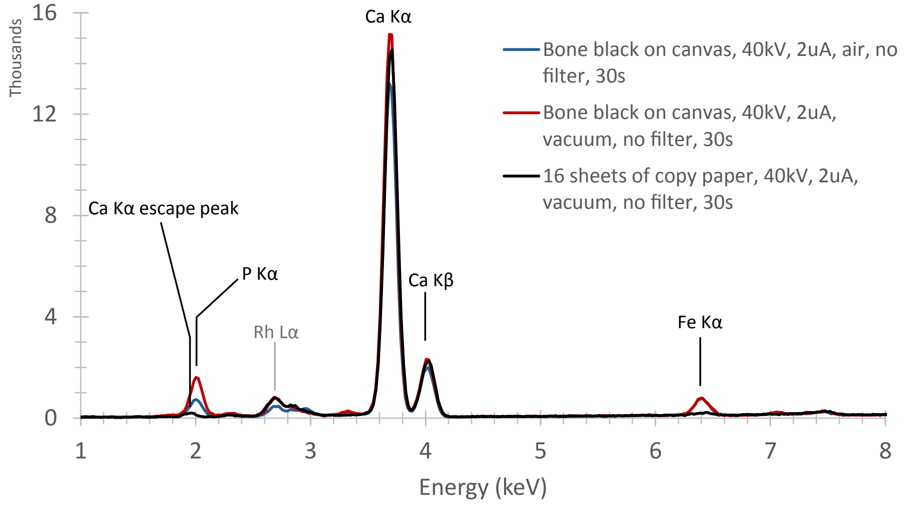


FIGURE 3.22c. Spectra for distinguishing real and artifact peaks: P Kα peak and Ca Kα escape peak.

- Copy paper typically contains calcium-based alkali reserves. One can visualize a Ca Kα peak (and its escape peak) by analyzing a stack of copy paper (a stack measuring 3 mm works well, which is approximately 16 sheets). In vacuum, the Ca Kα peak intensity will be similar compared to that observed in air. The Ca Kα escape peak intensity will also be similar compared to that observed in air.

EXPLANATION OF OBSERVATIONS

The vacuum pump removes air from the path of the beam inside the instrument. Since nitrogen and argon in air can attenuate (absorb) low-energy X-rays, the use of a vacuum should help increase the intensity of low-energy peaks, here the P Kα peak. If the peak was the Ca escape peak, the peak intensity will not be as affected by the vacuum.

Effect of accelerating potential

Spectra used in addressing the following questions from exercise 3.1c are shown in figure 3.23.

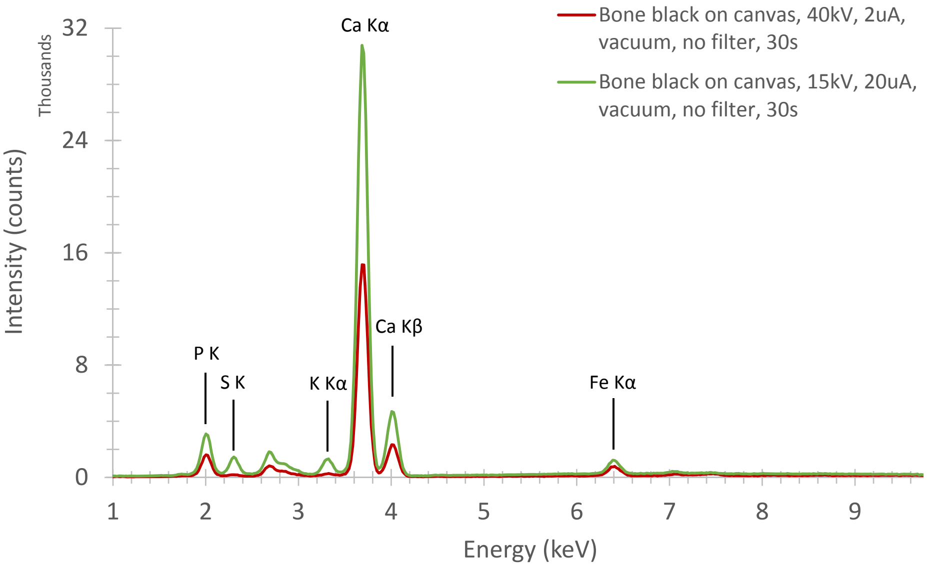


FIGURE 3.23. Spectra for analysis of bone black on canvas (effect of accelerating potential) in exercise 3.1c. Data collected using a Bruker Tracer III-SD, Rh tube.

6: Which accelerating potential (voltage) setting is better for low Z elements: 15 kV or 40 kV? Why?

- The 15 kV accelerating potential is better suited to the excitation of light elements (P, S, Ca). Characteristic peaks of these elements appear more intense in the spectrum collected at 15 kV as opposed to 40 kV.

EXPLANATION OF OBSERVATIONS

For a specific X-ray line in the sample to be excited, the accelerating potential (in kV) must be greater than the excitation potential of the X-ray line (in keV). Most efficient excitation happens at or right above the energy of the excitation potential. The center of the continuum (bremsstrahlung) excitation is around 7.5 kV when the accelerating potential is set to 15 kV. This value is much closer to the excitation potential for Fe (7.11 keV), Ca (4.04 keV), and P (2.15 keV) than the center of the continuum excitation (around 20 kV) when the accelerating potential is set to 40 kV.

EXERCISE 3.1d:

Alizarin Crimson on Canvas: Exploring Low Z Elements and Possible Spectral Interferences

EXPECTED OUTCOMES TO EXERCISE QUESTIONS

Elemental composition of the paint layer

Spectra used in addressing the following questions from exercise 3.1d are shown in figure 3.24a.

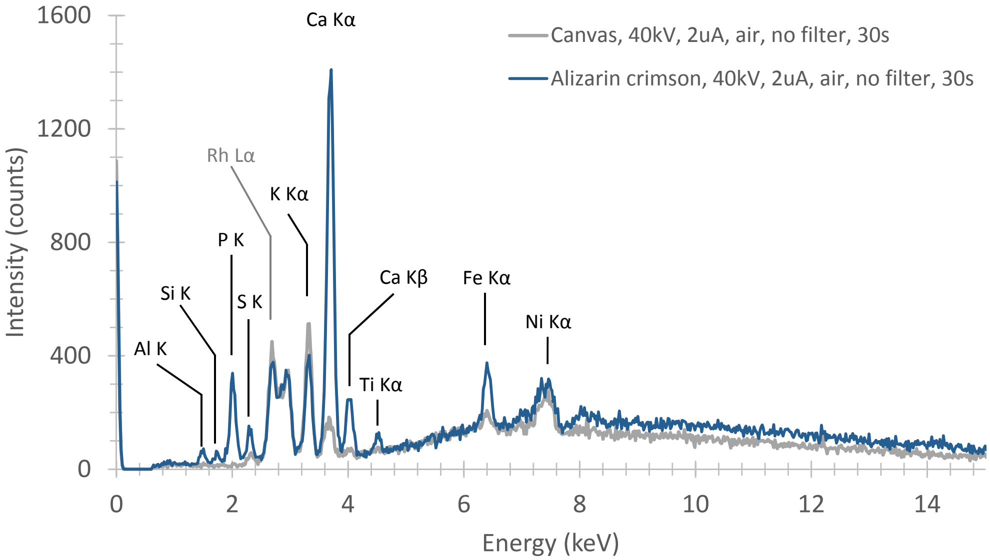


FIGURE 3.24a. Spectra for analysis of alizarin crimson on canvas and canvas substrate in exercise 3.1d. Data collected using a Bruker Tracer III-SD, Rh tube.

1: What are the elements contributing to the background (canvas background and instrument)?

- Overlaying the spectrum of the canvas support with the spectrum of alizarin on the canvas support helps visualize which elements in the spectrum may have contributions from the canvas and which are due to the pigment.
- Detectable elements in the canvas support are K and Ca.
- Comparison of the canvas support spectrum to the spectrum of clean polyethylene foam or PMMA tile helps determine whether low-intensity peaks are instrument contributions or not.

2: What is the elemental composition of the alizarin crimson paint?

- Elements unique to the alizarin paint: Al, Si, P, S, K, Ca, Ti, Fe. Alizarin is an organic dye affixed onto an inert substrate. Alum (potassium aluminum sulfate) is typically involved along with an alkali, potentially a calcium compound. Al, S, and K were all detected. Ca is also present, along with P. The exact nature of inorganic compounds present would need to be established using a complementary analytical technique such as fiber optic reflectance spectroscopy (FORS) and/or multispectral/hyperspectral imaging (MSI/HSI) techniques.

Effect of vacuum

Spectra used in addressing the following questions from exercise 3.1d are shown in figure 3.24b.

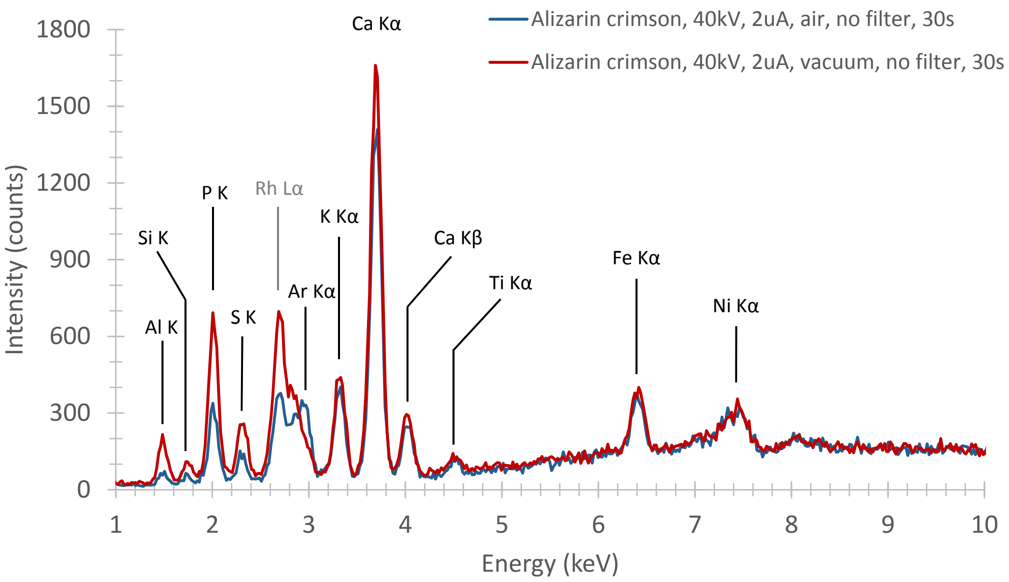


FIGURE 3.24b. Spectra for analysis of alizarin crimson on canvas (effect of vacuum) in exercise 3.1d. Data collected using a Bruker Tracer III-SD, Rh tube.

3: How does the vacuum affect the spectral response?

- The effect of vacuum is most noticeable for paint and canvas components with low-energy peaks: Al, Si, P, S, K, and Ca. These peaks appear more intense in spectra obtained with the vacuum pump.
- The intensity of the Ar peak (argon is 0.93% of the atmosphere) is lower in the spectrum obtained while using a vacuum pump to remove air from the interior of the instrument.
- Rh L peaks, which represent Rayleigh scattering of the excitation radiation by the sample, also appear more intense in spectra obtained with the vacuum pump.
- The effect of the vacuum pump on Fe, which has higher-energy X-ray peaks, is minimal.

EXPLANATION OF OBSERVATIONS

The vacuum pump removes air from the path of the beam inside the instrument. Since nitrogen and argon in air can attenuate (absorb) low-energy X-rays, the use of a vacuum should help increase the intensity of low-energy peaks.

Effect of accelerating potential

Spectra used in addressing the following questions from exercise 3.1d are shown in figure 3.25.

4: Which are the better conditions (voltage, current) for this paint mock-up, given its elemental makeup?

- The 15 kV accelerating potential is better suited to the excitation of light elements (Al, Si, P, S, K, Ca). Characteristic X-ray fluorescence emission peaks of these elements appear more intense in the spectrum collected at 15 kV as opposed to the spectrum collected at 40 kV.

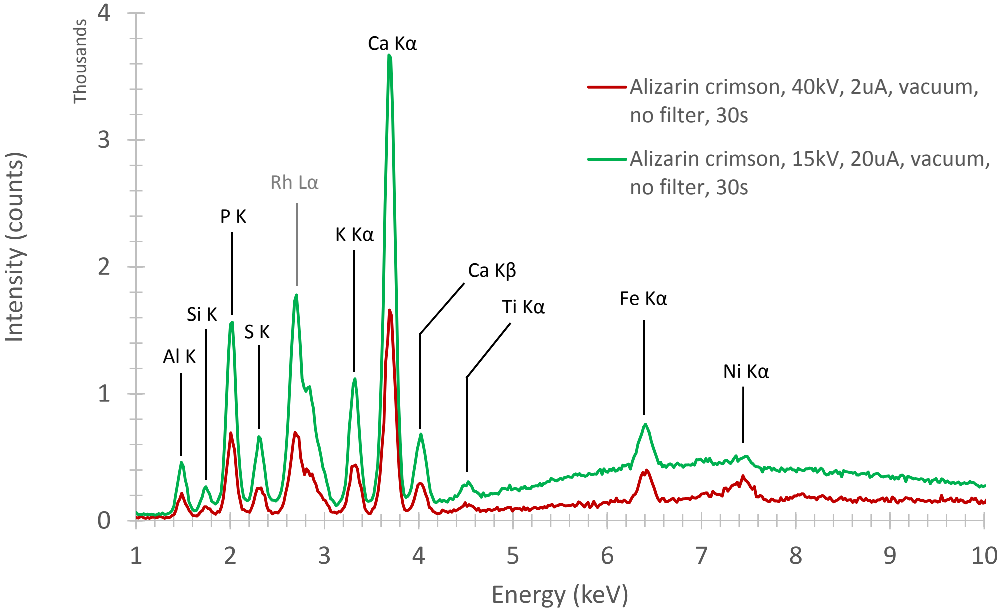


FIGURE 3.25. Spectra for analysis of alizarin crimson on canvas (effect of accelerating potential) in exercise 3.1d. Data collected using a Bruker Tracer III-SD, Rh tube.

EXPLANATION OF OBSERVATIONS

For a specific X-ray line in the sample to be excited, the accelerating potential (in kV) has to be greater than the excitation potential of the X-ray line (in keV). Most efficient excitation happens at or right above the energy of the excitation potential. The center of the continuum (bremsstrahlung) excitation is around 7.5 kV when the accelerating potential is set to 15 kV. This value is much closer to the excitation potential of the light elements than the center of the continuum excitation (around 20 kV) when the accelerating potential is set to 40 kV.

EXERCISE 3.1e:

Copper Alloy (Brass) Coupon: Spectral Artifacts Created by High Count Rates

EXPECTED OUTCOMES TO EXERCISE QUESTIONS

Effect of current

Spectra used in addressing the following questions from exercise 3.1e are shown in figure 3.26.

1: How do the identified elements compare to the expected composition of the copper alloy?

- The copper alloy contains Cu, Zn, and low amounts of Pb, Ni, and Fe. This alloy can be characterized as brass, a copper-zinc alloy.

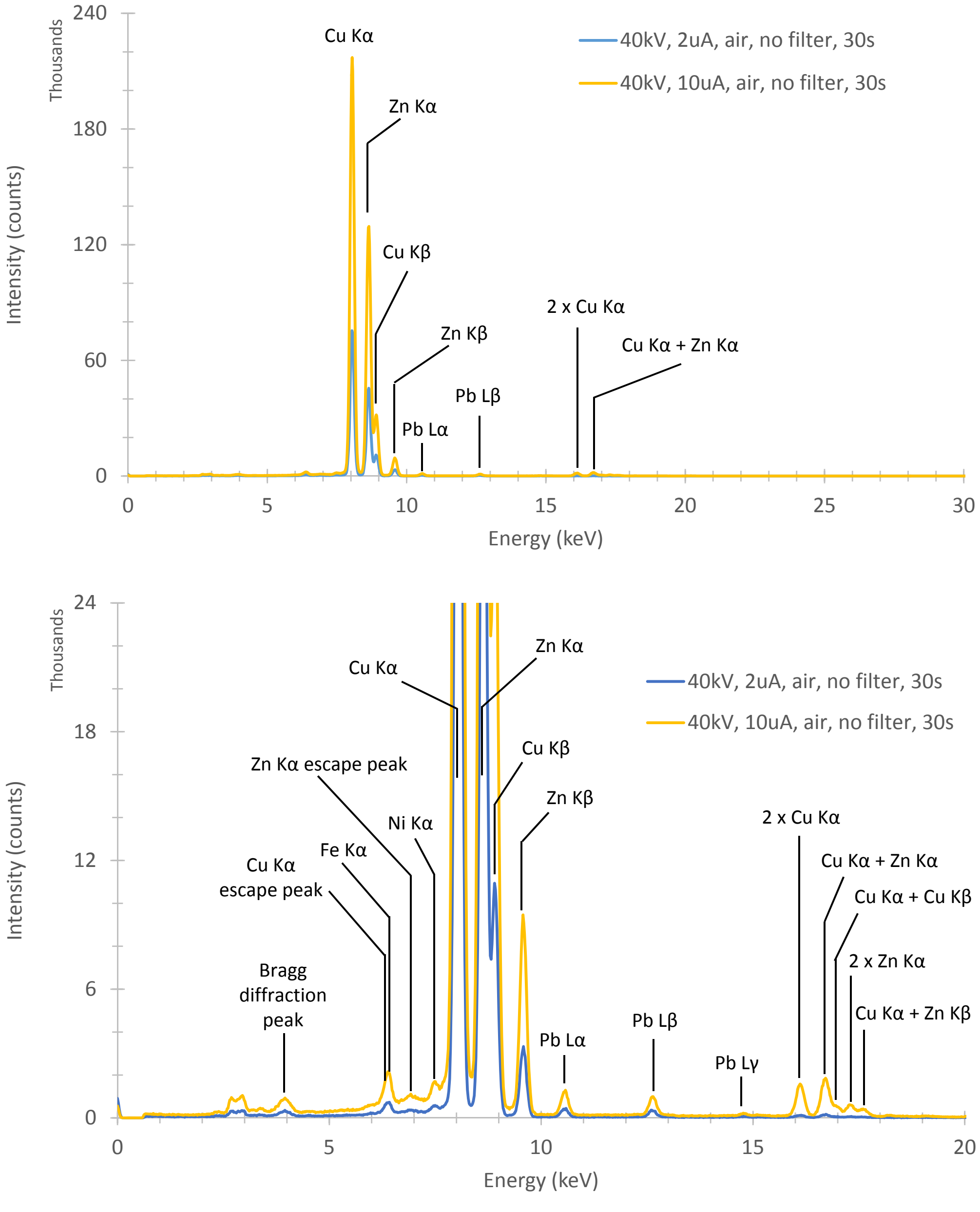


FIGURE 3.26. Spectra (with detail, bottom) for analysis of copper alloy (brass) coupon (effect of current) in exercise 3.1e. Data collected using a Bruker Tracer III-SD, Rh tube.

2: How would you determine whether peaks are coming from the instrument or from the sample?

- To determine if a peak is an instrumental artifact, it is helpful to compare the spectrum of the sample or object with the spectrum of clean polyethylene foam or PMMA tile.

3: Are there spectral artifacts? If so, what is the origin of these artifacts? How can you determine whether these are real or artifact peaks?

- There are several peaks that are spectral artifacts. The spectrum obtained at a higher current contains more spectral artifacts.
- The Cu Kα escape peak appears at 6.31 keV (8.05–1.74 keV). This peak occurs very close to the Fe Kα peak at 6.40 keV. Because of this overlap, it can be difficult to determine whether the copper alloy contains trace amounts of iron.
- The Zn Kα escape peak appears at 6.90 keV (8.64–1.74 keV). This peak occurs very close to the Co Kα peak at 6.93 keV. Because of this overlap, it can be difficult to determine whether the copper alloy contains trace amounts of cobalt.
- Several sum (pulse pile-up) peaks are present in the spectra. These peaks occur when two photons arrive at the detector simultaneously. Although sum peaks are often the result of two photons of the same energy arriving at the detector (e.g., Cu Kα + Cu Kα), they can be the combination of photons relating to any intense X-ray lines (e.g., Cu Kα + Cu Kβ; Cu Kα + Zn Kα).
- At 3.94 keV, there is a relatively broad low-intensity peak. This peak is likely due to Bragg diffraction of a specific energy of the excitation spectrum by the crystal structure of the copper alloy.

4: How would you determine the optimal conditions (voltage, current, filter, acquisition time, vacuum/He or no vacuum/He) to analyze the metal alloy?

- The 40 kV accelerating potential is well suited to the analysis of copper alloys, as it is able to excite efficiently the K lines of transition metals and the L lines of heavy metals. The lower-current setting produces fewer and less intense sum peaks. An excitation filter containing Al (and possibly other metal foil layers) is frequently used for copper alloy analysis.

EXERCISE 3.1f:

Lead-Tin Solder Disk: Detecting High and Low Z Elements and Determining Spectral Artifacts

EXPECTED OUTCOMES TO EXERCISE QUESTIONS

Effect of vacuum

Spectra used in addressing the following questions from exercise 3.1f are shown in figure 3.27.

1: What are the elements identified for the lead-tin solder? What are the elements identified from the instrument?

- The lead-tin solder contains Pb and Sn. Additionally, the low-intensity Ni peak indicates the presence of some nickel. Note that the intensity of this peak exceeded that of the peak contributed by the instrument (visualized by analyzing clean polyethylene foam).
- To determine if a peak is an instrument artifact, it is helpful to compare the spectrum of the sample or object with the spectrum of clean polyethylene foam or PMMA tile.

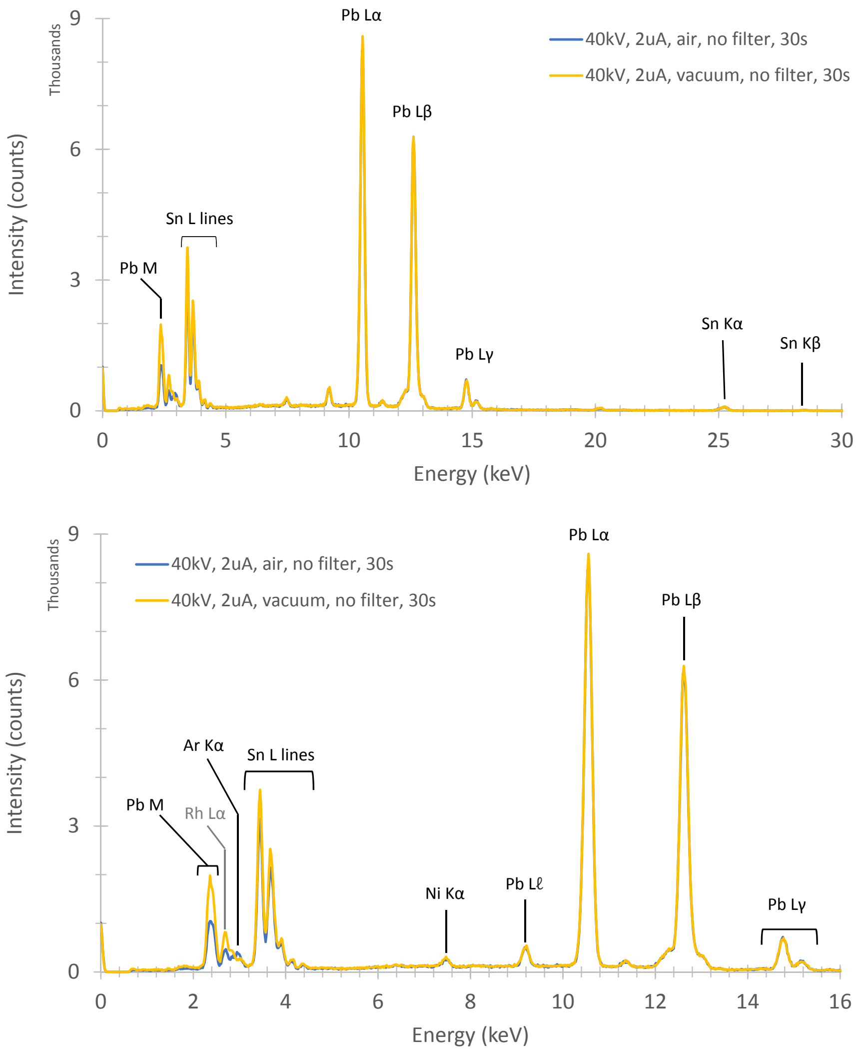


FIGURE 3.27. Spectra (with detail, bottom) for analysis of lead-tin solder (effect of vacuum) in exercise 3.1f. Data collected using a Bruker Tracer III-SD, Rh tube.

2: What is the effect of vacuum?

- The effect of vacuum is most noticeable for the low-energy X-ray lines generated by the solder components: the Pb M peaks. The Sn L peaks also appear to be slightly more intense when using vacuum, but the effect is much less noticeable. The Pb M and Sn L peaks are clearly visible without the use of the vacuum pump.
- The intensity of the Ar peak (argon is 0.93% of the atmosphere) is lower in the spectrum obtained while using a vacuum pump to remove air from the interior of the instrument.
- Rh L peaks, which represent Rayleigh scattering of the excitation radiation by the sample, also appear more intense in spectra obtained with the vacuum pump.
- The effect of the vacuum pump on the higher-energy X-ray lines (Pb L lines, Sn K lines) is minimal.

EXPLANATION OF OBSERVATIONS

The vacuum pump removes air from the path of the beam inside the instrument. Since nitrogen and argon in air can attenuate (absorb) low-energy X-rays, the use of a vacuum should help increase the detection efficiency of low-energy peaks.

Effect of current

Spectra used in addressing the following questions from exercise 3.1f are shown in figure 3.28.

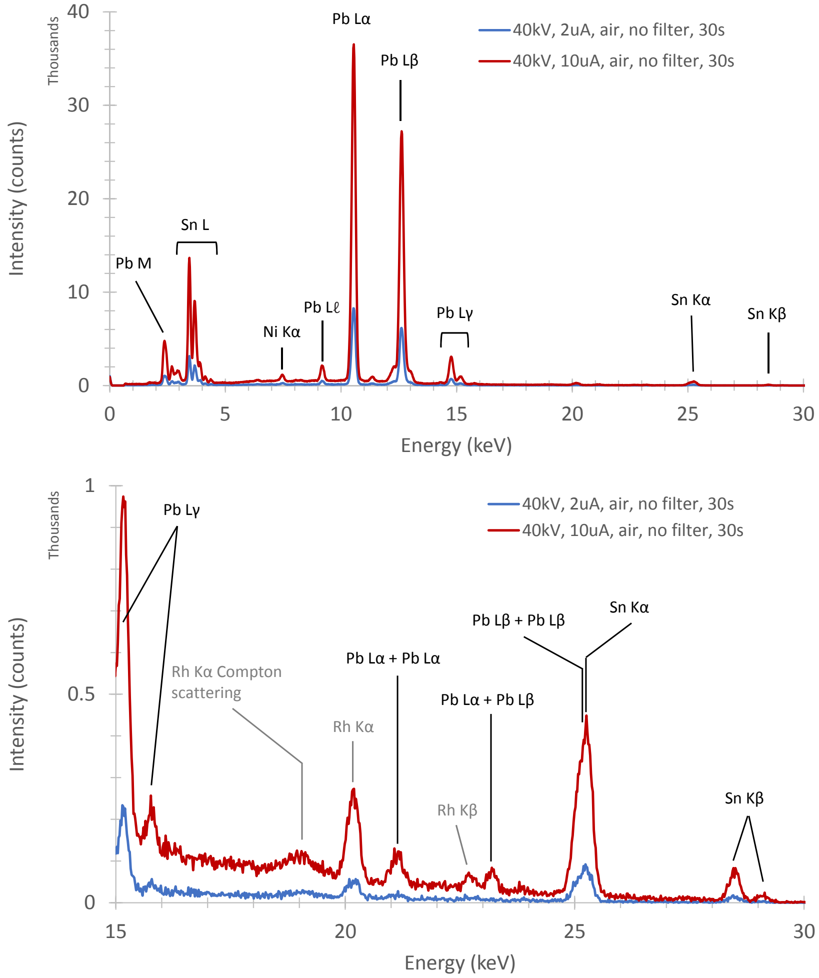


FIGURE 3.28. Spectra (with detail, bottom) for analysis of lead-tin solder (effect of current) in exercise 3.1f. Data collected using a Bruker Tracer III-SD, Rh tube.

3: Comparing the low- and high-current conditions, are there spectral artifacts in these spectra? If so, what is the origin of these artifacts? How can you check whether a peak is real or an artifact?

- The lead-tin solder contains Pb, Sn, and low or trace amounts of Ni.
- Several peaks are spectral artifacts. The spectrum obtained at higher current contains more spectral artifacts. The sum (pulse pile-up) peaks that are present in the spectra are as follows:
    - Pb Lα + Pb Lα (21.10 keV)
    - Pb Lα + Pb Lβ (23.16 keV)
    - The energy of one sum peak (Pb Lβ + Pb Lβ = 25.22 keV) overlaps with the $K\alpha_1$ peak of Sn at 25.27 keV.

4: How would you determine the optimal conditions (voltage, current, filter, acquisition time, vacuum, or air) to analyze the metal alloy?

- The 40 kV accelerating potential is well suited to the analysis of lead alloys, as it is able to excite efficiently the K lines of transition metals and the L lines of heavy metals. The lower-current setting produces fewer and less intense sum peaks. To improve the signal-to-noise ratio for the low-intensity Sn Kα peak, a longer collection time would be helpful.

EXERCISE 3.2a:

Cadmium Red Lines on Titanium White Ground with Various Line Widths

EXPECTED OUTCOMES TO EXERCISE QUESTIONS

Effect of line width

Spectra used in addressing the following questions from exercise 3.2a are shown in figure 3.29.

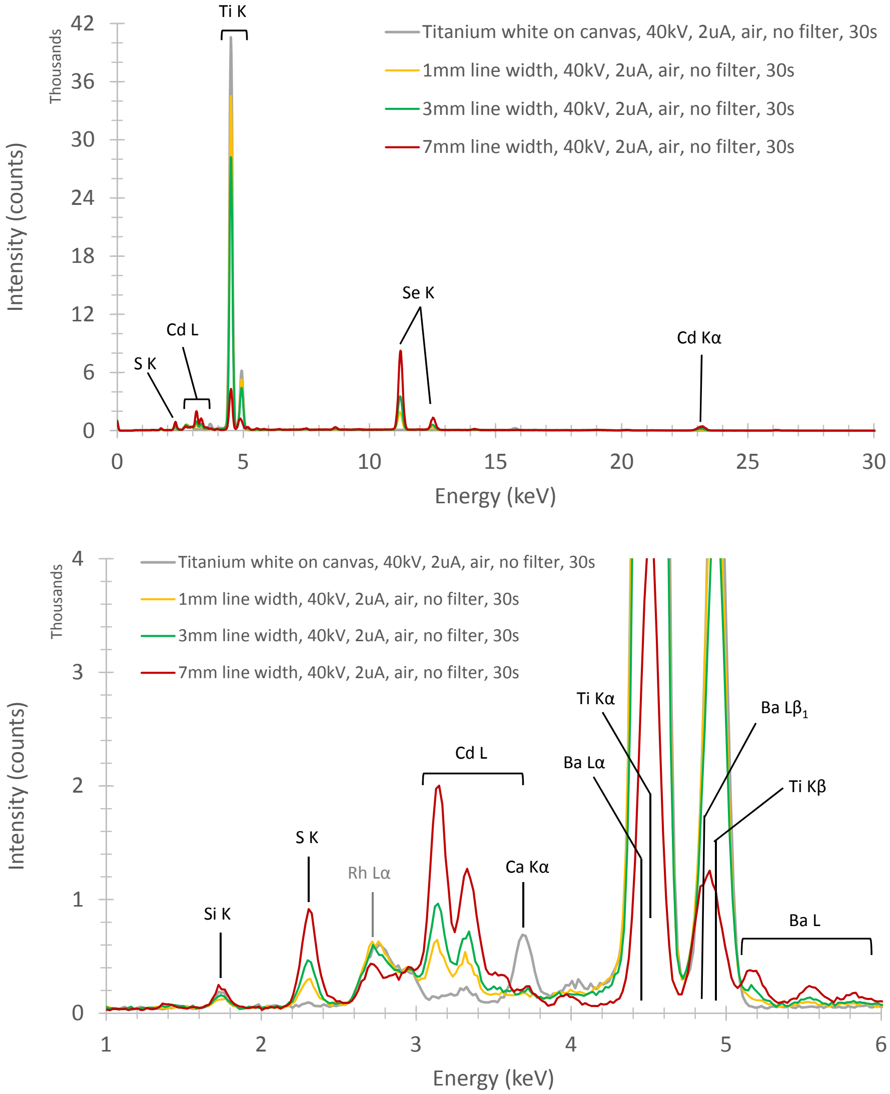
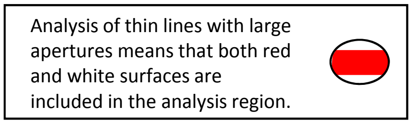


FIGURE 3.29. Spectra (with detail, bottom) for analysis of cadmium red lines on titanium white ground on canvas (effect of line width) in exercise 3.2a. Data collected using a Bruker Tracer III-SD, Rh tube.

1: How are the spectra affected by the line widths? Which line width completely covers the spot size?

- Thinner red lines do not completely cover the instrument's aperture (when analyzed with a Bruker Tracer III-SD). When analyzing 1 mm and 3 mm wide lines, the spectrum represents a combination of results for the following layer sequences: cadmium red, titanium white, canvas support; titanium white and canvas support.
- For the Bruker Tracer III-SD, the 7 mm wide line completely fills the instrument's aperture. The spectrum represents analysis of the following layer sequence only: cadmium red, titanium white, canvas support (see fig. 3.30).



Analysis of thin lines with large apertures means that both red and white surfaces are included in the analysis region.

FIGURE 3.30. Analysis of thin lines with a large-sized aperture means that neighboring color fields will impact the resulting spectrum; here, both red and white surfaces are included in the analysis region.

2: In each of the three line widths, is the titanium detected in the spectra due to the underlying paint or from the exposed sides?

- To understand which peaks relate to which layers, compare the spectra of the widest red line with those of titanium white on canvas and the bare canvas.
    - Elements unique to titanium white on canvas: Ti, Ca, Zr, Nb. Titanium white contains TiO_2.
    - Elements unique to cadmium red paint: S, Cd, Ba, Se. These elements relate to the presence of: CdS, CdSe, $BaSO_4$ (likely with traces of $SrSO_4$).
    - Elements that may be present in both titanium white paint and cadmium red paint: Si, Zn, Sr.
- As the width of the red lines increases, the proportion of cadmium red relative to titanium white in the area analyzed increases. There is an increase in the intensity of peaks related to the cadmium red paint: S, Cd, Ba, Zn, Se, Sr. There is a decrease in the intensity of peaks related only to the titanium white paint: Ti, Ca.

3: The Ti K lines overlap with the Ba L lines. How do you approach understanding the peak positions in this region with the presence of both Ti and Ba in this mock-up?

- Titanium peaks are present in spectra due to the excitation and detection of titanium both underneath and adjacent to the red lines when analyzing the narrower lines.
- Analysis of the 7 mm wide line, which fills the aperture of the Bruker Tracer III-SD completely (see fig. 3.29, detail), shows clearly the presence of Ba L lines, but the positions and relative intensities of the X-ray peaks at 4.51 keV and 4.89 keV indicate that Ti K lines are also present in the spectrum. Because no titanium white is visible in the region analyzed, the Ti K lines must be related to the titanium white layer under the cadmium red layer (fig. 3.31).

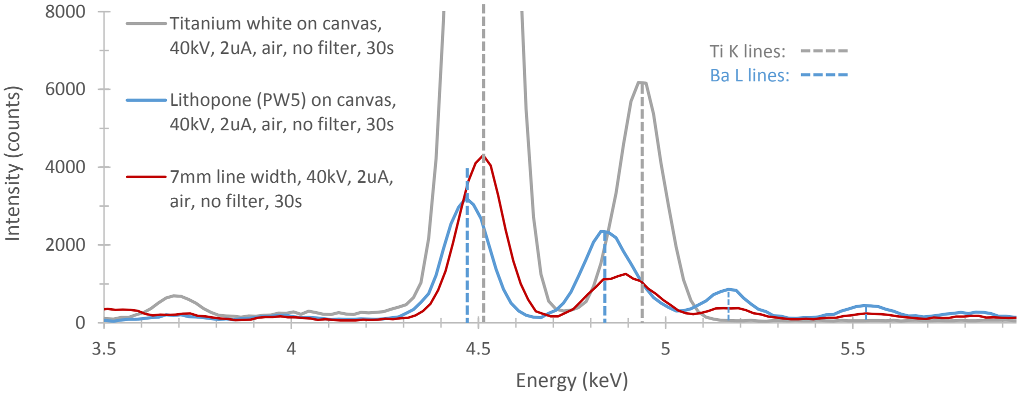


FIGURE 3.31. Details of overlaid spectra of titanium white paint on canvas, lithopone paint on canvas, and the cadmium red 7 mm line width paint on titanium white mock-up. For the cadmium red 7 mm line width, both titanium and barium are present and the peaks are shifted in between from the titanium only case and the barium only case.

EXERCISE 3.2b:

Lead-Tin Solder with Malachite Paint Layers: Effects of “Corrosion” Layers

EXPECTED OUTCOMES TO EXERCISE QUESTIONS

Effect of corrosion thickness

Spectra used in addressing the following questions from exercise 3.2b are shown in figure 3.32.

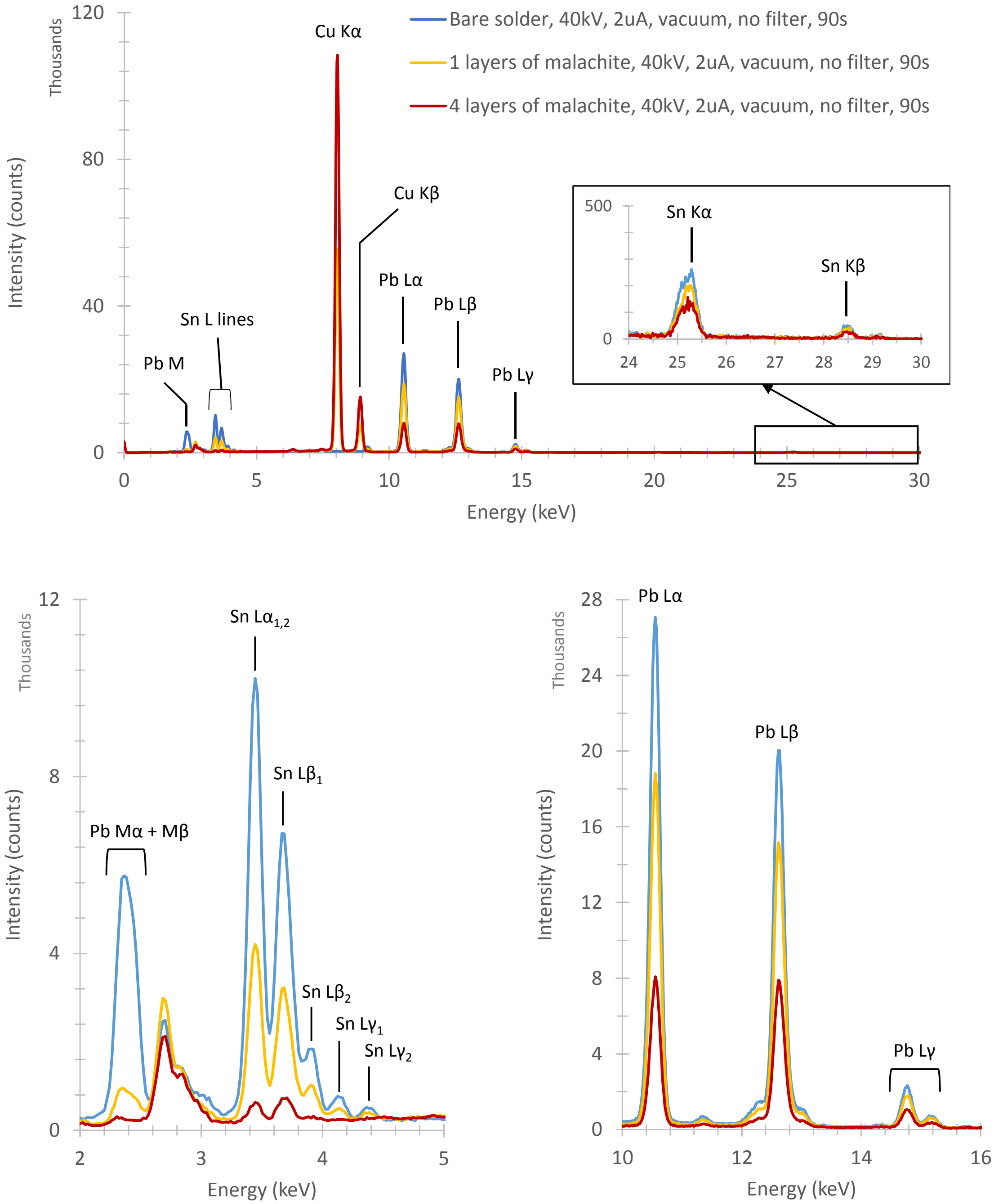


FIGURE 3.32. Spectra (with details, bottom left and right) for analysis of lead-tin solder with simulated copper-based corrosion (effect of corrosion thickness) in exercise 3.2b. Data collected using a Bruker Tracer III-SD, Rh tube.

1: What is the composition of the bare solder?

- The lead-tin solder contains Pb, Sn, and low or trace amounts of Ni (see fig. 3.27).

2: How are the spectra affected by the thin and thick layers of malachite, that is, “corrosion”?

- The presence of a copper-based corrosion layer over the lead-tin solder causes a decrease in the intensity of peaks related to the solder; thicker corrosion layers cause a greater decrease in intensity.

3: How are different parts of the energy spectrum affected by the corrosion layer? Explain.

- The lower the energy of the X-ray line, the greater the reduction in intensity due to the presence of a corrosion layer.

(greatest effect) Pb M > Sn L > Pb L > Sn K (least effect)

- Lower-energy X-ray lines within an X-ray line family (Sn L lines, Pb L lines, Sn K lines) are more affected by the corrosion layer than higher-energy lines.
- The Sn Lα lines are reduced in intensity relatively more than the Sn Lβ and Lγ lines.
- The Pb Lα line is reduced in intensity relatively more than the Pb Lβ and Lγ lines.

4: What is the nominal Lα/Lβ ratio for the Pb L lines? How does the corrosion layer(s) affect this ratio? What conclusions can be drawn about the layering based on the Pb Lα/Lβ ratio?

- Nominal intensity ratio of Pb Lα : Pb Lβ is 100:66 (or about 3:2). The thicker corrosion layer causes the intensity ratio to be almost 1:1.
- If the intensity of Pb Lα approaches that of Pb Lβ, it is likely that Pb atoms are mostly located beneath the surface analyzed.

EXPLANATION OF OBSERVATIONS

The corrosion layer impacts both the excitation and the detection of the X-ray lines in the lead-tin solder due to its position between the X-ray source and the solder (excitation) and between the solder and the detector (detection).

- X-ray photons from the X-ray tube must pass through the corrosion before they can arrive at the lead-tin solder and cause the excitation of characteristic X-ray photons for Pb and Sn. The copper-containing malachite will absorb some of the excitation photons before they can reach the lead-tin solder. Thus, the intensity of the excitation spectrum is lowered by the malachite corrosion layer. Overall, this leads to lowered excitation of characteristic Pb and Sn X-ray lines.
- Pb and Sn characteristic X-ray fluorescence photons must pass through the malachite layer before they can be detected. The copper-containing malachite will absorb some of the characteristic Pb and Sn X-ray photons on their way to the detector. Cu will absorb X-ray photons strongly at or just above the K line excitation potential: 8.97 keV. Pb Kα (10.55 keV) photons are more strongly absorbed by Cu than Pb Kβ (12.61 keV) photons because they are closer in energy to the excitation potential. Cu will also strongly absorb low-energy photons such as Pb M and Sn L lines.

The graph in figure 3.33 shows variation of the mass attenuation coefficient (MAC) of Cu with photon energy.

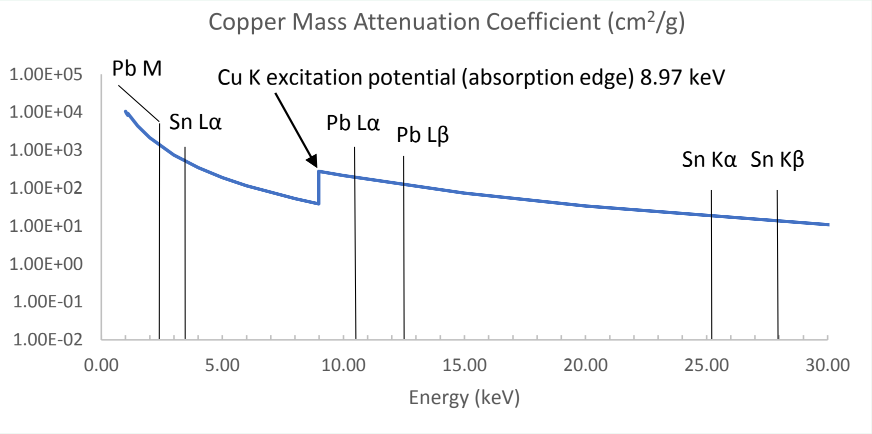


FIGURE 3.33. Graph showing how Cu MAC varies with photon energy. Higher values on the Y axis indicate stronger absorption of X-rays by Cu.

EXERCISE 3.2c:

Titanium White and Lithopone Painted Layers on Canvas: Paint Layers

EXPECTED OUTCOMES TO EXERCISE QUESTIONS

Analysis of unmixed paints on canvas

Spectra used in addressing the following questions from exercise 3.2c are shown in figures 3.34 and 3.35.

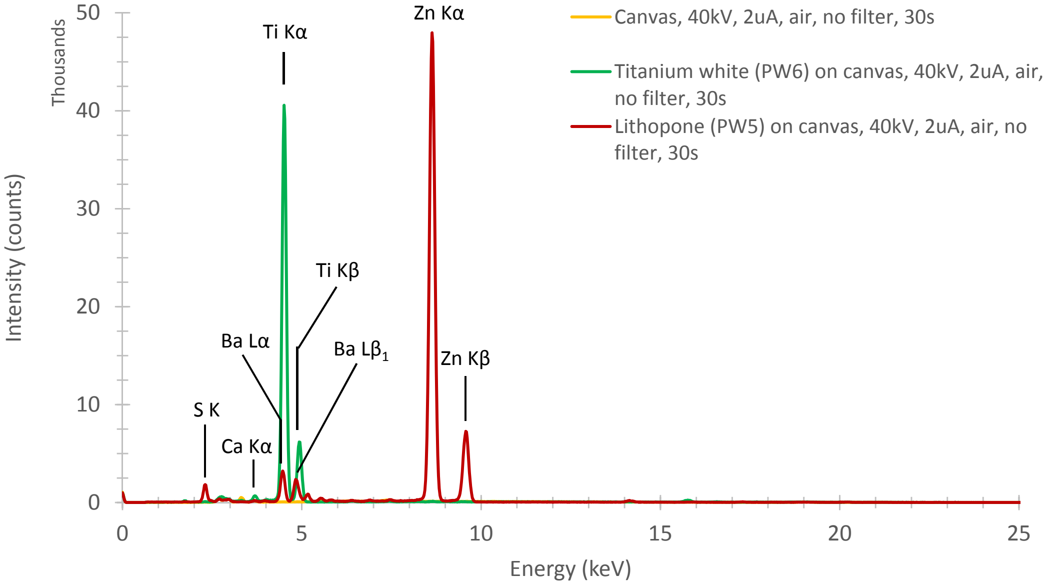


FIGURE 3.34. Spectra for analysis of canvas substrate, titanium white (PW6) only, and lithopone (PW5) only (analysis of unmixed paints on canvas) in exercise 3.2c. Data collected using a Bruker Tracer III-SD, Rh tube.

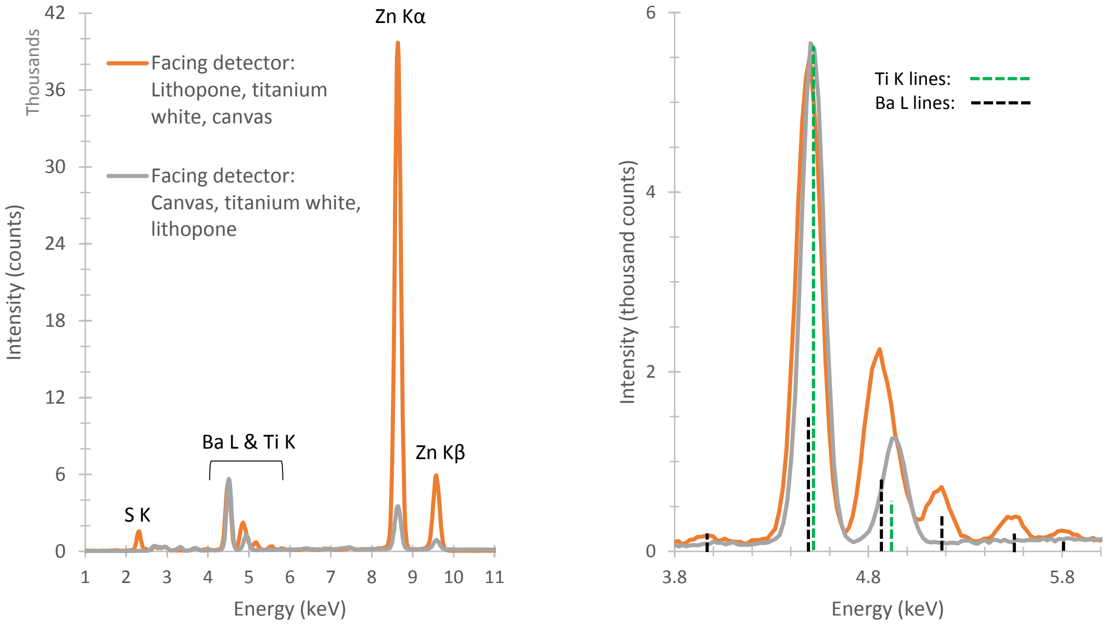


FIGURE 3.35. Spectra (with detail, right) for analysis of layered titanium white (PW6) and lithopone (PW5) (analysis of layered mock-up: canvas/titanium white/lithopone) in exercise 3.2c. Data collected using a Bruker Tracer III-SD, Rh tube.

1: What is the purpose of measuring the bare canvas, the titanium white on canvas only, and the lithopone paint on canvas only?

- Lithopone (PW5) contains barium sulfate ($BaSO_4$) and zinc sulfide (ZnS). Titanium white (PW6) is titanium dioxide.
- The analysis of bare canvas helps in understanding that elements relate to the support under the two layers of white paint. The analyses of lithopone on canvas as well as titanium white on canvas help in understanding what elements each paint layer can contribute to the spectra.

Analysis of layered mock-up: Canvas / titanium oxide / lithopone

2: How do the spectra from the front and back sides differ?

- Analysis from the front means that the detector faces lithopone, with titanium white and canvas layers following. The elements relating to lithopone (S, Ba, Zn, and possibly Ca) have the most intense peaks in the spectrum. The presence of Ti, in the volume of material analyzed, is difficult to discern. The positions and relative intensities of the X-ray peaks at 4.50 keV and 4.86 keV do not line up exactly with Ba $L\alpha$ and $L\beta$ lines and thus suggest that Ti K lines are also present in the spectrum.
- Analysis from the back means that the detector faces canvas, with titanium white and lithopone layers following. Peaks for elements associated with the canvas support are present in the spectrum: K, Ca. The sulfur (S) peak is of very low intensity, and the intensity is comparable to that of bare canvas. If S K X-rays are excited in the lithopone layer, they may be mostly or completely absorbed before they get to the detector. Titanium K lines are clearly detectable (relating to the titanium white layer), but Ba L lines appear to be absent from the spectrum. Note that the Ti $K\beta$ line is a little more intense relative to Ti $K\alpha$ than would nominally be expected. This indicates that Ti is not on the surface and that there is a layer (the canvas) between the titanium dioxide and the detector that causes greater attenuation of the lower-energy Ti $K\alpha$ line than the higher-energy Ti $K\beta$ line.

3: The Ti K lines overlap the Ba L lines. How do you approach understanding the peak positions in this region with the presence of both Ti and Ba in this mock-up? (See also the answers to questions for exercise 3.2a.)

- Analysis of the mock-up from the front detects the presence of S, Ba, and Zn. Based on this, the presence of $BaSO_4$ may be inferred along with either ZnO or ZnS.
- Analysis of the mock-up from the back suggests that a Ti-rich layer is present near the canvas, underneath the layer with S, Ba, and Zn. The lowered intensity of Zn, when analyzed from the canvas side, suggests that Zn is part of the top layer of paint.

EXERCISE 3.2d:

Lead-Tin Solder Disk with Aluminum Sheets

EXPECTED OUTCOMES TO EXERCISE QUESTIONS

Attenuation of spectral components

Spectra used in addressing the following questions from exercise 3.2d are shown in figure 3.36.

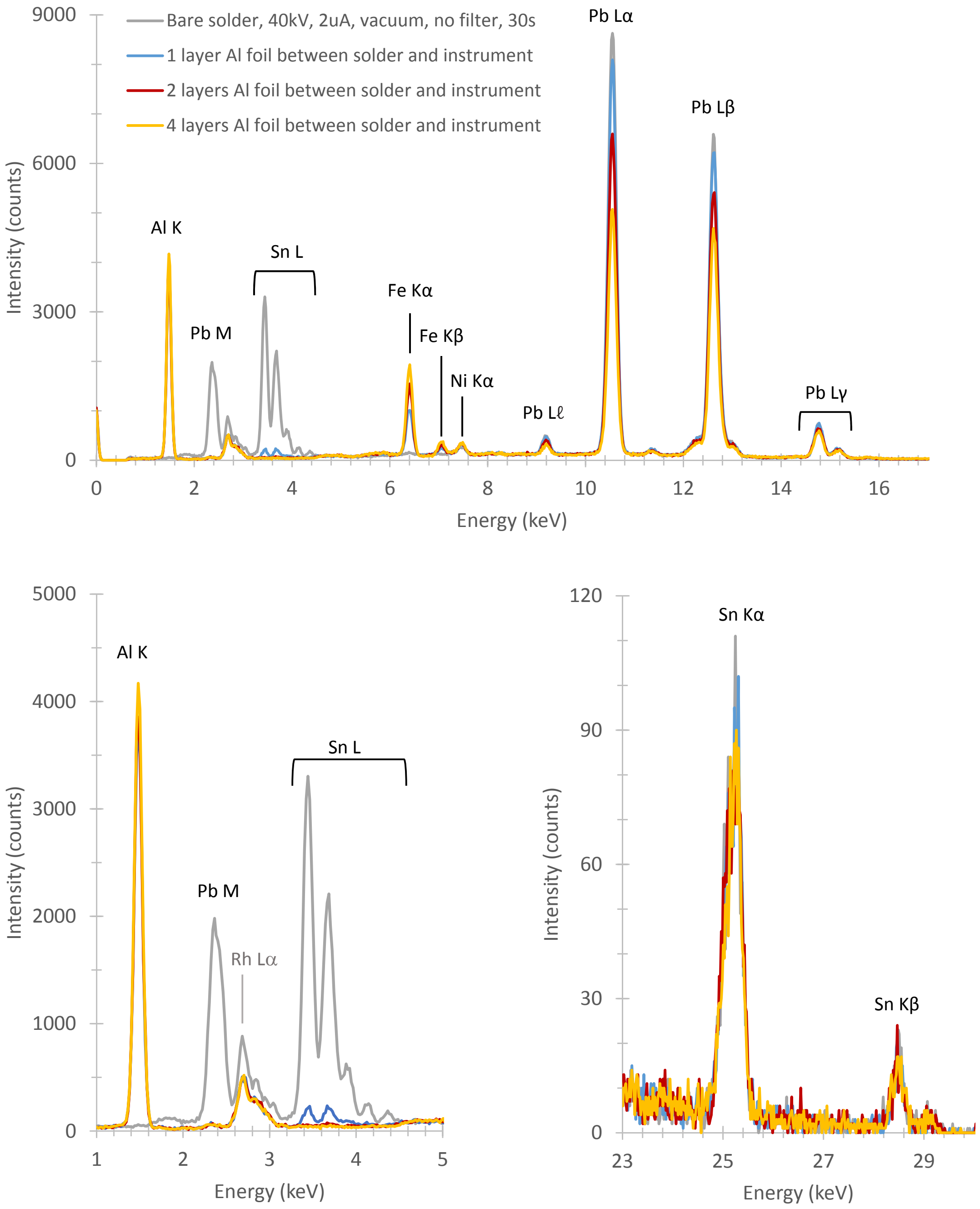


FIGURE 3.36. Spectra (with details, bottom left and right) for analysis of lead-tin solder with aluminum sheets (attenuation of spectral components) in exercise 3.2d. Data collected using a Bruker Tracer III-SD, Rh tube.

1: What is the Pb Lα/Lβ line ratio in the bare solder disk?

- Note that analysis of household aluminum foil indicates that there is some Fe present in addition to Al.
- The Pb Lα/Lβ ratio in the bare solder disk is approximately 1.3. This is lower than the nominal intensity ratio of Pb Lα : Pb Lβ, which is 100:66, or about 1.5.
- Self-absorption of Pb Lα lines by the Sn component of the solder lowers the intensity of the Pb Lα line relative to the Pb Lβ line.

2: How did the Al sheets affect the spectra of the lead-tin solder? How many sheets were needed to see the attenuation effect on the Pb Lα and Pb Lβ lines? On the Sn K lines? On the Sn L lines?

- Aluminum foil sheets lower the intensity of Pb and Sn peaks.
- Even a single aluminum foil sheet causes attenuation of both Pb Lα and Pb Lβ peaks.
- The Sn Kα line intensity is attenuated by four aluminum foil sheets. The Sn Kβ line intensity does not appear to be attenuated, even by four aluminum foil sheets.
- The Sn L lines are strongly attenuated by only a single aluminum foil sheet and are completely attenuated by two sheets.
- The Pb M lines are completely attenuated by a single aluminum foil sheet.

3: What general conclusions can you draw about how the different parts of the energy spectrum are affected by attenuation; that is, are the lower Z elements more sensitive to attenuation compared to the higher Z elements?

- The lower the energy of the X-ray fluorescence emission peak, the more susceptible it is to attenuation.
- Elements with low atomic numbers (low Z) have low-energy X-ray peaks and thus are very susceptible to attenuation.
- Elements with high atomic numbers (high Z) have L and M line families (see chap. 2, fig. 2.3) with low energies that are susceptible to attenuation. Some of these lines of relevance include the following: M lines: Pt, Au, Hg, Pb, Bi; L lines: Pd, Ag, Cd, Sn, Sb.

To serve as an ideal interleaving material, aluminum plates or sheets should be free of iron (and other contaminants) because the characteristic X-ray lines Fe Kα and Kβ have sufficient energy to pass through paper or parchment and arrive at the detector.

EXERCISE 3.2e:

Layered Titanium White and Phthalocyanine Green 7 (PG7) with Sheets of Copy Paper for Attenuation of the Copper (Cu) Peak

EXPECTED OUTCOMES TO EXERCISE QUESTIONS

Attenuation of spectral components

Spectra used in addressing the following questions from exercise 3.2e are shown in figure 3.37.

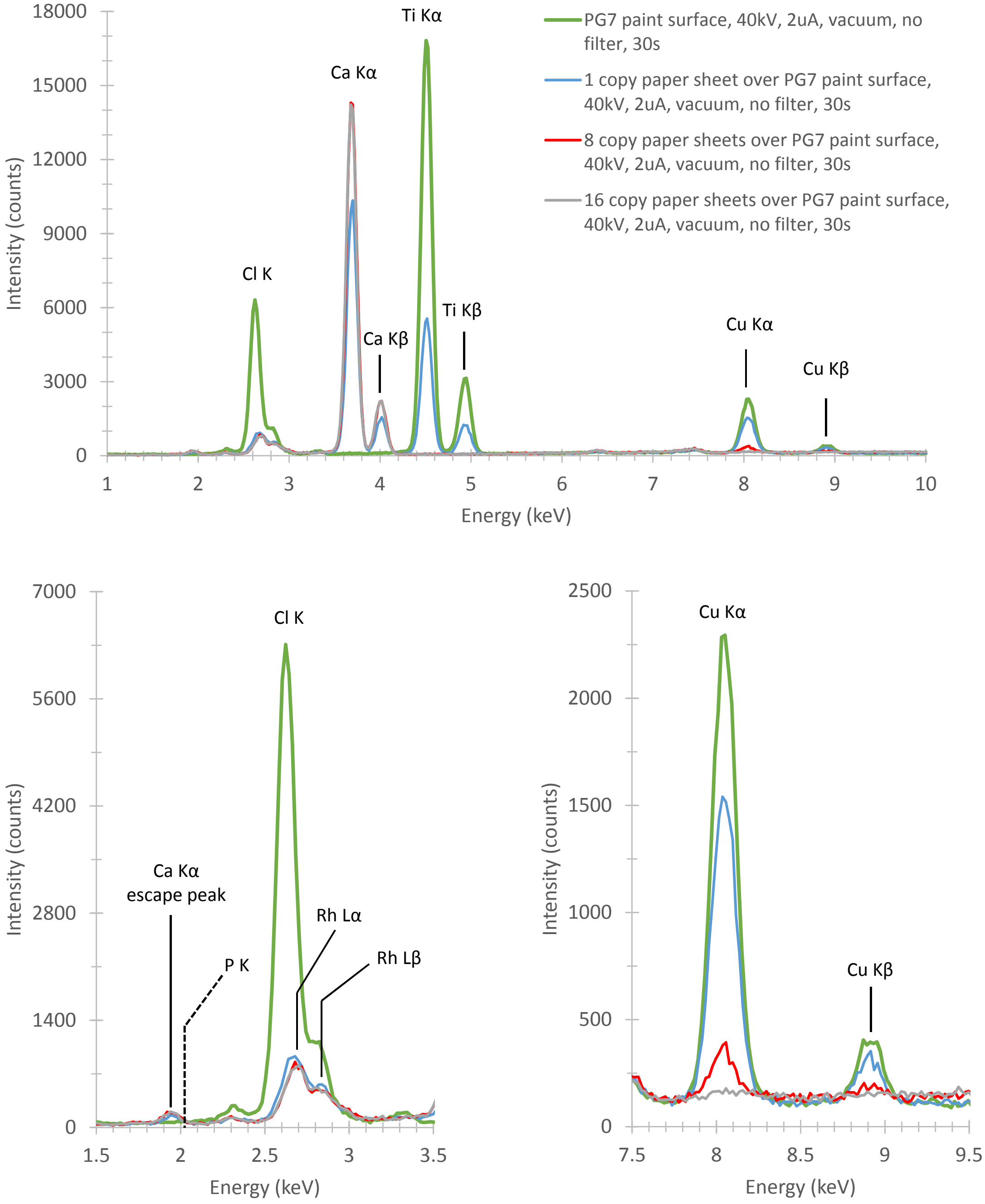


FIGURE 3.37. Spectra (with details, bottom left and right) for analysis of copy paper layers between phthalo green surface and instrument (attenuation of spectral components) in exercise 3.2e. Data collected using a Bruker Tracer III-SD, Rh tube.

1: What is the elemental composition of the painted surface?

- The green paint layer contains Cl and Cu. Phthalocyanine (phthalo) green has the molecular formula $C_{32}Cl_{16}CuN_8$. Ti peaks relate to the titanium white “ground layer” applied to the canvas before the green layer. Collect and examine spectra of bare canvas and bare canvas with a layer of titanium white to help distinguish which peaks may relate exclusively to the green layer containing phthalo green. See exercise 3.2c.

2: How did the sheets of paper affect the paint spectrum? Which elements were most impacted?

- Copy paper contains Ca, which relates to the use of alkali reserves in paper.
- Placing copy paper sheets between the green surface and the detector of the XRF instrument causes attenuation of the peaks related to the paint films. An increase in the intensity of peaks (Ca) related to the paper can also be noted.
- The Cl K peaks at 2.62 keV are most impacted. Even a single layer of copy paper causes the almost complete elimination of the Cl K peak from the spectrum.
- The Cu K peaks are also attenuated by the copy paper sheets but to a lesser extent than Cl K peaks. The Cu Kα peak is more strongly attenuated by copy paper than the Cu Kβ peak because it has a lower energy. The placement of paper sheets (here, 3 mm total thickness, approximately 16 sheets, was used to visualize the effect) between the green surface and the XRF instrument causes the complete elimination of Cu K peaks from the spectrum.

3: Why did it require more paper sheets to see the attenuation effect compared to the aluminum sheets in exercise 3.2d with the lead-tin solder?

- Aluminum foil has a higher density (pure Al is 2.699 g/cm^3) than copy paper (approximately 0.74 g/cm^3). The ability of a material to attenuate X-ray photons increases with density. Therefore, one would expect that a single sheet of aluminum foil would cause a greater decrease in peak intensities of Cl and Cu than a single sheet of copy paper of the same thickness.

EXERCISE 3.2f:

Varying Ratio of Titanium White and Lithopone Mixtures

EXPECTED OUTCOMES TO EXERCISE QUESTIONS

Resolution of overlapping Ti and Ba peaks

Spectra used in addressing the following questions from exercise 3.2f are shown in figure 3.38.

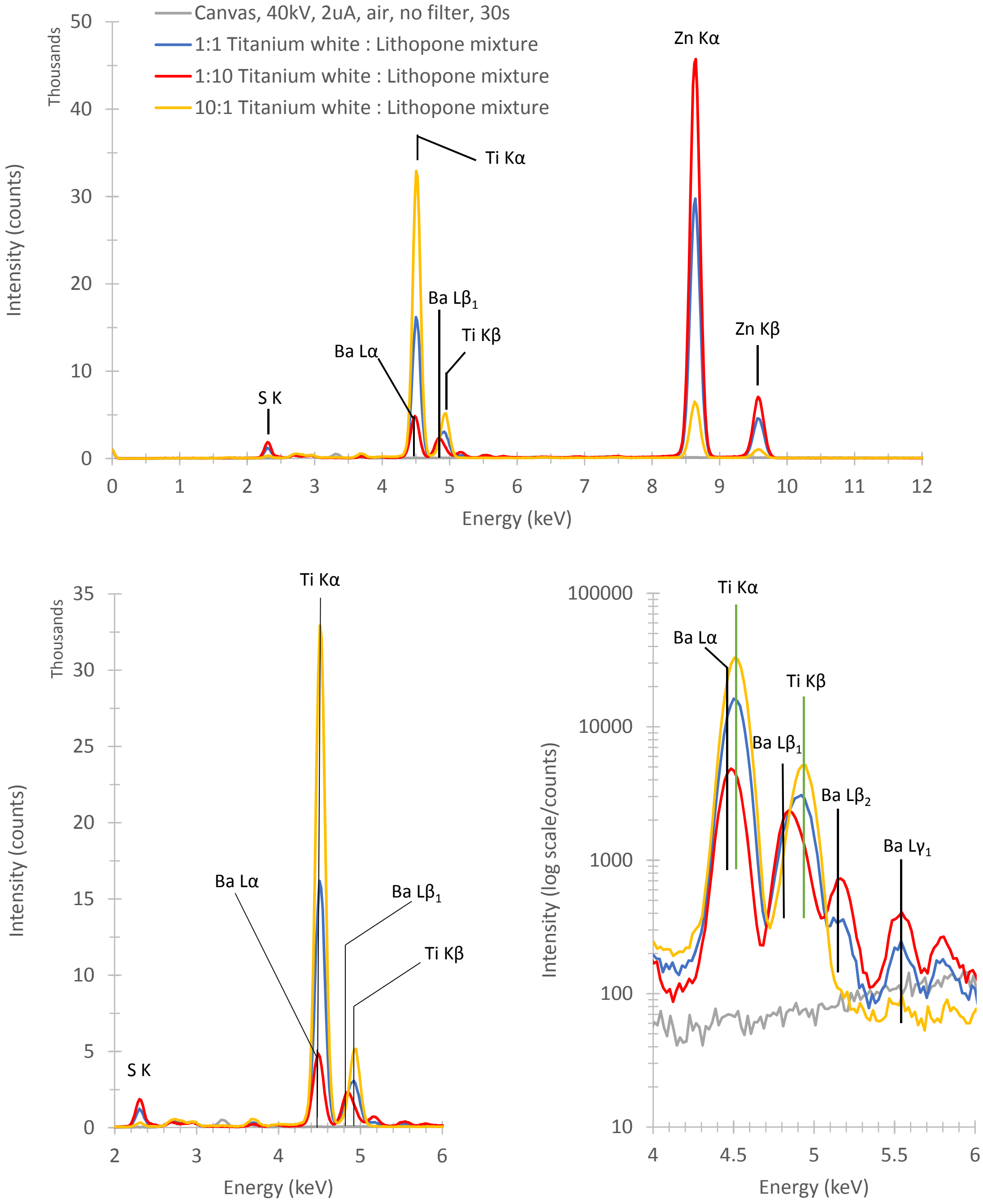


FIGURE 3.38. Spectra (with details, bottom left and right) for analysis of ratio of titanium white and lithopone mixtures (resolution of overlapping Ti and Ba peaks) in exercise 3.2f. Data collected using a Bruker Tracer III-SD, Rh tube.

1: How do the different ratios of titanium white and lithopone affect the spectra?

- Lithopone (PW5) contains barium sulfate ($BaSO_4$) and zinc sulfide (ZnS). Titanium white (PW6) is titanium dioxide. Different ratios of titanium white and lithopone cause changes in the relative intensities of Ti K vs. Ba L, S K, and Zn K peaks.
  - 10:1 mixture of titanium white and lithopone: the presence of Ba L lines is difficult to visualize unless one examines the region of the Ti K and Ba L lines using a logarithmic scale. In this case, the Ba $L\gamma_1$ peak becomes visible. The presence of Zn K lines is clear, and this observation should indicate that some other material is present in addition to a titanium-containing white pigment.
  - The spectrum of the 1:1 mixture shows a very subtle shift in the position of X-ray peaks from the Ti $K\alpha$ and Ti $K\beta$ positions to slightly lower energies due to the detection of more Ba $L\alpha$ and Ba $L\beta_1$ X-ray fluorescence photons. The Ba $L\beta_2$ and Ba $L\gamma_1$ peaks become clearly visible without the need to inspect the spectrum using a logarithmic scale. The presence of S K and Zn K lines is clear.
  - The spectrum of the 1:10 mixture of titanium white and lithopone displays peaks at 4.49 keV and 4.84 keV, which occupy positions between the Ti $K\alpha$ and Ba $L\alpha$ peaks and the Ba $L\beta_1$ and Ti $K\beta$ peaks, respectively. This is a very subtle indication of the presence of Ti in the volume of material analyzed in addition to Ba. Other Ba L lines are clearly visible, as are S and Zn peaks, which also indicate the presence of lithopone.

Mixtures vs. layers of titanium white and lithopone on canvas

Spectra used in addressing the following questions from exercise 3.2f are shown in figure 3.39.

2: In comparing the Ti/Ba layers (see exercise 3.2c; D, front; E, back) and mixtures spectra, can you distinguish which are mixtures and layers? Explain.

- Lithopone (PW5) contains barium sulfate ($BaSO_4$) and zinc sulfide (ZnS). Titanium white (PW6) is titanium dioxide.
- Comparison of spectra of layered vs. mixed titanium white and lithopone on canvas finds two spectra that appear very similar—the 1:10 titanium white to lithopone mock-up, and the layered mock-up (canvas, titanium white, lithopone) analyzed with the lithopone layer facing the instrument. It is clear from the spectra that Ba is present due to the detection of Ba $L\alpha$ lines. It may be more difficult to determine whether Ti is present based on these spectra. It is also clear that Zn is present in the material analyzed.
  - The detection of the S K peak indicates that S is present in the top region of the sample. This is because S K photons are low energy and it is unlikely that they would be detected if they were present in an underlying layer.
  - Based on the detection of S and Ba, one may infer that $BaSO_4$ is present as that is the most common form of Ba in cultural heritage materials.
  - Based on the co-occurrence of Ba and Zn, one may consider that lithopone is present and that S is present in both $BaSO_4$ and ZnS.
  - Without prior knowledge about the composition and layer structure of these two samples, it would be difficult to determine whether the spectra represent a mixture of Ba- and Ti-containing compounds or whether the spectra represent two or more separate layers containing compounds of Ba and Ti.

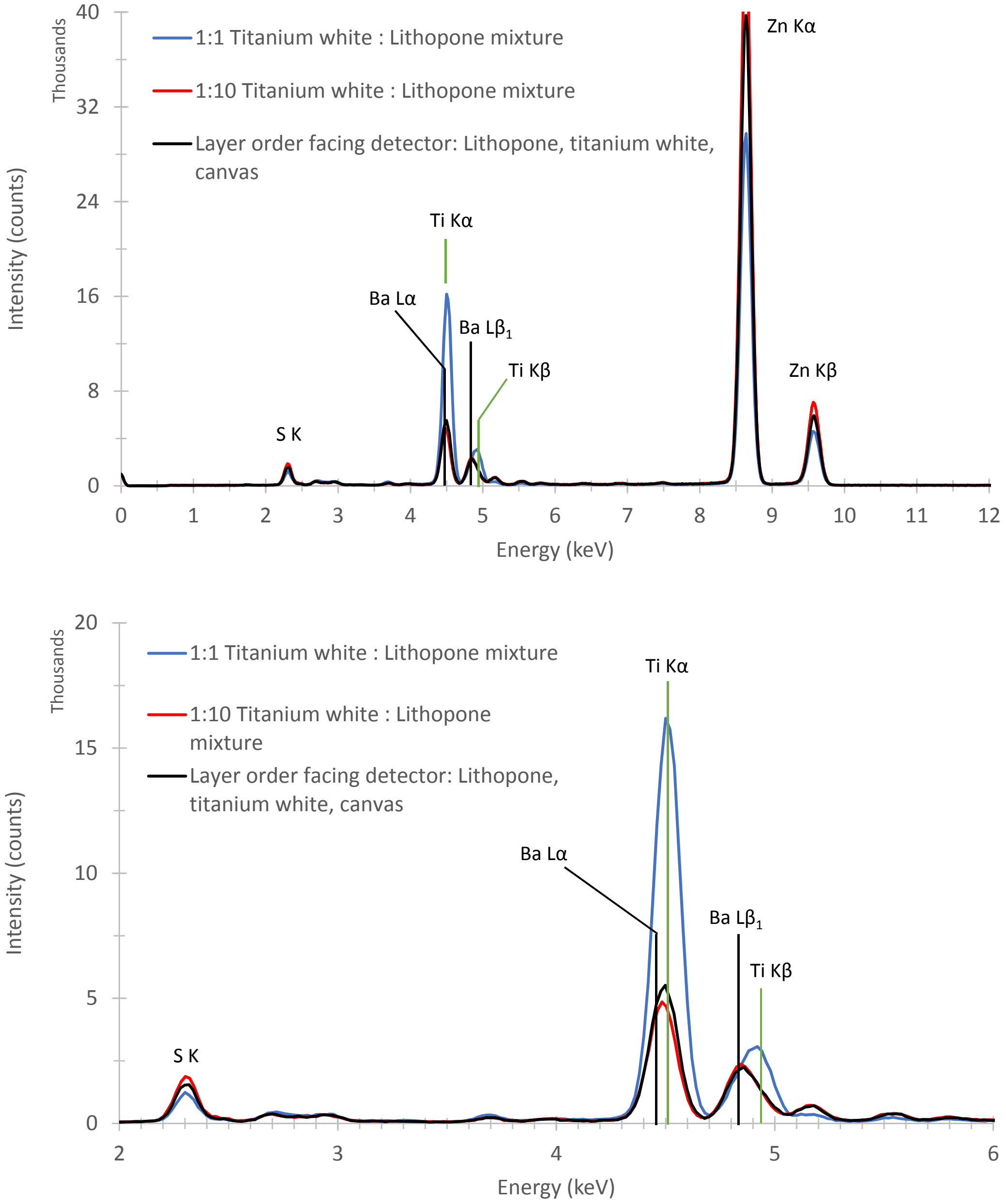


FIGURE 3.39. Spectra (with detail, bottom) for analysis of ratio of titanium white and lithopone mixtures (mixtures vs. layers on canvas) in exercise 3.2f. Data collected using a Bruker Tracer III-SD, Rh tube.

EXERCISE 3.3a:

Prussian Blue Serial Dilution with Titanium White

EXPECTED OUTCOMES TO EXERCISE QUESTIONS

Limits of color perception vs. iron detection via XRF

Spectra used in addressing the following questions from exercise 3.3a are shown in figure 3.40.

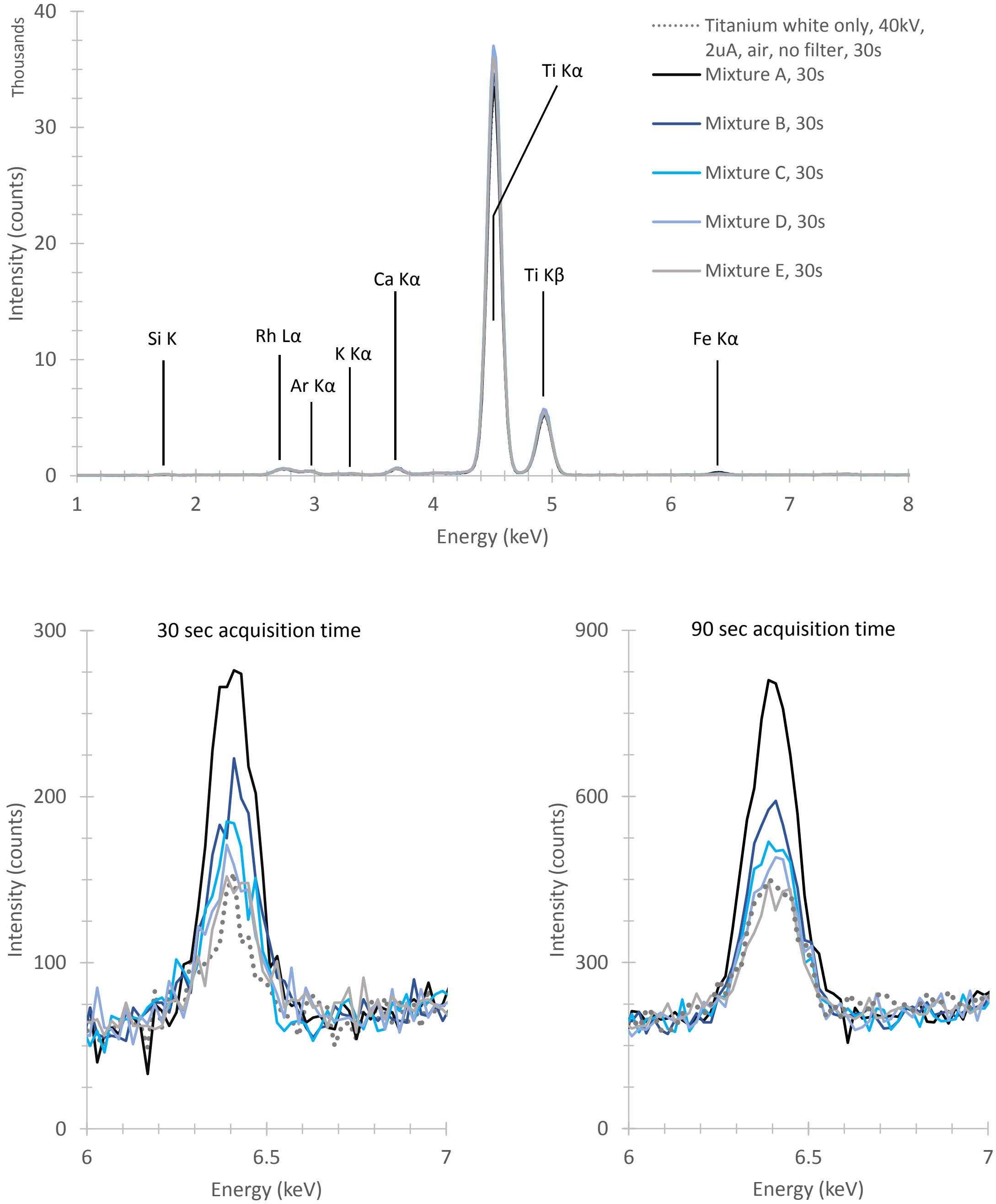


FIGURE 3.40. Spectra for sensitivity analysis of dilution of Prussian blue with titanium white in exercise 3.3a. Fe Kα peak at 30s acquisition time is shown at bottom left; Fe Kα peak at 90s acquisition time is shown at bottom right. Data collected using a Bruker Tracer III-SD, Rh tube.

1: What is the elemental composition of the serial dilutions?

- The elemental composition includes Ti, Ca, K, Fe, Si.
- Rh peaks relate to the anode material of the X-ray tube. Ar is detected as it is part of the atmosphere. The use of a vacuum pump or He flush would eliminate or lower the Ar peak intensity.
- Comparison to the spectrum of bare canvas indicates that the canvas likely contributes the K peak. Examination of the spectrum of titanium white paint on canvas indicates that Ti is present as TiO_2. Titanium white paint also contributes the Si and Ca peaks.
- The detection of Fe peaks may relate to the presence of Prussian blue (PB27), which is ferric ferrocyanide ($Fe_4[Fe(CN)_6]_3$). It is important to check whether the intensity of the Fe peaks exceeds the intensity of iron peaks in spectra of the bare canvas and canvas with titanium white paint.

2: At what dilution is it difficult to determine the presence of Prussian blue?

- Visually, the presence of Prussian blue can be inferred from the perception of a blue hue. Prussian blue is a pigment with a very high tinting strength. Although mixture E has very little Prussian blue relative to titanium white, it still has a perceptibly blue hue. The ratios of Prussian blue to titanium white in the five mixtures are shown in table 3.20.
- Chemically, the presence of Prussian blue correlates with the presence of iron (Fe) peaks in spectra. The intensity of the Fe Kα peak in the spectrum of mixture E (palest blue) is similar to the intensity of the Fe Kα peak in the spectrum of titanium white on canvas. Thus, based on the detection of iron only, it is not possible to infer the presence of Prussian blue.

TABLE 3.20. Ratios of Prussian blue to titanium white paint in the various mixtures.

Mixture	Prussian blue to titanium white paint ratio (weight ratio)
A	1: 1200
B	1: 2400
C	1: 4800
D	1: 9600
E	1: 19200

3: Would a longer acquisition time help in determining the presence of the iron (Fe) peak? Why or why not?

- The use of a longer acquisition time helps to determine with greater confidence that the Fe Kα peak is of greater intensity in the spectrum of mixture D than in the spectrum of titanium white paint only.
- The use of a longer acquisition time causes an improvement in the signal-to-noise ratio of spectra. This can be seen in the background region on both sides of the Fe Kα peak in spectra acquired for 90s: the “zigzag” signal in the background has a smaller amplitude relative to the height of the Fe Kα peak. To facilitate this comparison, the y-axes (intensity) of the spectra have been adjusted so that the height of the Fe Kα peak for mixture A is approximately the same in spectra collected with 30s and 90s real time.

EXERCISE 3.3b:

Black-and-White Photograph, with and without PMMA Backing

EXPECTED OUTCOMES TO EXERCISE QUESTIONS

Analysis of areas with increasing image density

Spectra used in addressing the following questions from exercise 3.3b are shown in figure 3.41.

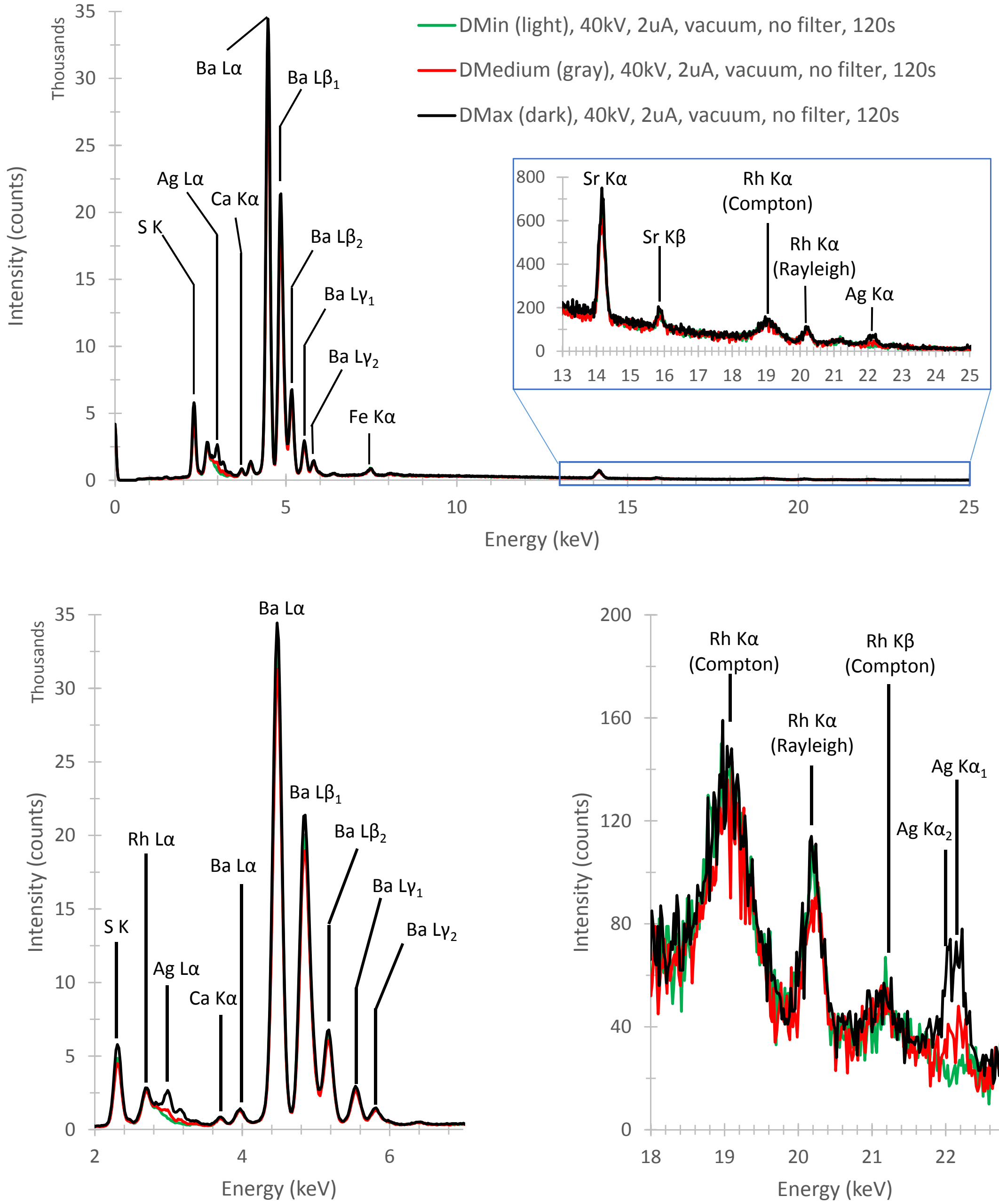


FIGURE 3.41. Spectra (with details, bottom left and right) for analysis of black-and-white photograph (analysis of areas with increasing image density) in exercise 3.3b. Data collected using a Bruker Tracer III-SD, Rh tube.

1: For silver gelatin prints, what are the elements of interest? What instrument conditions would you use to observe these elements?

- Ag is the primary image-forming material. Given the thinness of the Ag imaging layer, the use of higher currents and long collection times help enhance the sensitivity of Ag detection. When available, the choice of larger X-ray spots is advised.
    - Ag L lines are enhanced when using 15–20 kV accelerating potential.
    - The Ag Lα peak (2.98 keV) overlaps with the Ar Kα peak (2.95 keV). The use of vacuum or He atmosphere helps eliminate or lower the intensities of Ar K peaks, and this enhances sensitivity of the technique to Ag L lines.
    - The use of a Ti filter suppresses the Rh L lines from the excitation spectrum when combined with the use of vacuum or He atmosphere; this can also improve sensitivity to the Ag L peaks.
    - Ag K lines are near the Rayleigh scattered Rh K lines, and in a Rh-anode instrument the detection of low-intensity Ag K lines can be difficult due to the relatively high spectral background in this region.
    - Ba, S, and Sr are present in the baryta layer as $BaSO_4$ with trace Sr impurity. Note that the Ba Kα (32.19 keV) and Ba Kβ (36.39 keV) peaks are difficult to excite with Rh-anode XRF instruments at 40 kV accelerating potential. Use of 45 kV accelerating potential helps with the detection of Ba K peaks.

Common image-toning agents include S, Se, and Au. Note that it can be difficult to judge the use of sulfur (S) toning in the presence of $BaSO_4$. Detection of S K peaks is enhanced when using low accelerating potential and high-current settings along with vacuum or He atmosphere. Detection of low-intensity Se K and Au L lines can be enhanced by using beam filters that contain Cu (such as a combined Al/Ti/Cu filter) along with high accelerating potential and high-current settings. Such filters lower the background in the region of the Se K and Au L lines. Some less common toning agents are iron and uranium.

"Blue" toners result in the creation of ferric ferrocyanide, which would be associated with elevated levels of Fe in areas of high image density (DMax). Detection of low-intensity peaks can be enhanced the same way Se K lines can. If the photographs were hand colored, elements associated with pigments may be present.

2: What is the elemental composition of the DMin area? How does this inform us about the elemental composition of the photograph substrate?

- The DMin area contains Al, S, Ca, Ba, Fe, and Sr. The photograph substrate contains a baryta layer ($BaSO_4$ + Sr) with low levels of Al, Ca, and Fe.

3: What is the elemental composition of the DMedium and DMax areas?

- The DMedium and DMax areas contain Ag in addition to the elements in the DMin area. There appear to be no toning materials present in addition to the silver (Ag) image-forming material.

4: Are any elements due to the instrument?

- Spectra also contain peaks due to Ni and Cu, which appear to be present due to instrument contributions based on comparisons with spectra of a clean polyethylene cube and a PMMA tile.

Effect of PMMA backing on spectra

Spectra used in addressing the following questions from exercise 3.3b are shown in figure 3.42.

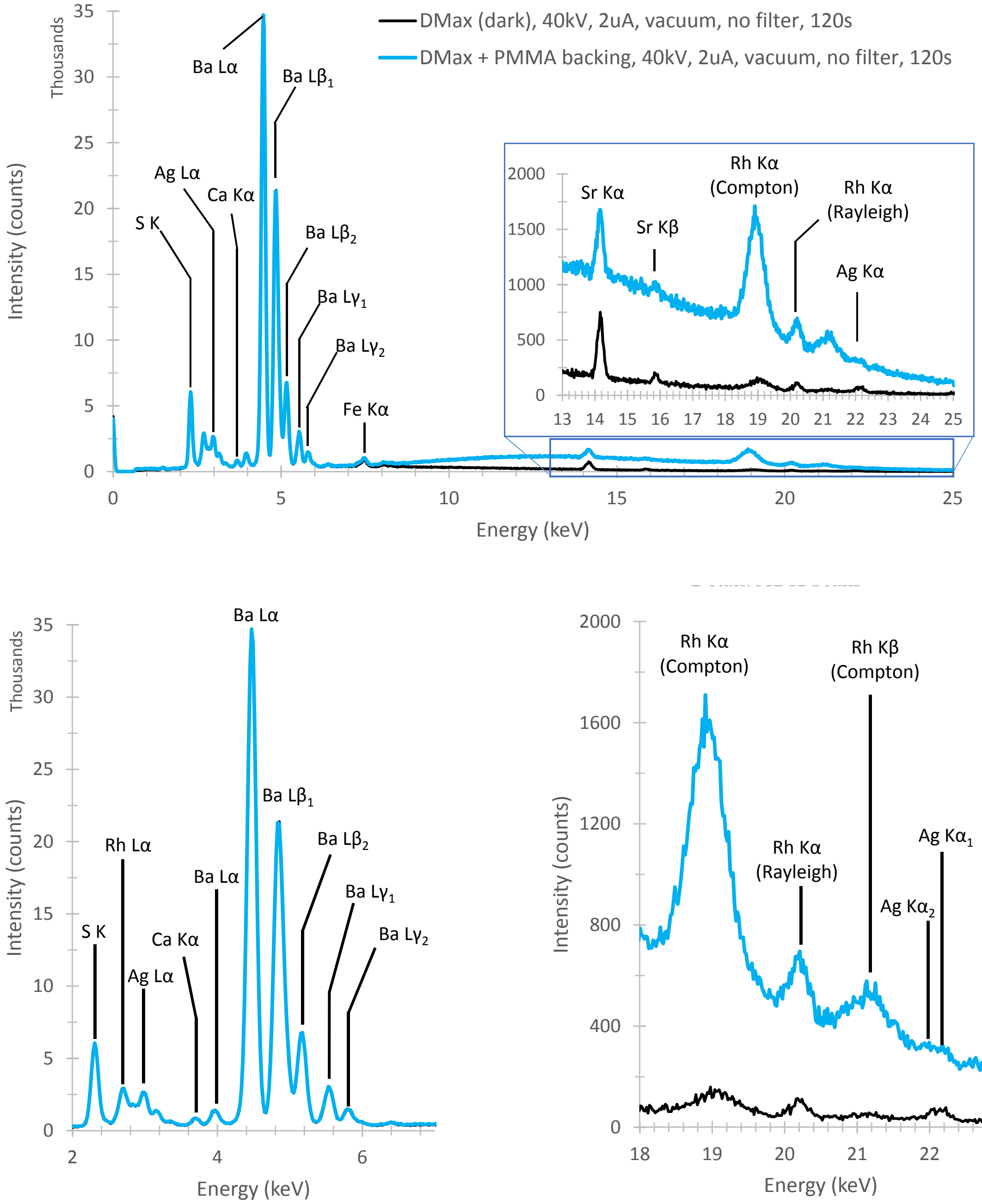


FIGURE 3.42. Spectra (with details, bottom left and right) for analysis of black-and-white photograph (effect of PMMA backing on spectra) in exercise 3.3b. Data collected using a Bruker Tracer III-SD, Rh tube.

5: What is the effect of the PMMA backing? How does the PMMA backing affect the interpretation of the spectral peaks? What could you do to counteract the effect of the mounting (here, PMMA backing) on the resulting spectra?

- The PMMA backing sheet causes an elevation in the intensity of the background starting around 8 keV. The spectrum appears to have a “hump” centered around 13–14 keV (see fig. 3.42, inset).
- Materials with low average atomic numbers are effective at scattering X-ray photons. By placing a PMMA backing sheet behind a photograph (instead of leaving an air space), scatter of the excitation spectrum is increased back toward the detector. Both the continuous (bremsstrahlung) portion and the characteristic Rh K lines of the excitation spectrum are scattered and detected.
- Due to the higher, sloped background of the spectrum obtained with the PMMA backing sheet, it becomes more difficult to distinguish low-intensity peaks from the background.
- The Sr Kβ peak becomes more difficult to distinguish from the background.
- The Ag Kα peak becomes more difficult to distinguish from the background.
- If there is a PMMA or matboard backing (or mounting) layer present, it may be helpful to use a multilayer beam filter containing a Cu layer and high-current settings to obtain spectra at 40–50 kV accelerating potential. These parameters would lower the intensity of the excitation spectrum above 10 keV and reduce the hump-shaped background that interferes with the detection of Sr and Ag.

EXERCISE 3.3c:

Albumen Photograph Print: Effect of Filter

EXPECTED OUTCOMES TO EXERCISE QUESTIONS

Analysis of areas with maximum image density

Spectra used in addressing the following question from exercise 3.3c are shown in figure 3.43.

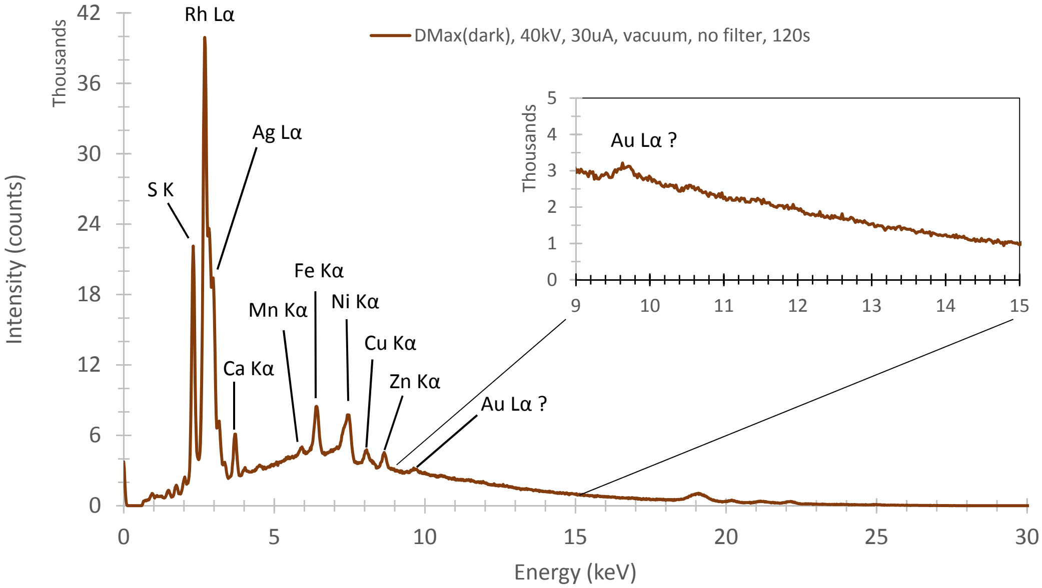


FIGURE 3.43. Spectra for analysis of albumen photographic print (analysis of areas with maximum image density) in exercise 3.3c.

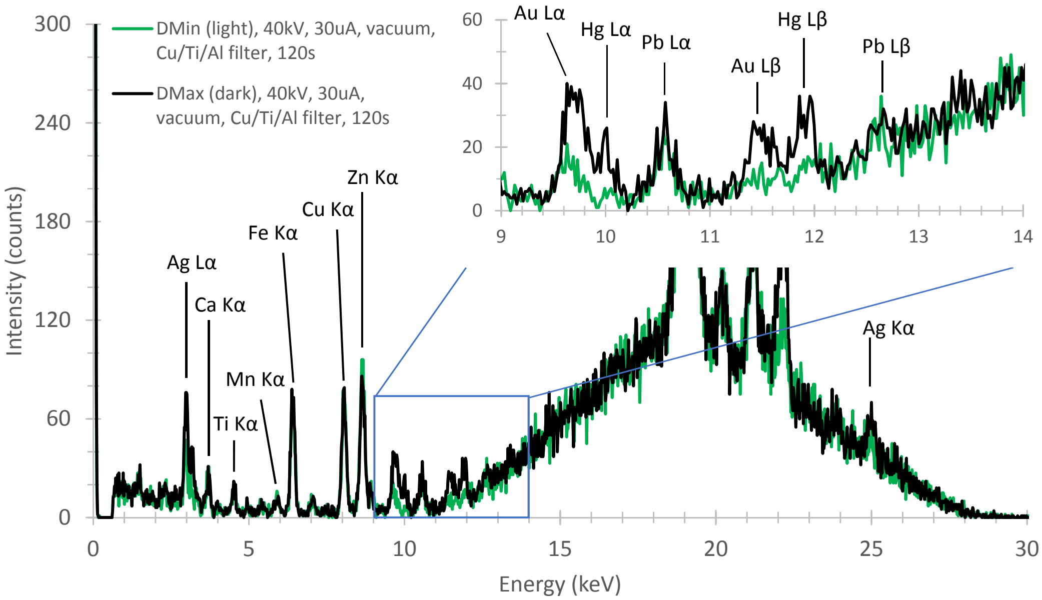


FIGURE 3.44: Spectra showing effect of filters on albumen photographs, with data collected using a Bruker Tracer III-SD, Rh tube, in exercise 3.3c.

1: How does the use of filters affect the analysis of photographs?

- Elements of interest for albumen photographic prints:
  - Ag is the primary image-forming material.
  - Gold (Au) and mercury (Hg) are frequently associated with albumen prints.
  - If the black-and-white albumen prints were hand colored (typically with watercolors), then elements associated with the pigments may be detected.
- The use of filters lowers the intensity of the excitation spectrum; therefore, higher-current settings and longer collection times are needed to acquire spectra.
- The use of Cu/Ti/Al filters with Rh-anode instruments can aid in the detection of several elements.
  - Low-intensity X-ray lines for Au L, Hg L, and Pb L families are difficult to detect when no filter is used because of the high sloping background resulting from scattered bremsstrahlung radiation from the X-ray tube.
  - Cu/Ti/Al filters absorb the bremsstrahlung radiation emerging from the X-ray tube up to around 15 keV. Low-intensity Au, Hg, and Pb peaks can be more easily detected when the background is lowered.
  - In the example shown (see fig. 3.44), the DMax area has higher-intensity Au and Hg lines than the DMin area. This indicates that gold and mercury are associated with the image-forming material (silver). Gold was a commonly used toning agent to improve the permanence of silver-based photographic prints.
  - In the example shown (see fig. 3.44), the Pb L lines have very similar intensities in the DMax and DMin areas. This indicates that lead is likely associated with the paper support of the albumen print.
- The detection of Ag L lines is hindered by the presence of intense Rh L lines from the excitation spectrum.
  - The use of a Cu/Ti/Al filter suppresses the Rh L lines from the excitation spectrum; this improves sensitivity to the Ag L peaks.
  - The Ag Lα peak (2.98 keV) overlaps with the Ar Kα peak (2.95 keV). The use of vacuum or He atmosphere helps eliminate or lower the intensities of Ar K peaks, and this enhances sensitivity of the technique to Ag L lines.

EXERCISE 3.3d:

Drawing Materials on Paper: Sensitivity, with and without PMMA Backing

EXPECTED OUTCOMES TO EXERCISE QUESTIONS

Sensitivity to minor components

Spectra used in addressing the following question from exercise 3.3d are shown in figure 3.45.

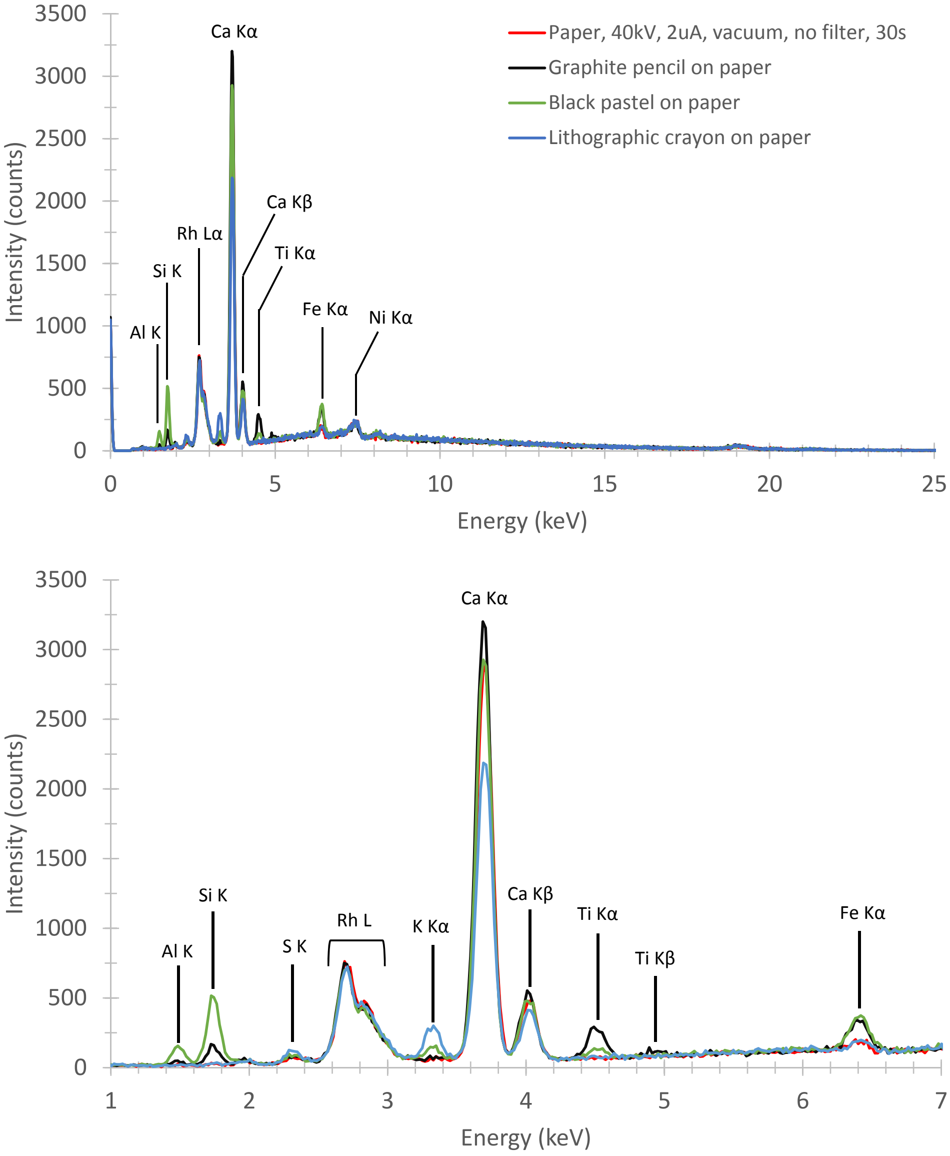


FIGURE 3.45. Spectra (with detail, bottom) for analysis of drawing materials on paper (sensitivity to minor components) in exercise 3.3d. Data collected using a Bruker Tracer III-SD, Rh tube.

1: What is the elemental composition of the watercolor paper substrate? What is the elemental composition of the drawing materials?

- The watercolor paper substrate contains Ca and low-intensity peaks for Fe. The latter are of greater intensity than Fe peaks in spectra of a clean polyethylene foam cube and a PMMA tile. Ca is likely present as $CaCO_3$, which may be added to paper to provide an alkaline reserve.

- The spectrum of the watercolor paper substrate also contains peaks corresponding to Ni and Cu, which appear to be present due to instrument contributions based on comparisons with spectra of a clean polyethylene foam cube and a PMMA tile.
- Graphite pencil contributes Al, Si, Ca, Ti, and Fe to the spectrum. These elements are likely present as additives to the graphite, a form of carbon. Common graphite pencil components include clay, which is most likely the source of Al, Si, Ti, and Fe. Ca may also be present in clay or as calcium carbonate. Ca and Fe peaks are more intense in the spectrum of the graphite on paper than in the spectrum of the paper substrate only.
- Black pastel contributes Al, Si, K, Ti, and Fe to the spectrum. Very low levels of S and Ca may be present. In addition to a carbon-based black, the formulation of the pastel likely includes clay (containing Al, Si, K, Ti, and Fe) and possibly chalk, a form of calcium carbonate (containing Ca). Pastels also contain an organic binding medium, such as a plant gum (e.g., gum Arabic) or methyl cellulose. Elements present in organic materials (H, C, O) cannot be detected using handheld or other air-path energy-dispersive XRF instruments.
- Black lithographic crayon contributes S and K to the spectrum. The color is most likely due to a carbon black (e.g., lamp black). The lithographic crayon does not appear to contain clay fillers. Traditional lithographic crayon ingredients may have included graphite, saltpeter (KNO_3), and lye (K_2CO_3). Lithographic crayons contain a high proportion of organic materials. Historically, the crayon medium ingredients were wax, natural resins, and tallow. Other organic ingredients may have included oil and stearic acid.

Impact of vacuum on spectra

Spectra used in addressing the following question from exercise 3.3d are shown in figure 3.46.

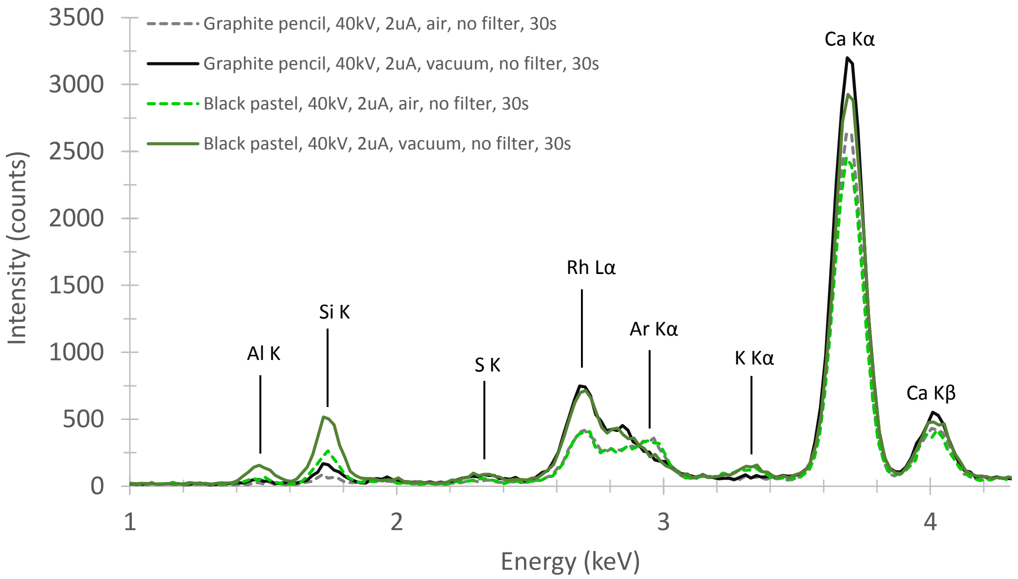


FIGURE 3.46. Spectra for analysis of drawing materials on paper (impact of vacuum on spectra) in exercise 3.3d. Data collected using a Bruker Tracer III-SD, Rh tube.

2: What is the effect of vacuum?

- The effect of vacuum is most noticeable for paper and drawing media components with low-energy peaks: Al, Si, S, K, and Ca. These peaks appear more intense in spectra obtained with the vacuum pump. Some instruments may be capable of detecting Na and Mg as well.
- The intensity of the Ar peak (argon is 0.93% of the atmosphere) is lower in the spectrum obtained while using a vacuum pump to remove air from the interior of the instrument.
- Rh L peaks, which represent Rayleigh scattering of the excitation radiation by the sample, also appear more intense in spectra obtained with the vacuum pump.

EXPLANATION OF OBSERVATIONS

The vacuum pump removes air from the path of the beam inside the instrument. Since nitrogen and argon in air can attenuate (absorb) low-energy X-rays, the use of a vacuum should help increase the intensity of low-energy peaks.

Effect of PMMA backing sheet on spectra

Spectra used in addressing the following question from exercise 3.3d are shown in figure 3.47.

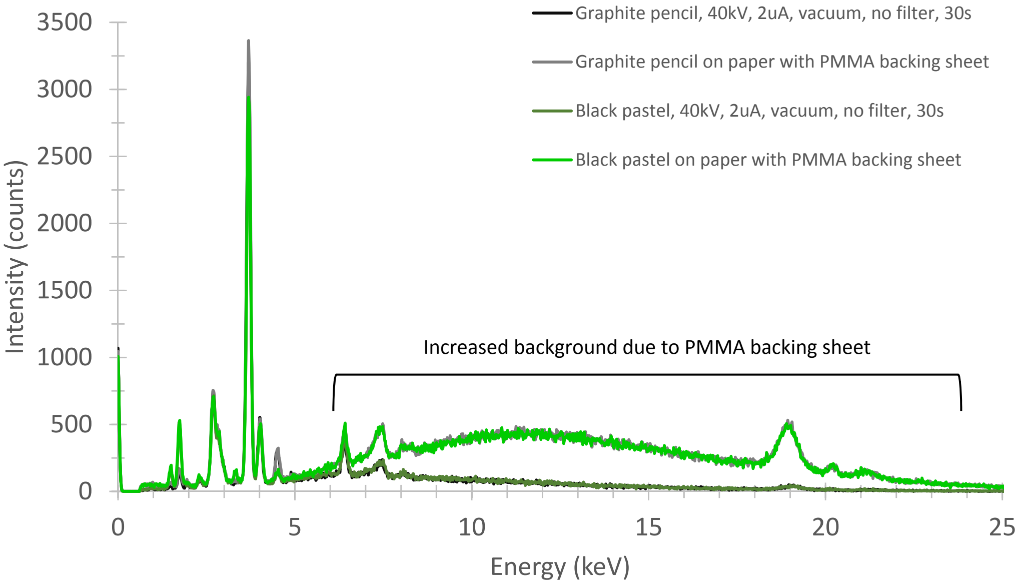


FIGURE 3.47. Spectra for analysis of drawing materials on paper (effect of PMMA backing sheet on spectra) in exercise 3.3d. Data collected using a Bruker Tracer III-SD, Rh tube.

3: How did the PMMA backing sheet affect the graphite pencil and black pastel spectra?

- The PMMA backing sheet causes an elevation in the intensity of the background starting around 6 keV. The spectrum appears to have a “hump” centered around 11–12 keV.

- Materials with low average atomic numbers are effective at scattering X-ray photons. By placing a PMMA backing sheet behind a paper substrate (instead of leaving an air space), scatter of the excitation spectrum is increased back toward the detector. Both the continuous (bremsstrahlung) portion and the characteristic Rh K lines of the excitation spectrum are scattered and detected.
- The drawing media in these mock-up samples do not appear to contain elements with X-ray peaks above 8 keV. Thus, the PMMA backing sheet does not impact the ability to distinguish low-intensity peaks from a sloped, high-intensity background.
- Analysis of drawings on paper created with a metal point, such as lead (Pb) or silver (Ag), could be impacted by the use of a PMMA backing sheet because Pb L peaks and Ag K peaks would likely be of low intensity and may be difficult to detect on a sloped, high-intensity background.

EXERCISE 3.4a:

Phthalocyanine Green 7 (PG7) Painted on Pleated Filter Paper

EXPECTED OUTCOMES TO EXERCISE QUESTIONS

Effect of flat and pleated areas

Spectra used in addressing the following questions from exercise 3.4a are shown in figure 3.48.

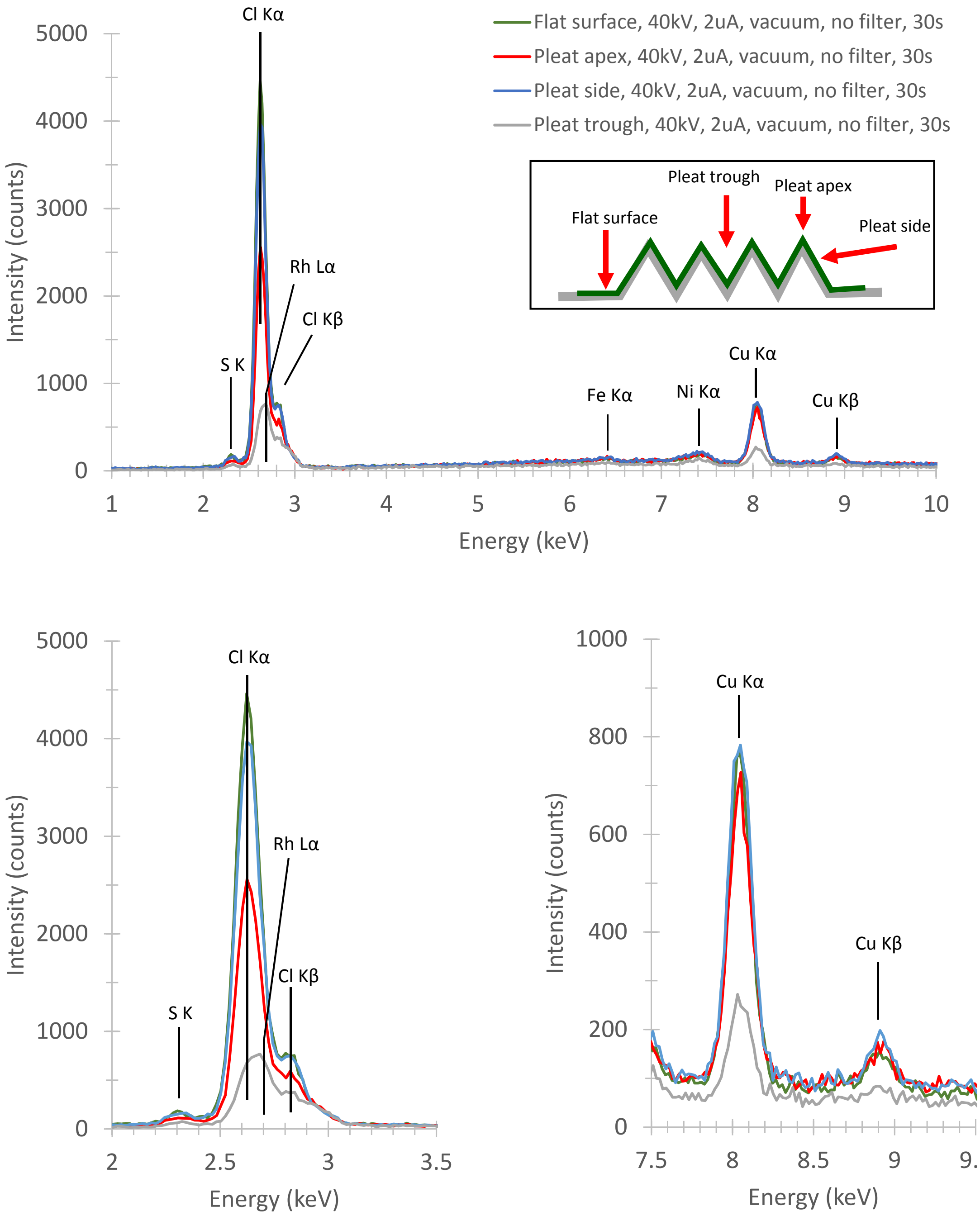


FIGURE 3.48. Spectra (with details, bottom left and right) for analysis of distance/topography for phthalo green (PG7) on filter paper (effect of flat and pleated areas) in exercise 3.4a. Data collected using a Bruker Tracer III-SD, Rh tube.

1: Does the relative intensity of the peaks change in the different sections? Calculate the ratio between copper (Cu) and chlorine (Cl) peak intensities. Which peak (Cu or Cl) is more affected by the attenuation?

- The green paint layer contains Cl and Cu. Phthalocyanine (phthalo) green has the molecular formula ranging from $C_{32}H_3Cl_{13}CuN_8$ to $C_{32}HCl_{15}CuN_8$.
- When the unpleated flat surface of the paper is analyzed, the instrument-sample geometry can be easily optimized. For handheld XRF units, the green flat surface will cover the entire instrument aperture.
- This measurement geometry optimizes the detection of Cl, as the Cl K peaks are low in energy and any air gaps between the green surface and the instrument aperture will result in the attenuation of the Cl K peaks.
- The ratio of Cl Kα to Cu Kα peak areas is the greatest in this configuration.
- Positioning the instrument to analyze the side of the pleated paper can be harder to achieve than the analysis of the unpleated flat surface.
- The Cl K and Cu K peak intensities are slightly lower than in the spectrum of the flat surface.
- The Cl K peak intensity is impacted more than the Cu K peak intensities, and the peak area ratios are lower than for the flat surface.
- The apex of a pleat presents a relatively small green surface for analysis. The Cl K and Cu K peak intensities are lowered compared to the unpleated flat surface and the side surface of a pleat.
- The Cl K peak intensity is impacted more than the Cu K peak intensities, and the peak area ratios are lower than for the flat surface and the side surface of a pleat.
- Positioning a trough over the instrument aperture of a handheld XRF unit means that there is a significant gap between the surface and the instrument nose.
- Cl K peaks are significantly attenuated due to the air gap between the instrument and the green surface. Cu K peaks are also attenuated, but not as much as the Cl K peaks because Cu K peaks have a higher energy. The Cl Kα : Cu Kα peak area ratio is the lowest for this measurement geometry.

2: Do you trust your ability to be consistent in holding the unit for the pleat apex, side, and trough sections? Why is this important?

- Consistent positioning of a handheld XRF unit is important to obtain consistent, comparable results. Positioning near an object with complex surface geometry is difficult. The use of a tripod and a horizontal arm is recommended to help position and hold the instrument steady relative to a surface.

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4. Practical Application of XRF to Cultural Heritage Materials

The exercises in this workbook are designed to help you understand how X-ray fluorescence (XRF) spectrometers work and how to recognize some of the challenges encountered in the collection and interpretation of XRF spectra. Mastering the operation of this instrument is only the first step, however. Though it's tempting to simply jump in and start collecting spectra, without proper planning and preparation it's unlikely you will get the good-quality data that will provide the information you need. This chapter discusses how to design an experiment using the scientific method to address specific research questions, identifies practical aspects of preparing and setting up for analysis of cultural heritage objects, provides tips for interpreting and reporting results, and outlines considerations for the use of complementary techniques.

4.1 The Scientific Method

Scientific research projects of any size always should be carried out using a systematic process called the scientific method. The basic components of the scientific method are outlined in figure 4.1. Everything begins with an observation, usually accompanied by the question "Why?" The scientific method helps answer this question through the formation of a *testable* hypothesis—an explanation of the observed phenomenon that can be probed with an experimental measurement. If the result of the experiment is consistent with the hypothesis, then the hypothesis has a good chance of being correct. This is an iterative process, and the odds that the hypothesis being tested is correct grows with each round of repeated testing. For a hypothesis to become a scientific *theory*, it must have stood up to multiple, rigorous rounds of testing.

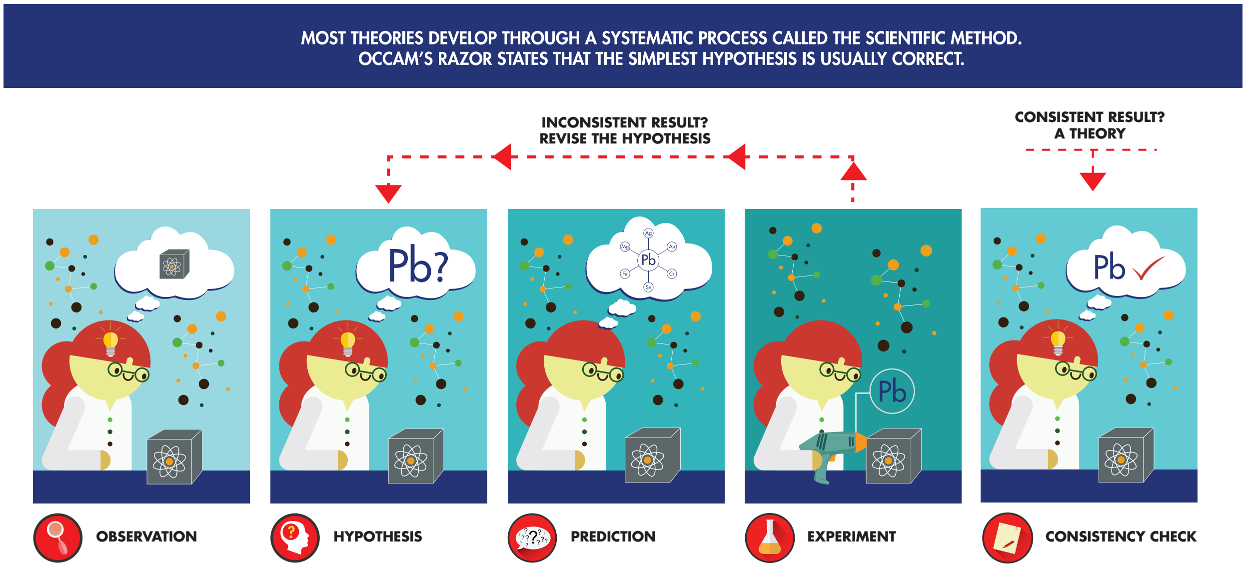

FIGURE 4.1. The basic components of the scientific method.

The scientific method can and should also be used in the study of cultural heritage materials. It can be applied to all levels of an investigation, from defining the overall scope of the project to understanding the results from a single analytical measurement. A well-designed scientific investigation involves continual questioning and re-evaluation. Typically, it is not sufficient to simply determine *what* something is; a well-designed study should also strive to understand *how* or *why* it got to be that way. When asked the purpose of an XRF study, a common reply is "I want to know what the pigments are in this painting/object." This, of course, may be an important step in the process, as long as the first step—developing a testable hypothesis to explain an observation—is well defined in the researcher's mind. *Why* is it important to identify the pigments? *How* will that information influence the understanding of the object or determination of a conservation treatment?

Once you become practiced at employing the scientific method, you may not need to articulate what you are seeking at each individual stage. For example, saying you want to identify pigments may become shorthand for the following:

- Observation: pigments are observed on this painting/object.
- Hypothesis/prediction: if this painting/object was made by artist X, then the predicted pigments are A, B, and C.
- Experiment: use XRF to identify/characterize detectable pigment.
- Evaluation: are the results consistent with the hypothesis?

Keeping in mind the basic process of the scientific method—observation, hypothesis, prediction, experiment—will ensure that the experiments being conducted remain focused on addressing a specific question. Asking "why" at every step will ensure that opportunities for new discoveries and insights are not missed. Further, bear in mind that the answer to "why" may not be achievable with XRF alone and may require the use of other techniques.

Employing the scientific method can be critical to correctly interpreting the information obtained from XRF results. To this end, we use the XRF analysis of layered white paint samples as an example (fig. 4.2).

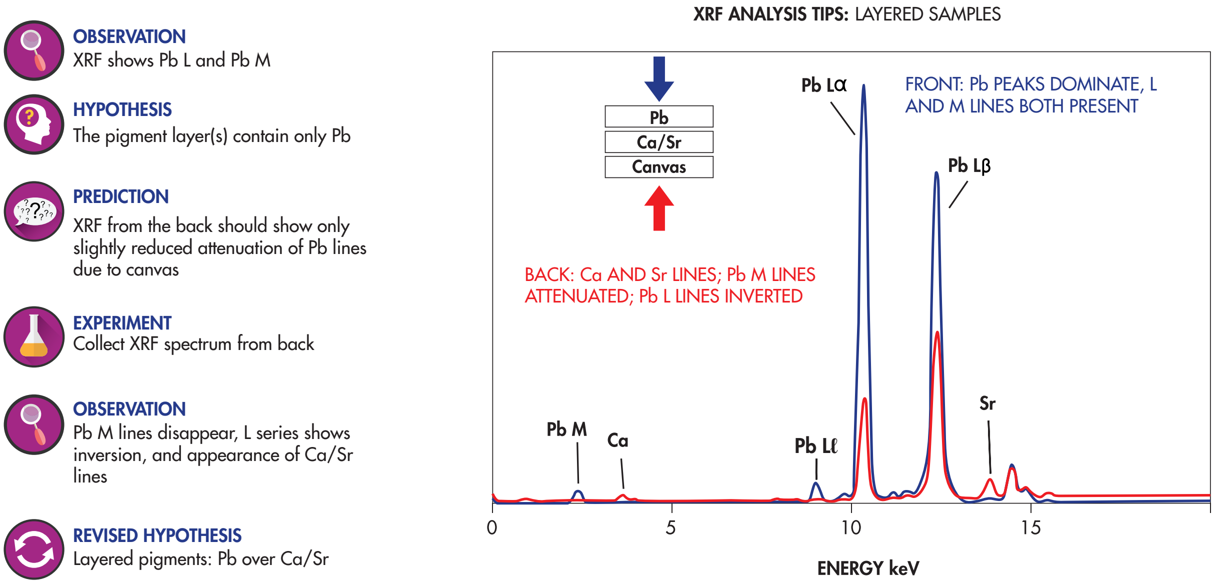

FIGURE 4.2. Spectra for XRF analysis of layered paint samples showing the application of the scientific method.

There may be something about the initial observation of a white pigment that leads to the hypothesis that the pigment lead white is present (e.g., it has a warm tone, the assumed date is historic, and/or the artist is known to have used lead white). This, of course, can be tested by collecting an XRF spectrum, which shows, as predicted, peaks attributable to Pb—both L and M emission lines (see fig. 4.2). This supports the initial hypothesis that a lead-containing pigment is present. The further observation that *only* lines attributable to Pb are present may lead to a subsequent hypothesis that a single layer of lead-containing pigment(s) is present. To test this hypothesis, it is predicted that an XRF spectrum collected from the back of the canvas should show only slight attenuation of the lower-energy Pb M lines relative to the higher-energy L lines due to the canvas, and perhaps also a slight attenuation of the lower-energy Lα line with respect to the Lβ line. However, when this experiment is conducted, the Pb M lines disappear and the Pb Lα line is strongly attenuated relative to the Lβ line. Furthermore, and significantly, XRF lines indicating the presence of Ca and Sr are now present, leading to the revised hypothesis that there is a calcium-containing layer under the lead-containing layer.

This hypothesis could be tested through the collection of a cross section and examination using complementary techniques. Of course, it is not always possible or practical to collect a spectrum from the reverse of a painting. In such a case, the XRF spectrum from the top surface alone would be interpreted as indicating that a single, lead-containing paint layer is present, and the underlying calcium-based layer would be missed.

The above example demonstrates another important tenet of scientific research: you can base conclusions on positive evidence, but you cannot prove something based on negative, or lack of, evidence. Or, as is often stated: "absence of evidence is not evidence of absence." The strongest conclusions are made based on positive results. For example, the presence of large peaks corresponding to lead allows the confident assertion that lead is present, but the lack of peaks corresponding to calcium can only be interpreted as indicating that no calcium is present above the detection limit.

It is important to remember that XRF is simply one tool and, while powerful, may not provide a full understanding of the system under investigation. As with most analytical techniques, it is best used in combination with other methods, even if the method is only visual observation. For example, visual observations of lacuna in the upper paint layer might have led to the hypothesis that multiple layers were present, and that collecting XRF spectra from both sides could provide additional information.

4.2 Conducting the Analysis

There is more to conducting an XRF study than simply collecting the spectra. Advance preparation regarding the object under study, as well as the physical presentation of the spectrometer to the object, is key to a successful analysis. The following sections provide practical tips on ways to prepare, set up, interpret, and report your data.

Preparation

To help understand issues critical to the study of an object, literature research, consultation of conservation/curatorial records, and discussion with colleagues to gather available information about the object's date, place, culture of origin, and history should be conducted before beginning any analysis. Once you have determined the scope of the research and established that XRF is the correct method to be used, there are additional recommended steps to take to help make the data collection go more smoothly.

- Have a good-quality color image on which you can record the spot locations of the XRF analysis. This can be done in many ways, including writing directly on the photo or printout or applying small adhesive dots on which the numbers are written (though this method covers more area, it often allows the analysis spots to be seen more easily on the image). Alternatively, a digital photo editor can be used, which has the advantage of producing a report-ready image. Choose what works best for you.
- Gather any previous technical imaging, such as ultraviolet (UV), infrared (IR), X-ray, and multispectral imaging (MSI). These of course should be examined prior to beginning analysis to help identify areas of interest, but having them on hand during analysis may be useful in interpreting the results as they are being collected and, based on new observations, may help identify new avenues of investigation.
- Have on hand a good flashlight, UV light, loupe, or other tools that will enable you to examine the surface closely. In particular, consult available treatment reports, noting any areas of damage, restoration, or corrosion that might impact the XRF analysis.
- Prepare a template to record experimental observations. For each XRF spectrum collected, you should record the operating conditions of the instrument (anode, voltage, current, filter, acquisition time, aperture size). While many instruments record these metadata automatically, it is good practice to note this information in your records as well. See chapter 2 for examples.
- Develop a game plan and budget your time. Pre-populating a template with a list of areas targeted for analysis can be helpful. Prioritizing areas of greatest interest is important, but keep in mind that it may be more efficient to collect data from all the spots in one general area before moving on to the next.
- During data collection, examine each spectrum to ensure that the spectral quality is sufficient; in particular, make sure *counts* and *dead time* are acceptable (see Glossary). Readjust parameters as appropriate. In addition, you should be performing a preliminary evaluation of each spectrum (i.e., identifying the majority of the peaks) as it is being collected, so that if something unexpected arises (e.g., an observation that would require you to revise your hypothesis), you can adjust your game plan to incorporate new analyses.
- Reserve time for data analysis and, if possible, time to come back to the object (not necessarily in the same session) to perform further analyses on any additional areas that may be identified through examination of the data.

Positioning the Instrument

One major advantage of handheld XRF spectrometers is their small size, which enables them to be easily positioned to examine large or complex-shaped surfaces. With that flexibility, however, comes additional preparation considerations: Should the instrument be handheld or can it be mounted on a tripod? What special precautions must be taken to ensure the safety of the instrument operator, other people nearby, and, of course, the safety of the art itself? While the instrument can be operated alone, it is often beneficial to have at least one other person present to help with the positioning and collection of data and, more importantly, to help monitor safety.

Handheld operation

Most handheld XRF spectrometers are designed to be operated by placing the nose of the instrument in direct contact with the surface of the object being analyzed. If this is acceptable and appropriate, it is good practice to make sure the nose of the instrument is clean by wiping it before moving the instrument to another spot to prevent cross-contamination. However, for most cultural heritage materials, it is generally preferable to place an isolating layer between the instrument and the object. This can be a thin sheet or

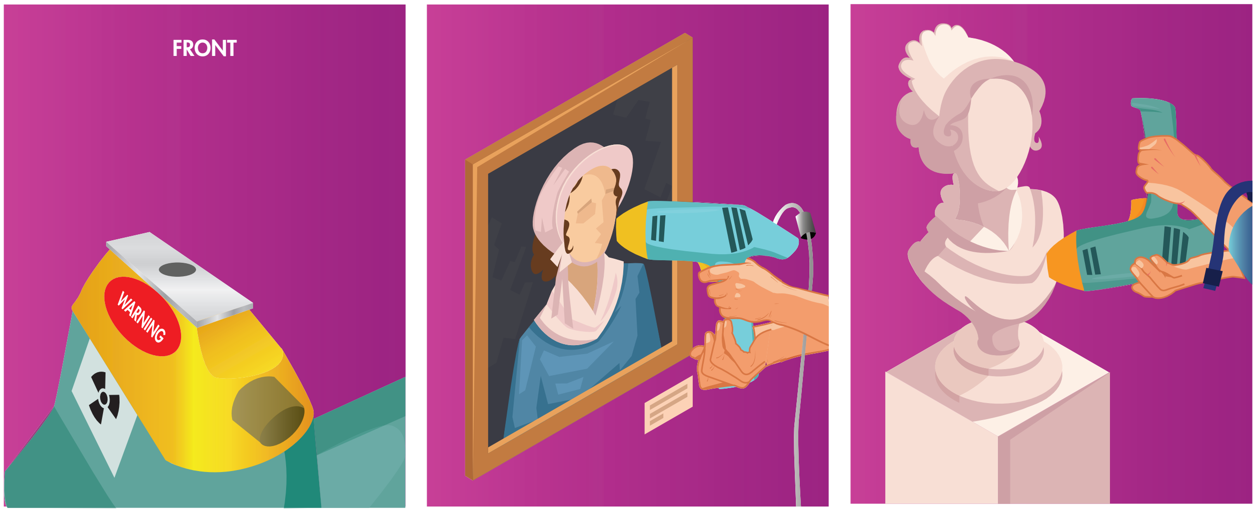

FIGURE 4.3. From left: placement of a sheet of insulating material on the nose for proper nose protection; and two proper hand positions on a handheld XRF instrument.

sheets of whatever material is acceptable to be in contact with the object: for example, Ethafoam, blotter paper, or glassine (fig. 4.3, left). In general, it is safer to adhere the isolating layer to the nose of the instrument, taking care not to cover the X-ray aperture, cameras, or other instrument components necessary to collect a spectrum. It is good practice to check the nose of the instrument between measurements to ensure that no material has been picked up that might lead to accidental cross-contamination.

Operating the instrument in the handheld mode allows hard-to-reach areas to be analyzed, but this often requires the operator to hold the instrument in an awkward position. The instrument should be held *only* by the designated handle or other grip location (see fig. 4.3). If the position is uncomfortable (e.g., held overhead or at an extended, unnatural length) or the acquisition time is long, it may be tempting to support the instrument with the other hand in a place other than at the grip. This is unsafe and must be avoided. If you feel you cannot adequately support the instrument at the approved grip locations, re-evaluate your setup. You may need to bring in some sort of additional physical support (e.g., a block, bolster, or strap).

Keep in mind that in some circumstances, turning the instrument upside down or sideways may help in reaching the area of interest. Regardless of the orientation of the instrument, before turning on the X-ray, always make sure you are aware of the beam direction. Make sure the beam is directed away from you, as the operator, and from any other people in the area (for further information, see the discussion of X-ray safety in chap. 1).

Tripod positioning and operation

For extended acquisitions and/or for objects with a simple geometry (e.g., for planar objects such as paintings, drawings, and photographs), it may be easiest—and safest—to use a tripod or other mechanical support. A tripod setup can be used for objects in either a vertical (mounted on a wall or an easel) or horizontal (on a table or other support) orientation (fig. 4.4). Use the mounting configuration recommended by the manufacturer of your specific instrument. It is helpful to attach the instrument to a geared lateral arm so that it can be translated along a short distance—toward and away from the object—in a controlled manner. These arms are available from most photography suppliers.

Regardless of what sort of support you use, make sure the instrument is securely mounted to prevent it from coming into contact with the object under study. Check that the setup is stable, placing counterweights as appropriate to provide balance so that the setup cannot tip over (see fig. 4.4). For tripods, this can

FIGURE 4.4. XRF instrument tripod setup with counterweights for an object mounted horizontally (left) and vertically (right).

usually be achieved by placing or hanging weighted bags on the back leg(s). The rough positioning can be done manually by placing the setup within a few inches of the object and ensuring that the lateral arm can extend far enough for the instrument to be in the proper position for analysis. The nose of the instrument should be as parallel to the surface as possible. (Keep in mind that the surface may not be perfectly flat.)

Once the rough positioning is complete, if you are using a geared lateral arm, slowly move the instrument to within 1–2 mm of the surface (or in direct contact, if that is deemed acceptable conservation practice). Ideally, the instrument should be placed as close as possible to the surface, but other considerations—such as the possibility of damaging or disturbing the surface and the degree of evenness of the surface—may limit this. See section 3.4 for a discussion of the effects of distance and/or topography. Once you have determined the optimal distance, note it and attempt to collect all analyses at this distance, if possible, to facilitate comparison between spectra.

***Tip:* All of the setup work should be done away from the cultural heritage material. If working with a new setup, it is highly recommended to use a mock-up to gain confidence in the setup and to assess the positioning.**

When using a tripod setup, as with handheld operation, always know the direction of the X-ray beam and ensure that it is pointed away from the operator or any other people who are in or may enter the area. Further safety measures include the use of remote triggers or other devices that allow for more distance between the operator and the instrument. See chapter 1 for a discussion of X-ray safety. Never leave the instrument unattended while it is running or in standby mode. During the collection of XRF spectra, always keep an eye on the setup to make sure that nothing has moved or changed position. Once the spectral acquisition is complete, it is good practice to move the spectrometer head away from the object, either manually or using the geared drive on the lateral arm, until it is time for the next measurement.

Reducing interferences

As demonstrated in the exercises in chapter 3, elements present in subsurface layers may show up in the XRF spectra (exercises 3.2a, 3.2b, and 3.2c). This is true whether the subsurface layers are part of the object or part of the mounting setup. Therefore, when planning an analysis, it is critically important to be aware of which, if any, of the support or other materials may be unintentionally included in the acquired spectra. This is most commonly encountered in the analysis of paper and parchment objects, as X-rays can easily penetrate the low Z matrix of the thin sheets and excite elements present in the matboard, the underlying pages (e.g., in bound manuscripts), or even the table. It is also a consideration, however, for paintings or for any other object placed on a secondary support for analysis.

If possible, when arranging the object, nothing (except air) should be directly behind the area of interest. For paintings, this might mean adjusting the position on an easel so that none of the components are directly behind the area of interest. For unmounted photographs, drawings, or other single-sheet objects, a simple solution is to construct a raised support that still allows the area of interest to be examined free from any underlying material. In figure 4.5, foam strips are used to elevate an archival blue-board with openings cut in the board for placement of the area of interest. Analysis from the top proceeds so as to ensure that there is only air below the area of interest and that the table top is sufficiently far to ensure that no X-ray peaks from its components reach the instrument.

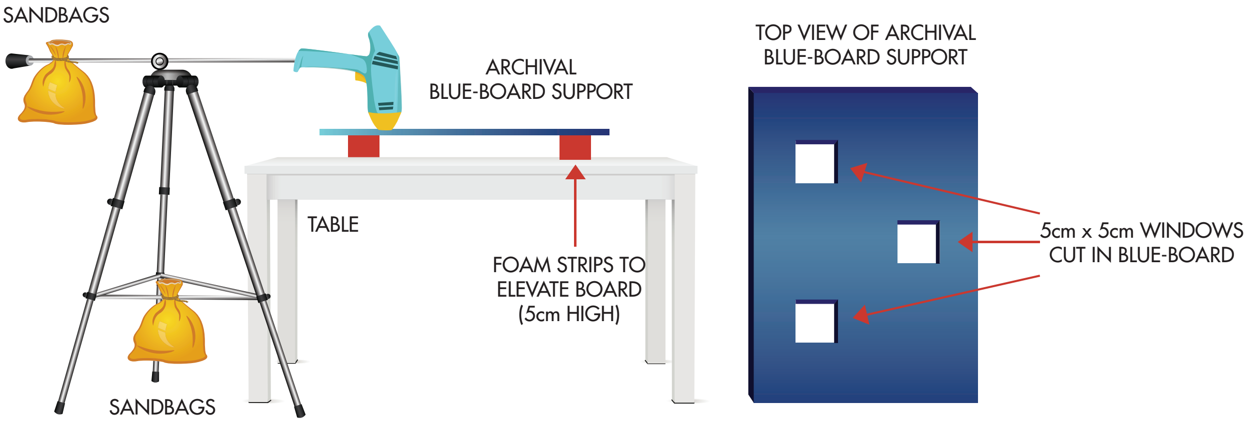

FIGURE 4.5. Graphic illustrating an analysis setup for unmounted sheets that provides support while still allowing the area of interest to be examined free from any underlying material. Here, foam strips are used to elevate an archival blue-board; openings are cut in the board for placement of the areas of interest. Analysis from the top proceeds so as to ensure that there is only air below the location of interest and that the table top is sufficiently far to ensure that no X-ray peaks from its components reach the instrument.

If the object cannot be separated from its support (e.g., it cannot be detached from the matboard or is in a bound book), then steps should be taken to minimize contribution from the support to the XRF signal. Suggested configurations for XRF analysis of manuscript illuminations or any similarly thin object that cannot be separated from its support, are shown in figure 4.6.

An XRF spectrum should always be collected from the support alone, whether the support is a matboard, easel, or table. This enables any elements present to be identified and their contribution to the overall XRF spectrum evaluated. If it is possible (and safe for the object) to place sheets of a low Z material such as Plexiglas or Teflon under the object, unwanted fluorescence signals from underlying supports can be

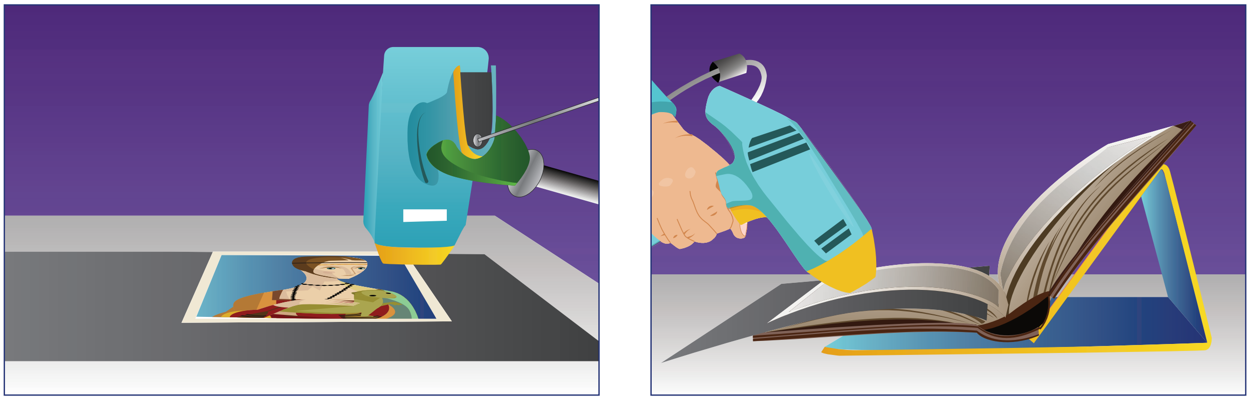

FIGURE 4.6. Setups for analysis of objects that cannot be separated from their supports. At left, the XRF instrument is secured to a tripod and arm and positioned over a sheet mounted on matboard. At right, the XRF instrument is handheld over a page in a bound book; an interleaving material has been placed between the pages to minimize spectral contributions from the leaves underneath.

minimized. See exercises and discussion on the use of interleaving materials to reduce unwanted fluorescence in the section titled "Interleaving Materials" in chapter 3. However, as explored in exercises 3.2d and 3.2e, as well as exercises 3.3b and 3.3c, low Z materials scatter X-rays more strongly than higher Z materials, and so the interleaving sheets, while reducing the unwanted fluorescence signal, may increase the scattering background. Therefore, selection of the thickness of an interleaving sheet will be guided primarily by the safety of the object; the material should be thick enough to reduce unwanted fluorescence but thin enough to avoid an increase in background scattering.

4.3 Interpreting the Data and Reporting Results

The spectral identification guide (see appendix 4) provides a suggested flow for the interpretation of features in XRF spectra. Do not wait until you have collected all your spectra to begin identifying the peaks. It is important to carry out some basic spectral identification during the analysis to make sure everything is running smoothly, and to identify any unusual or interesting findings that might warrant further, unplanned investigation. After all the data have been collected, each spectrum should be carefully and thoroughly reexamined to make sure that *all* the peaks have been correctly identified.

How the results are organized to prepare for report writing is largely a matter of personal preference. If only a few spectra have been collected from an object, it may be simplest to note the elements identified directly on the image next to the spot location, using a callout or other annotation tool on a digital image. If a larger number of spectra have been taken, it is generally more efficient to compile the results into a table (see table 4.1 for an example). In this table, list the elements identified for each spot (along with some indication of the relative intensity of the peaks, keeping in mind that peak height is not always a good measure of relative abundance) and any relevant notes or observations. Entering the results in a spreadsheet allows them to be easily reorganized to facilitate comparison of areas of similar color, shape, texture, or whatever aspect is being investigated.

Once you have identified the elements in each spectrum, the next step is to use that information to draw conclusions about the material under study. For metal objects, the relationship between the elements present is generally relatively straightforward. The detection of zinc together with copper, for example, may indicate a brass, but if it contains tin and lead in addition to copper, then it is classified as a bronze. However, as shown in exercises 3.1b (varnish layer) and 3.2b (corrosion layer), material on the surface, such

TABLE 4.1. Sample summary of XRF analysis data. Under “Elemental Analysis,” bold font denotes probable major elements; roman font indicates elements present in lesser quantities; and italics indicate minor/trace relative amounts. Relative amounts are not quantitative. XRF may suggest the presence of certain materials, but it does not conclusively identify the molecular phase. Thus, we use language to indicate this uncertainty.

Area of Analysis	Description/Color	Elemental Analysis	Possible Pigments
1	Red orange angel	**Pb**, Hg, *Cu*, *Fe*	Red lead, possible trace vermilion (either with red lead or on verso)
2	Bright red flower	**Cu**, **Hg**, Pb, *Fe*	Vermilion (note a blue initial on verso, which is likely azurite)
3	Yellow of flower petals	**Pb**, Sn, *Cu*, *Fe*	Lead-tin yellow
4	Golden yellow on angel’s robe	**Pb**, Fe, Ca, *Cu*, *Sr*	Iron earth, lead white
5	Brown violin	**Fe**, Pb	Iron earth, lead white
6	Pale green in bottom arch	**Pb**, Cu, Fe	Lead white, azurite or copper green, possible iron earth
7	Green book	**Pb**, **Cu**, Sn, Fe	Lead white, azurite or copper green, lead-tin yellow, possible iron earth
8	Dark blue background	**Cu**, Fe, Pb, *As*	Azurite (suspect ultramarine over azurite)
9	White cloth	**Pb**, Cu, *Sr*, *Fe*, *Au*	Lead white, azurite nearby?
10	Ink note	**Fe**, Ca, Cu, *Hg*, *Mn*	Iron-based ink?
11	Parchment	**Ca**, Fe, Pb, *Sr*	Chalk preparation
12	Parchment with paper backing	Ca	Chalk preparation

as dirt or corrosion products, can significantly affect the XRF spectrum. It should be noted when such factors may be present.

Because most pigments are molecular compounds, they cannot be definitively identified by XRF alone (see “Complementary Techniques”). However, in many cases inferences about the possible pigments present may be made from the XRF data by utilizing additional information, in the form of either visual analysis or research into the types of materials expected for the object’s date, location, and/or artist. Some may be very clear cut—the detection of mercury, for example, is a fairly reliable indicator of the presence of vermilion (mercuric sulfide, HgS). By contrast, the detection of copper may indicate the presence of a number of copper-based pigments, such as malachite, azurite, emerald green, and verdigris. Therefore, in reporting the XRF results, it is important to indicate the level of certainly of the inferred pigments. Note that in the sample table (see table 4.1) the interpretation column is labeled “Possible Pigments,” and further levels of certainty are indicated by the terms *likely*, *suspect*, or, more simply, a question mark.

In deciding how to organize and report your results, always make sure to look for and note any of the possible interferences that may affect your interpretation of the spectra. Those most commonly encountered have been explored in the exercises in this workbook and include the following:

- Inhomogeneous/layered samples
- Area of interest smaller than aperture
- Shielding from varnish/dirt/patina on surface
- Rough or complex surface shapes
- Contamination on instrument window
- Overlap of peaks (e.g., Pb/As or Ba/Ti)
- Artifact peaks, such as sum or escape peaks

As an example, you might note that a detected element may be due to an adjacent area if the spot size of the instrument is too large to examine only the area of interest, or that since the Sn Kα line appears at the same energy as the Pb Lα sum peak, its presence is confirmed by detection of the Sn Kβ line. Bear in mind there are numerous factors that can affect an XRF spectrum, and it is important to be able to recognize them.

4.4 Different Modalities of XRF

Once it is determined that XRF is the appropriate tool to use, it also must be determined whether a single point analysis is sufficient or whether some distribution information—in the form of either a line or an area scan—is necessary. For objects that are relatively homogeneous in composition, such as metal sculpture or large color fields on a painting, single-spot analyses are typically sufficient. However, it must be kept in mind that XRF spectra can be significantly affected by the presence of surface contaminants or corrosion (in the case of metals), or by the presence of subsurface layers in painted objects or complex constructions. For objects that may be inseparable from a substrate (such as a photograph or a mounted manuscript illumination), spectra should be collected from the area of interest as well as an area of the background. As a rule, a minimum of three spots should be analyzed for each feature of interest to check for consistency.

If the feature being analyzed is smaller than the aperture of the spectrometer, the spectrum by default will contain information from the feature together with the surrounding area. As above, collection of a background spectrum may be helpful, but if the feature is very small, such as a drawing line or solder join, there may be insufficient material present for a simple subtraction to work. In these cases, a line scan may be helpful. If available, instruments with smaller apertures or polycapillary optics attached to a motorized stage that can move the spot with precision will provide the best result. As an alternative, adequate line scans can be performed with a handheld spectrometer by collecting point spectra at regular intervals and plotting the intensity of the individual element peaks at each position against the distance along the line.

Objects consisting of a complex mixture of components, constructed of different elements, may benefit from area scanning. Macro-XRF scanners can generate large-scale distribution maps of individual elements and are increasingly being utilized in cultural heritage. Such scanners can provide incredible detail about an artist's technique or even reveal hidden paintings. However, if this technology is not available, coarse XRF maps can be generated manually in the same way as the line scans described above, using handheld XRF spectrometers. As of this writing, efforts are under way to develop a means of generating area maps from handheld XRF spectrometers, either by attaching the instrument to a simple x-y scanner or by doing mathematical calculations to interpolate between the points, which will make at least some form of area mapping more readily available.

4.5 Complementary Techniques

Although XRF spectroscopy can be a useful and versatile tool, it may not be the most appropriate or the only tool necessary to answer questions that arise through the scientific method. The selection of analytical tools should be driven by the research goals: What information is desired, and which tool would best provide that information? More often than not, the answer is that a variety of complementary tools are required in order to achieve a thorough understanding of the object under investigation.

Visual and Imaging Analysis

The first step in the scientific method is observation; likewise, the first step in most analytical studies of works of art should be visual analysis. This may begin with a close visual examination, usually under magnification, and perhaps utilizing other regions of the electromagnetic (EM) spectrum, such as ultraviolet or infrared radiation. Observations should be noted, and photographs used for documenting spots for subsequent XRF analysis. Visual analysis also may include examination using multiple discrete sections of the EM spectrum, perhaps in the form of multi- or hyperspectral imaging. If one of these modalities is employed, it can provide additional information in the form of reflectance spectra that can help characterize classes of materials. Image analysis based on reflectance spectra can be used to generate distribution maps showing areas with similar properties, which, again, can help identify areas to be targeted for XRF analysis.

Molecularly Specific Identification Techniques: Inorganics

The information provided by XRF spectroscopy is only elemental—it cannot provide information about the particular form in which the elements are present. For some materials, elemental analysis alone may be sufficient to address the research question under investigation. As discussed earlier, while the general alloy of metals or the identity of many pigments may be inferred from the elemental composition, if more specific or definitive identification is desired, another technique may need to be employed. For many pigments, Raman spectroscopy provides a nice complementarity to the XRF data. If the Raman spectrometer is equipped with a fiber-optic or extension arm, Raman spectra may be taken directly from the work of art without having to remove a sample. Portable Raman spectrometers are also available, but in general these do not allow the operator to have sufficient control over the power of the laser, and accidental burning may occur.

As with any instrument, before examining any cultural heritage material, tests should be conducted on mock-ups to determine the appropriate and safest conditions for conducting the analysis. Raman spectroscopy has found particular use in the study of illuminated manuscripts, in which the pigments are thinly bound and sampling is typically not an option. The prevalence of binding medium in paintings, however, tends to produce fluorescence that masks the Raman signal of the pigments.

Another technique that can provide complementary information to help identify and characterize crystalline materials is X-ray diffraction (XRD). For pigment analysis, Raman spectroscopy has largely supplanted XRD, but certain materials—most notably, corrosion products and natural stones—are still best characterized by XRD. Most X-ray diffractometers require the removal of a small sample for analysis. Some recently developed portable instruments can be operated in reflection, allowing analysis to be performed in situ.

Infrared spectroscopy likewise can also provide complementary chemical information, in particular for the identification of oxides. However, as with XRD, most Fourier-transform infrared (FTIR) spectroscopy instruments require the removal of a sample for analysis. IR mapping may be performed on prepared cross sections. Portable reflectance IR spectrometers have been developed and may be suitable for specific questions.

Molecularly Specific Identification Techniques: Organics

XRF cannot detect the elements present in organic compounds—C, N, and O—and so a complementary technique is necessary to identify any organic materials that are suspected to be present. Raman spectroscopy can identify many organic pigments, including indigo, modern azo dyes, and natural organic reds such as madder and alizarin. Fiber-optic reflectance spectroscopy (FORS) may be used to help characterize a number of commonly encountered pigments and organic colorants. Similarly, multi- or hyperspectral imaging has proven useful in the characterization of a number of organic pigments and in distinguishing classes of organic binding media in situ. At present, though, the identification of binding media typically requires the removal of a sample for analysis by either FTIR spectroscopy or gas chromatography–mass spectrometry (GC-MS).

Quantification of Elemental Composition

For metals and alloys, a quantitative analysis of individual components is often desired. There are many methods for performing quantitative analysis based on XRF data, but to be effective, in general, they require spectra to be collected under carefully controlled conditions and from well-prepared surfaces. For most cultural heritage materials, it is not possible to prepare a surface that is completely free of any surface contaminants, including dirt, patina, or other coatings. As explored in exercises 3.1b and 3.2b, even the presence of a thin layer of material can affect the relative heights of the fluorescence lines. However, if spectra of sufficient reproducibility and quality can be obtained, quantitative analysis may be approached either by using a fundamental parameters approach (in which a modeling program such as PyMca is used to calculate the contributions to the spectra) or by generating a calibration curve (in which the response to a series of standards is tested) to which the unknown spectrum can be compared. Both approaches require considerable input in terms of development of the models and/or appropriate reference materials. Because both are not direct measures of the individual components, the level of accuracy may vary depending on factors such as the robustness of the model and complexity of the samples.

The most accurate method to determine the quantity of individual elements in a sample is through direct measurement, for example, as afforded by inductively coupled plasma mass spectrometry (ICP-MS), in which a small amount of the sample is removed and vaporized so that the amount of each element can be measured using a mass spectrometer. While this method is the most accurate, it also requires the removal and consumption of a sample, which for many objects may not be allowable.

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Appendix 1
Acquisition Parameters for Instrument Models

A1.1 Flexibly Adjustable Handheld and Portable Units (HH Flex)

Bruker Tracer Handheld Units; Bruker ELIO and CHRONO portable units

While the accelerating potential (voltage) and current can be flexibly adjusted for these models, the range of adjustability depends on the maximum power output and allowed voltage and current ranges. Bruker Tracer models can be used with a vacuum pump or with a He gas supply in addition to their basic operation with air as the atmosphere. Bruker ELIO and CHRONO models can be operated with air and He as the atmosphere. Most of the flexible models used for the analysis of cultural heritage objects allow users to choose whether to use a filter.

Tracer III-SD (2 W maximum output)
Tracer III-SD models have an X-ray tube with a maximum power output of 2 W. At 40 kV, the maximum current is 30 µA. At 15 kV, the maximum current is 55 µA (table A1.1). Filters that are available for the Tracer III-SD are listed in table A1.3.

Tracer 5 series, ELIO and CHRONO (4 W maximum output)
Tracer 5 series models, as well as ELIO and CHRONO models, have X-ray tubes with a maximum power output of 4 W. Tracer 5 models have 6–50 kV voltage and 4.5–195 µA current ranges. ELIO and CHRONO models have 10–50 kV and 5–200 µA current ranges (table A1.2).

TABLE A1.1. Instrument parameters for the Bruker Tracer III-SD model.

Parameter	Mode	Voltage (V)	Current (I)*	Atmosphere	Filter
High V, Low I, Air	N/A	40 kV	2 µA	Air	None
High V, Low I, Vac.	N/A	40 kV	2 µA	Vacuum or He	None
High V, High I, Air	N/A	40 kV	10 µA	Air	None
High V, High I, Vac.	N/A	40 kV	10 µA	Vacuum or He	None
Low V, Low I, Air	N/A	15 kV	10 µA	Air	None
Low V, Low I, Vac.	N/A	15 kV	10 µA	Vacuum or He	None
Low V, High I, Air	N/A	15 kV	20 µA	Air	None
Low V, High I, Vac.	N/A	15 kV	20 µA	Vacuum or He	None

*For HH Flex type instruments, current choice should take into account the maximum power rating for the X-ray tube.

TABLE A1.2. Instrument parameters for the Tracer 5 series, ELIO and CHRONO models.

Parameter	Mode	Voltage (V)	Current (I)*	Atmosphere	Filter
High V, Low I, Air	N/A	50 kV	10 µA	Air	None
High V, Low I, Vac	N/A	50 kV	10 µA	Vacuum or He	None
High V, High I, Air	N/A	50 kV	40 µA	Air	None
High V, High I, Vac	N/A	50 kV	40 µA	Vacuum or He	None
Low V, Low I, Air	N/A	20 kV	40 µA	Air	None
Low V, Low I, Vac	N/A	20 kV	40 µA	Vacuum or He	None
Low V, High I, Air	N/A	20 kV	80 µA	Air	None
Low V, High I, Vac	N/A	20 kV	80 µA	Vacuum or He	None

*For HH Flex type instruments, current choice should take into account the maximum power rating for the X-ray tube.

TABLE A1.3. Available filters for the Bruker Tracer III-SD model.

Blue	0.0254 mm (1 mil) Ti
Yellow	0.0254 mm (1 mil) Ti / 0.3048 mm (12 mil) Al
Green	0.0254 mm (1 mil) Cu / 0.0254 mm (1 mil) Ti / 0.3048 mm (12 mil) Al
Red	0.1524 mm (6 mil) Cu / 0.0254 mm (1 mil) Ti / 0.3048 mm (12 mil) Al

Source: Bruker.

A1.2 Thermo Scientific Handheld Units (HH Mode)

The Thermo Scientific Niton handheld X-ray fluorescence (XRF) spectrometers belong to the category of instruments with preset modes (also known as programs or methods). In this workbook, we use HH Mode to refer to these instruments. Each mode is designed to optimize the detection and quantification of ranges of elements relevant to a variety of analytical challenges. Applications include alloy identification, precious metals, mining, soil, plastics, and lead in paint. Consult the manufacturer for up-to-date information about instrument models and modes.

The modes available depend on the Niton analyzer model. Each Niton mode involves the collection of one to four spectra using a different combination of accelerating potentials (kV) and filters. The current is adjusted by the instrument based on the intensity of the X-ray signal detected and cannot be set by the user (table A1.4).

Given the wide variety of Niton models, this section of the appendix deals with the one most frequently encountered in cultural heritage applications, the Niton XL3t GOLDD+, and the most common modes used (table A1.5). To ensure detection of low-energy and high-energy X-ray lines in the exercises in this workbook, always collect spectra under every beam condition within the mode/program of your choice.

TABLE A1.4. Thermo Scientific Niton analyzer models, including their various modes and beam conditions.

Model	Anode	Voltage (V)	Current (I)	Detector	Modes Available
XL3t GOLDD+	Ag	6–50 kV	0–200 µA	Large area SDD	“Varies by Application” Metal Alloy, Electronics Alloy, Precious Metals, Soil, Mining, RoHS Plastics, TestAll, Thin Film, etc.
XL3t	Au	50 kV max	100 µA max	SiPIN	
XL2 GOLDD	Ag	45 kV max	100 µA max	Large area SDD	
XL2	Ag	45 kV max	80 µA max	SiPIN	

Source: Thermo Scientific.

TABLE A1.5. Instrument parameters of several modes of the Thermo Scientific Niton XL3t GOLDD+.

Mode/Program	Beam Condition	Voltage (V)	Filter	Atm.	Exercise Acquisition Conditions
Alloy & Coatings	Main	50 kV	Al	Air	High Voltage
	Low	15 kV	Fe	Air	Low Voltage
	High	—	—	—	—
	Light	8 kV	None	Air	Low Voltage
Mining Soil & Thin Film	Main	50 kV	Al	Air	High Voltage
	Low	20 kV	Cu	Air	Low Voltage
	High	50 kV	Mo	Air	High Voltage
	Light (not in Soil mode)	8 kV	None	Air	Low Voltage

Source: Thermo Scientific.

A1.3 Olympus Handheld Units (HH Mode)

The Olympus Vanta handheld XRF spectrometers belong to the category of instruments with preset modes (also known as programs or methods). In this workbook, we use HH Mode to refer to these instruments. Each mode is designed to optimize the detection and quantification of ranges of elements relevant to a variety of analytical challenges. Applications include alloy identification, mining and exploration, consumer safety, scrap processing, environmental testing, and coating thickness measurement. Consult the manufacturer for up-to-date information about instrument models and methods.

Each Olympus Vanta method is associated with a preset accelerating potential (tube voltage) and filter. The tube current is adjusted by the instrument based on the intensity of the X-ray signal (counts) detected and cannot be set by the user. Users have access only to methods they have purchased. Olympus Vanta methods include Alloy, Alloy Plus, Precious Metals, RoHS, RoHS Plus, GeoChem (1 beam), GeoChem (2 beam), GeoChem REE (2 beam), Car Catalyst, Coating, Lead Paint, and Soil (table A1.6).

The methods listed in table A1.7 involve the collection of multiple "exposures." Each exposure is a spectrum collected using different parameters. To ensure detection of low-energy and high-energy X-ray lines in the exercises in this workbook, always collect spectra under both high-voltage and low-voltage conditions within the method of your choice. Export spectra in .csv format to allow you to learn the following parameters:

- Tube Voltage (units = kV) and Tube Current (μA)
- Filter (atomic number) and Filter Thickness (assumed units = μm)

TABLE A1.6. Olympus Vanta analyzer models with their various modes and beam conditions.

Model	Anode	Power	Voltage (V)	Current (I)	Detector	Methods Available
M series	Rh	4 W	8–50 kV	5–200 μA	Large area SDD	Alloy Plus, Precious Metals, GeoChem (2-beam), GeoChem-REE (2-beam), Car Catalyst (W tube), RoHS & RoHS Plus (W tube)
M series	W	4 W	8–50 kV	5–200 μA		
C series	Rh	4 W	8–40 kV	5–200 μA	SDD	Alloy Plus, Precious Metals, GeoChem (2-beam), Car Catalyst (W tube), RoHS (W & Ag tubes)
C series	W	4 W	8–40 kV	5–200 μA		
C series	Ag	4 W	8–50 kV	5–200 μA		
L series	W	2 W	8–35 kV		SiPIN	Alloy, Precious Metals, GeoChem (1-beam), Car Catalyst (only W tube)

Source: Olympus.

TABLE A1.7. Olympus Vanta instrument parameters for methods commonly used in the analysis of cultural heritage materials.

Method	Anode	Voltage (V)	Filter*	Atm.	Exercise Acquisition Conditions
GeoChem 2 spectra collected	Rh	40 kV	Al 2000 µm (?)	Air	High Voltage
		10 kV	None	Air	Low Voltage
GeoChem REE 2 spectra collected	Rh	50 kV	Cu 350 µm (?)	Air	High Voltage
		10 kV	None	Air	Low Voltage
Soil 3 spectra collected	Rh	40 kV	Cu 150 µm (?)	Air	High Voltage
		40 kV	Al 2000 µm (?)	Air	High Voltage
		15 kV	None	Air	Low Voltage

*Material was inferred from manufacturer information. Thickness was assumed to be given in µm as units.
Source: Olympus.

A1.4 Flexibly Adjustable Models with Higher-Power X-ray Tube (Flex)

Bruker Artax, Bruker M6 Jetstream, Bruker M4 Tornado, and Other Instruments (including custom built)

As in the case of handheld and more portable models, the accelerating potential (voltage) and current can be flexibly adjusted for the Bruker Artax, Bruker M6 Jetstream, Bruker M4 Tornado, and other instrument models. Range of adjustability depends on maximum power output and allowed voltage and current ranges. Instruments with an open architecture design can be used with a He gas supply in addition to their basic operation with air as the atmosphere. Instruments featuring a closed sample chamber may be able to use either He or vacuum atmosphere for analysis in addition to air. Note that the use of vacuum atmosphere in a closed chamber instrument would not be appropriate for materials that are negatively impacted by low-humidity environments, such as works on paper, canvas or parchment, wood objects, bone or ivory, and lacquer.

Many of these models have an X-ray tube with a Rh anode and a maximum power output of 30 W if they are equipped with polycapillary X-ray optics (Bruker M6, M4, and Artax 800), or 50 W if they are equipped with collimator type X-ray optics (Bruker Artax 200 and Artax 400). At 50 kV the maximum current is 600 µA for the 30 W models and 1000 µA for the 50 W models. The current setting is limited at lower voltage values (table A1.8). Filters that are available for the Bruker Artax are listed in table A1.9.

TABLE A1.8. Instrument parameters for higher-powered X-ray tubes (Flex models).

Parameter	Mode	Voltage (V)	Current (I)*	Atmosphere	Filter**
High V, Low I, Air	N/A	50 kV	100 μA	Air	None
High V, Low I, Vac	N/A	50 kV	100 μA	He	None
High V, High I, Air	N/A	50 kV	400 μA	Air	None
High V, High I, Vac	N/A	50 kV	400 μA	He	None
Low V, Low I, Air	N/A	20 kV	100 μA	Air	None
Low V, Low I, Vac	N/A	20 kV	100 μA	He	None
Low V, High I, Air	N/A	20 kV	200 μA	Air	None
Low V, High I, Vac	N/A	20 kV	200 μA	He	None

*For Flex type instruments, current choice should take into account the maximum power rating for the X-ray tube.

**"None" indicated because user can choose and manually insert the available filters. See table A1.9 for available filters for the Artax.

TABLE A1.9. Filters available for Bruker ArTax.

Filter Material	Thickness (mm)
Al	0.1; 0.2; 0.315
Ni	0.0125; 0.025
Zr	0.015
Mo	0.0125

Source: Bruker.

Appendix 2
Instructions for Mock-Up Samples

Directions on how to make the mock-ups are given in the following sections. Under the "Materials" heading, specific paint products have been recommended; these have been analyzed by the authors to verify their composition and determine there are no fillers, impurities, and so forth. Some of the recommended paint materials are tube paints (Winsor & Newton Designers Gouache series; Golden Acrylics) and some are dry pigments (Kremer Pigments) that will require grinding and mixing with acrylic medium using a glass muller. Instructions for using the muller to make paint-outs are given at the end of this appendix. You have the choice of making all the paint mock-ups using dry pigments instead of tube paints. If you decide to use different tube paints or dry pigments from what is recommended, you will need to prepare paint-outs on bare canvas to verify the composition of the paints and pigments. Appendix 3 is a list of the materials and instrument suppliers discussed throughout this workbook.

The authors are aware that using acrylic-based or gouache-based paints on unprimed canvas can result in a brittle film after a period of time. The decision to use these types of paints was motivated primarily by their ease of use and fast drying times, allowing suitable mock-ups to be prepared relatively easily and quickly. The recommendation of using unprimed canvas allows the creation of a mock-up that avoids having the priming layer contribute to the spectral response.

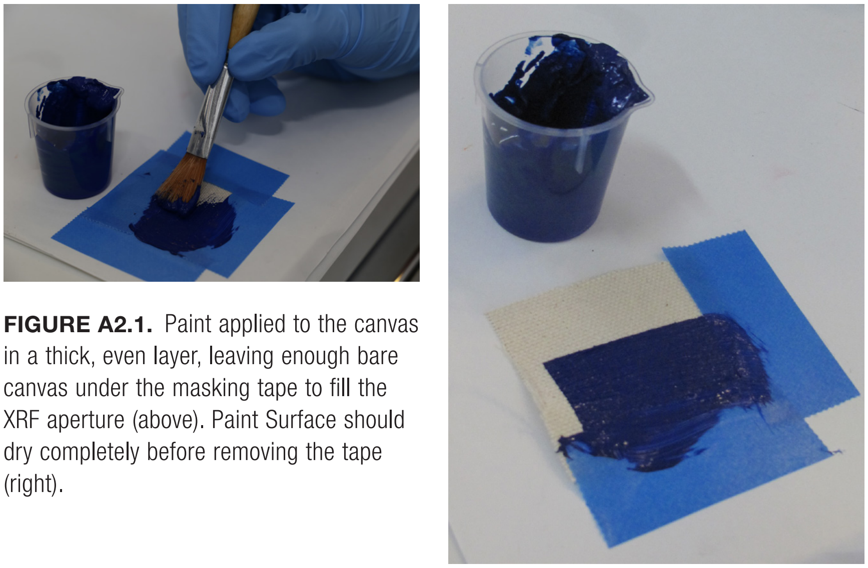

FIGURE A2.1. Paint applied to the canvas in a thick, even layer, leaving enough bare canvas under the masking tape to fill the XRF aperture (above). Paint Surface should dry completely before removing the tape (right).

FIGURE A2.2. Use of weighted ropes to flatten the paint mock-up on top of the XRF stage and head. Here, the painted surface is directly facing the XRF aperture. Ropes should be kept away from the aperture so as not to contribute to spectral response.

General tips and notes on materials used:

- For the paint mock-ups on canvas, tape down the canvas using painter's tape and create a mask for the painted area large enough to cover the XRF aperture. Make sure to leave a similarly sized area of the canvas bare.
- Make sure the paint layer is thick and even—described as "good" coverage—so that the underlayer (where applicable) or canvas does not show through (fig. A2.1a). If needed, apply several coats unless otherwise instructed (e.g., in some exercises, a specific number of layers is required).
- Allow the paint mock-ups on canvas to dry completely before removing the tape (fig. A2.1b). This will prevent the canvas from curling and help the mock-up lie flat. This is important because you do not want to introduce an unintentional air gap between the sample and nose of the XRF instrument. If the canvas becomes curled, use weighted ropes to make it lie flat (fig. A2.2).
- Label the mock-ups accordingly (XRF workbook, exercise number, paints and pigments used). Place the mock-ups in a dedicated location—in a box or in sleeves in a notebook—so they can be easily referred to when necessary.

EXERCISE 3.1b:

Instructions for Mock-Up

Materials:

- Winsor & Newton Designers Gouache Ultramarine (tube paint)
- Winsor & Newton Designers Gouache Cobalt Blue (tube paint)
- Canvas, unprimed

Directions:

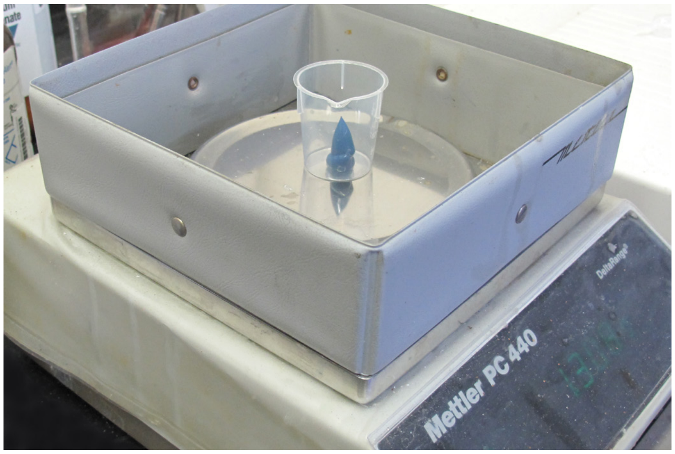

FIGURE A2.3. Tube paints measured using a scale for weight ratios.

1. Place an empty cup on the scale and tare to zero. By weight, measure out equal amounts of ultramarine and cobalt blue gouache paint in the cup (fig. A2.3). Mix thoroughly.
2. Cut the bare canvas into a (minimum) 50 × 50 mm square. Using painter's tape, tape down the bare canvas to a Plexiglas sheet or other smooth, cleanable surface. Mask the canvas, leaving an open area large enough to cover the XRF aperture. The masked area should also be large enough to cover the XRF aperture, as this will be the background measurement of the bare canvas (see chap. 2, exercise 2.3c). Apply the paint mixture to the open area of the canvas.
3. Reapply mixture as needed to create a paint layer with good coverage.
4. Let dry completely before removing the tape.

EXERCISE 3.1c:

Instructions for Mock-Up

Materials:

- Kremer bone black (dry pigment)
- Canvas, unprimed
- See end of this appendix for additional tools and materials.

Directions:

1. Prepare bone black acrylic paint (see end of this appendix).
2. Cut the bare canvas into a (minimum) 50 × 50 mm square. Using painter's tape, tape down the bare canvas to a Plexiglas sheet or other smooth, cleanable surface. Mask the canvas, leaving an open area large enough to cover the XRF aperture. The masked area should also be large enough to cover the XRF aperture, as this will be the background measurement of the bare canvas (see chap. 2, exercise 2.3c). Apply the paint mixture to the open area of the canvas.
3. Reapply paint as needed to create a paint layer with good coverage.
4. Let dry completely before removing the tape.

EXERCISE 3.1d:

Instructions for Mock-Up

Materials:

- Winsor & Newton Designers Gouache alizarin crimson (tube paint)
- Canvas, unprimed

Directions:

1. Cut the bare canvas into a (minimum) 50 × 50 mm square. Using painter's tape, tape down the bare canvas to a Plexiglas sheet or other smooth, cleanable surface. Mask the canvas, leaving an open area large enough to cover the XRF aperture. The masked area should also be large enough to cover the XRF aperture, as this will be the background measurement of the bare canvas (see chap. 2, exercise 2.3c). Apply the paint to the open area of the canvas.
2. Reapply paint as needed to create a paint layer with good coverage.
3. Let dry completely before removing the tape.

EXERCISE 3.2a:

Instructions for Mock-Up

Materials:

- Winsor & Newton Designers Gouache cadmium red (tube paint)
- Winsor & Newton Designers Gouache titanium white (PW6, tube paint)
- Canvas, unprimed

Directions:

1. Cut the bare canvas into a 50 × 100 mm rectangle. Using painter's tape, tape down the bare canvas to a Plexiglas sheet or other smooth, cleanable surface. Mask the canvas by the edges.
2. On the canvas, paint a layer of titanium white. Reapply as needed to create a paint layer with good coverage. Let dry completely.
3. After the titanium white underlayer is completely dry, paint cadmium red lines of three different widths (1 mm, 3 mm, and 7 mm), providing sufficient space between the lines so that the XRF aperture, when placed on one of the lines, does not overlap with an adjacent line.
4. Let dry completely before removing the tape. See figure A2.4 for a photo of the completed mock-up.

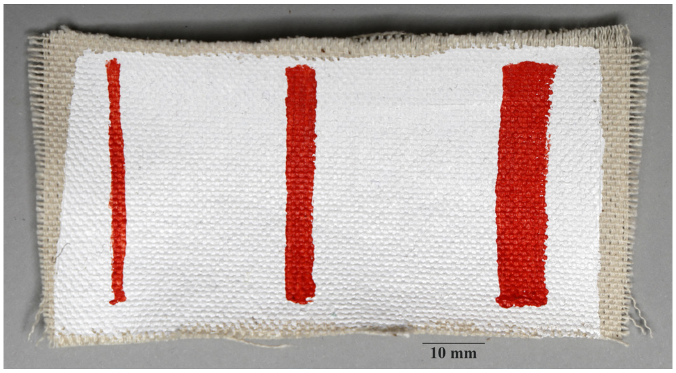

FIGURE A2.4. Photo of mock-up: cadmium red lines of varying widths painted on top of a titanium white underlayer on top of bare canvas.

EXERCISE 3.2b:

Instructions for Mock-Up

Materials:

- Cookson Electronics Alpha Fry solder wire: lead (50%), tin (50%). Gauge: 3.175 mm thick (or similar); contains no core flux.
- Wire cutter
- Rubber mallet or small hammer
- Kremer malachite (dry pigment)
- See end of this appendix for additional tools and materials.

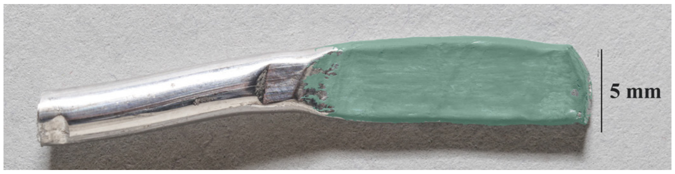

FIGURE A2.5. Example of malachite painted on flattened wire surface.

Directions:

1. Prepare malachite acrylic paint using the instructions at the end of this appendix.
2. Cut three pieces of solder wire, each approximately 30 mm in length.
3. Flatten the pieces of wire using the rubber mallet or small hammer.

— Wire A remains bare.

— On wire B, paint one layer of malachite on the smoother side of the flattened wire.

— On wire C, paint four layers of malachite on the smoother side of the flattened wire (fig. A2.5).

EXERCISE 3.2c:

Instructions for Mock-Up

Materials:

- PW5: Kremer lithopone (dry pigment) OR Winsor & Newton Designers Gouache zinc white (tube paint)
- PW6: Kremer titanium white (dry pigment) OR Winsor & Newton Designers Gouache permanent white (tube paint)
- Canvas, unprimed
- See end of this appendix for additional tools and materials if you are using Kremer dry pigments.

Directions:

1. Prepare lithopone acrylic paint and titanium white acrylic paint, following the instructions at the end of this appendix if you are using Kremer dry pigments.
2. Cut the bare canvas into three pieces, each (minimum) 50 × 50 mm square. Using painter's tape, tape down each bare canvas piece to a Plexiglas sheet or other smooth, cleanable surface. Mask the canvas pieces, leaving an open area large enough to cover the XRF aperture. The masked area should also be large enough to cover the XRF aperture, as this will be the background measurement of the bare canvas (see chap. 2, exercise 2.3c).

3, On one of the bare canvas pieces, paint the titanium white ONLY on the open area of the canvas. Reapply paint as needed to create a layer with good coverage. Let dry completely.

4. On the second bare canvas piece, paint the lithopone ONLY on the open area of the canvas. Reapply paint as needed to create a layer with good coverage. Let dry completely.
5. On the third bare canvas piece, first paint the titanium white on the open area of the canvas. Reapply paint as needed to create a layer with good coverage. Let dry completely. After the titanium white underlayer is completely dry, paint the lithopone layer, again making sure to attain good coverage.
6. Let dry completely before removing the tape.

EXERCISE 3.2e:

Instructions for Mock-Up

Materials:

- PG7: Kremer pigment green 7 (dry pigment) OR Golden Acrylics phthalo green (blue shade; tube paint)
- PW6: Kremer titanium white (dry pigment) OR Winsor & Newton Designers Gouache permanent white (tube paint)
- Canvas, unprimed
- Sheets of copy paper to a total thickness of approximately 3 mm (approximately 16 sheets)
- See end of this appendix for additional tools and materials.

Directions:

1. Prepare PG7 acrylic paint and titanium white acrylic paint, following the instructions at the end of this appendix if using Kremer pigments.
2. Cut the bare canvas into a (minimum) 50 × 50 mm square. Using painter's tape, tape down the bare canvas to a Plexiglas sheet or other smooth, cleanable surface. Mask the canvas, leaving an open area large enough to cover the XRF aperture. The masked area should also be large enough to cover the XRF aperture, as this will be the background measurement of the bare canvas (see chap. 2, exercise 2.3c).
3. Paint the titanium white on the open area of the bare canvas. Reapply as needed to create a layer with good coverage. Let dry completely.
4. After the titanium white underlayer is completely dry, paint the PG7 layer, again making sure to attain good paint coverage.
5. Let dry completely before removing the tape.

EXERCISE 3.2f:

Instructions for Mock-Up

Materials:

- PW5: Kremer lithopone (dry pigment) OR Winsor & Newton Designers Gouache zinc white (tube paint)
- PW6: Kremer titanium white (dry pigment) OR Winsor & Newton Designers Gouache permanent white (tube paint)
- Canvas, unprimed
- See end of this appendix for additional tools and materials if you are using Kremer dry pigments.

Directions:

1. Cut the bare canvas into three pieces, each (minimum) 50 × 50 mm square. Using painter's tape, tape down each piece of bare canvas to a Plexiglas sheet or other smooth, cleanable surface. Mask the canvas, leaving an open area large enough to cover the XRF aperture. The masked area should also be large enough to cover the XRF aperture, as this will be the background measurement of the bare canvas (see chap. 2, exercise 2.3c).
2. Prepare lithopone acrylic paint and titanium white acrylic paint, following the instructions at the end of this appendix if you are using Kremer dry pigments.
3. Mix the two prepared paints from step 2 in the following mixtures, with the proportions calculated by weight (for both the acrylic paints made from the dry pigments and the gouache tube paint):

Titanium white: lithopone	1:1
Titanium white: lithopone	10:1
Titanium white: lithopone	1:10

4. Apply each of these paint mixtures to the open area of one of the masked canvas squares.
5. Let dry completely before removing the tape.
6. Be sure to label each mock-up carefully.

EXERCISE 3.3a:

Instructions for Mock-Up

Materials:

- Winsor & Newton Designers Gouache Prussian blue (tube paint)
- Winsor & Newton Designers Gouache permanent white (PW6; tube paint)
- Canvas, unprimed

Directions:

1. Cut a long strip of bare canvas. The strip should be large enough to cover the XRF nosepiece. Using painter's tape, tape down the bare canvas to a Plexiglas sheet or other smooth, cleanable surface. (***Note:*** If easier and safer to handle, cut the strip into individual squares, one for each mixture. Make sure to label each square carefully!)
2. Mix the Prussian blue with titanium white, proportions calculated by weight, as noted in table A2.1.

TABLE A2.1. Weight ratio and dilution factor of Prussian blue to titanium white.

Mixture	Weight Ratio	Dilution Factor to Mixture A
A	0.01 g Prussian blue with 12 g titanium white	1
B	1:1 of mixture A:titanium white	0.5
C	1:1 of mixture B:titanium white	0.25
D	1:1 of mixture C:titanium white	0.125
E	1:1 of mixture D:titanium white	0.063
F	Titanium white only	n/a

3. Paint a square of mixture A on the prepared canvas. Next to it, paint a square of mixture B. Repeat with each remaining mixture. (The series of squares should be large enough to cover the XRF aperture.) Use the schematic and photo in chapter 3, figures 3.10 and 3.11 as a guide. In addition to mixtures A–E, mixture F is titanium white paint only and is used as the background measurement.
4. Let dry completely before removing the tape.

EXERCISE 3.4a:

Instructions for Mock-Up

Materials:

Kremer pigment green 7 (PG7; dry pigment) OR Golden Acrylics phthalo green (blue shade; tube paint)

Two Whatman filter paper sheets

See end of this appendix for additional tools and materials.

Directions:

1. Prepare PG7 acrylic paint, following the instructions at the end of this appendix if using Kremer pigment.
2. Using painter's tape, tape down the edges of the bare Whatman paper to a Plexiglas sheet or other smooth, cleanable surface.
3. Apply PG7 paint to both filter paper sheets, leaving a portion of each sheet unpainted. This unpainted area should be large enough to cover the XRF aperture, as this will be the background (substrate) measurement (see chap. 2, exercise 2.3c).
4. Let dry completely before removing the tape.
5. Leave one of the painted filter papers flat. For the second painted filter paper, fold into pleats. You should have three or four pleats (fig. A2.6; see chap. 3, fig. 3.14).

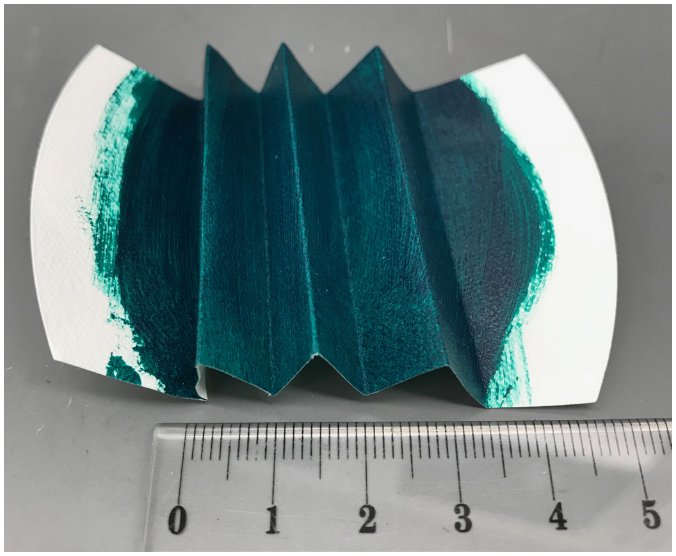

FIGURE A2.6. Photo of mock-up on Whatman filter paper painted with PG7 and folded to make pleats.

Dry Pigments and Acrylic

To make paint-outs for the exercises, only pigments and media are used; fillers, driers, and other components that make up traditional and contemporary paints are not included. The main reason for using an acrylic medium is because of its relative nontoxicity and its fast drying time, which allows the mock-ups to be made quickly and easily.

Note: Before creating complex mock-ups, always paint out individual pigments on unprimed canvas or filter paper and evaluate the composition using XRF analysis to make sure you understand the elemental components (i.e., whether there are impurities, fillers, etc.).

Tools:

- Thick glass sheet
- Glass muller
- Small containers with lids
- Brushes
- Canvas, unprimed
- Distilled water
- Winsor & Newton Ox Gall or any non-ionic surfactant (water miscible) that contains only organic components (i.e., will not contribute to the XRF signal, such as Kodak's Photoflo, propylene glycol) (fig. A2.7)
- Pigments
- Golden GAC 100 (acrylic medium)
- Spatula
- Pipettes and bulb
- Paper towels or wipes (preferably lint free) and acetone for cleaning
- Nitrile gloves

Directions:

1. Place a small amount of pigment on the glass sheet (fig. A2.8).
2. Add 1 or 2 drops of distilled water.
3. Add 1–3 drops of Ox Gall (only if needed based on wettability of pigment).
4. Place the muller in the middle of the pigment and grind (fig. A2.9). Add more distilled water as needed.

FIGURE A2.7. Tools and materials used in creating acrylic paint with dry pigments, including Winsor & Newton Ox Gall, spatulas, pipette, cup, distilled water, and paintbrushes. Jars of dry pigments can be seen in the background.

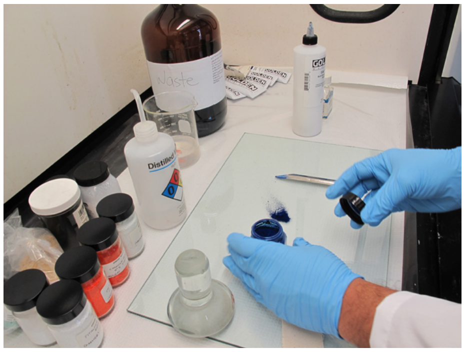

FIGURE A2.8. Small amount of dry pigment added to glass sheet in a fume hood.

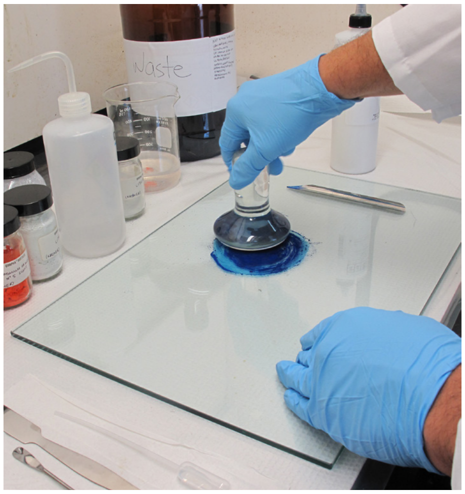

FIGURE A2.9. Grinding of dry pigment with the glass muller.

5. Add Ox Gall as needed, but do not add too much, as it will disrupt the quality of the paint (fig. A2.10). More water and Ox Gall will require a longer drying time.
6. Continue grinding until the consistency is like that of an oil slick (fig. A2.11).
7. Add 5–10 mL acrylic medium to the center of the paint circle (fig. A2.12).
8. With both hands, use the muller to grind and mix slowly, moving in a circular motion until paint is evenly mixed.
9. Scrape the paint into the middle of the glass sheet (fig. A2.13). Collect the paint in a disposable jar.
10. Use a brush to paint onto canvas.
11. **Always dispose of solid waste and liquid waste in appropriate containers and label the contents accordingly.**
12. Check local regulations for appropriate waste disposal practices. Golden Paints suggests the following (https://www.goldenpaints.com/waste-disposal):
    - "Even with water-based products, it is best to discard a solid instead of washing everything down the drain. Also, liquid paint should not be taken to a landfill. If allowed to dry, film-forming paints such as acrylics lock pigments in place and help prevent them from moving around in the groundwater. Allow residual paints and mediums to dry in the container. Dispose of as is, or remove the subsequent paint skin, leaving a fairly clean container. GOLDEN Acrylics are packaged in HDPE plastic, which can then be reused or recycled in many areas."
    - "Before using water to clean palettes, brushes, containers and other tools, wipe them with a paper towel and allow it to dry before disposal. This makes the wash water stay cleaner longer and keeps paint solids from going down the drain."

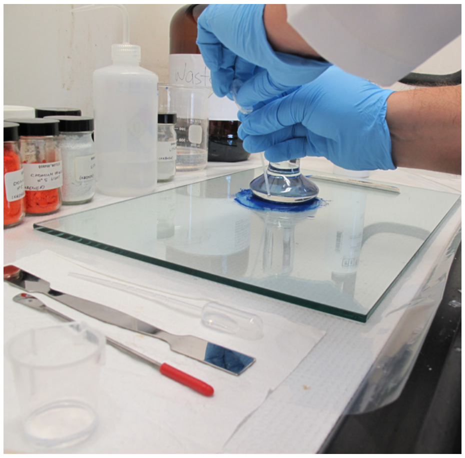

FIGURE A2.10. Addition of distilled water and Ox Gall as needed.

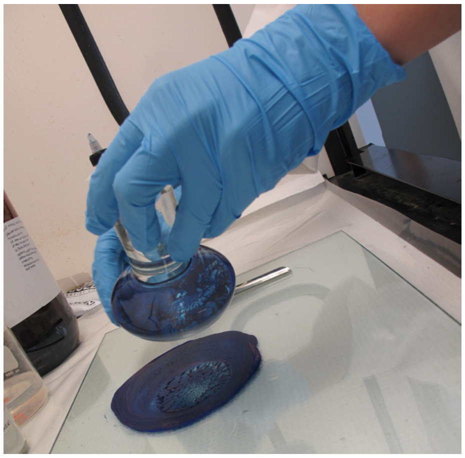

FIGURE A2.11. Consistency of paint after grinding should resemble an oil slick.

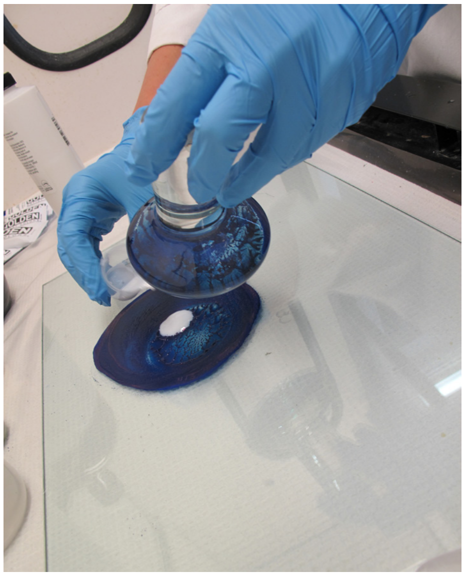

FIGURE A2.12. Addition of acrylic medium to center of the paint circle.

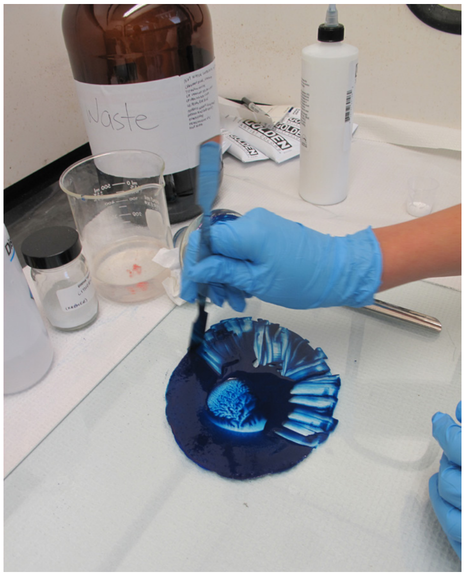

FIGURE A2.13. Paint being scraped toward the middle of the glass sheet before transferring to a jar.

Appendix 3
Materials and Instrument Suppliers

Winsor & Newton Designers Gouache

http://www.winsornewton.com/na/shop/water-colour/designers-gouache?colourid=50947270

Tube Paint Color	*Color Number and Product Code*
Ultramarine (PB29)	Color number: 660; Product code: 605660
Cobalt blue (PB28)	Color number: 178; Product code: 605178
Alizarin crimson (PR83)	Color number: 4; Product code: 605004
Cadmium red (PR108)	Color number: 94; Product code: 605094
Permanent white (PW6)	Color number: 512; Product code: 0614512
Zinc white (PW7 = lithopone)	Color number: 748; Product code: 614748
Prussian blue (PB27)	Color number: 538; Product code: 605538

Winsor & Newton Ox Gall

http://www.winsornewton.com/na/search-results?searchterm=ox+gall&Search.x=0&Search.y=0
Product code: 3221766

Kremer Pigments

http://shop.kremerpigments.com/en/

Dry Pigments	*Product Number*
Bone black (PBk9)	47100
Malachite natural	10300
Lithopone	46100
Titanium white rutile	46200
Phthalo green dark (bluish, PG7)	23000

Golden Acrylics

https://www.goldenpaints.com/products/colors/heavy-body

Tube Paint Color	*Product Number*
Acrylics Phthalo green (blue shade, PG7)	1270 (series 4)

Golden Medium

https://www.goldenpaints.com/products/medium-gels-pastes/special-purpose-mediums
GAC-100 Multi-purpose acrylic polymer
Product number: 3910

Cookson Electronics

https://www.acehardware.com/departments/tools/welding-and-soldering-tools/soldering-accessories/24650

Alpha Fry solid wire solder with tin/lead (50/50), gauge 3.175 mm (0.125 in.) thick, contains no core flux (Product #23505 or #24650)

Handheld XRF Manufacturers

Below are the manufacturers mentioned in this workbook; it is not intended to be a complete list of what is available on the market. (Websites current as of January 2020).

Bruker
https://www.bruker.com/products/x-ray-diffraction-and-elemental-analysis/handheld-xrf.html

https://www.bruker.com/products/x-ray-diffraction-and-elemental-analysis/micro-xrf-and-txrf.html

Thermo Scientific
https://www.thermofisher.com/us/en/home/industrial/spectroscopy-elemental-isotope-analysis/portable-analysis-material-id/portable-xrf-analyzer-selection-guide.html

Olympus
https://www.olympus-ims.com/en/landing/the-vanta-series/

SciAps
https://www.sciaps.com/xrf-handheld-x-ray-analyzers/x-series/

Spectro
https://www.spectro.com/products/xrf-spectrometer/xsort-xrf-gun-handheld-analyzer

Elvatech
https://elvatech.com/products/

Appendix 4
X-ray Energy Lines, Spectral Overlaps, and Interpretation Guide

A4.1 Periodic Table and X-ray Energy Lines

Key to Energy Values in keV

K_{α} $K_{\beta1}$
Au
79
$L_{\alpha1}$ $L_{\beta1}$

Group IA	IIA	IIIB	IVB	VB	VIB	VIIB	Group VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
H **1**																	**He** **2**
0.052 **Li** **3**	0.110 **Be** **4**											0.185 **B** **5**	0.282 **C** **6**	0.392 **N** **7**	0.526 **O** **8**	0.677 **F** **9**	0.851 **Ne** **10**
1.04 1.07 **Na** **11**	1.25 1.30 **Mg** **12**											1.49 1.55 **Al** **13**	1.74 1.83 **Si** **14**	2.02 2.14 **P** **15**	2.31 2.46 **S** **16**	2.62 2.82 **Cl** **17**	2.96 3.19 **Ar** **18**
3.31 3.59 **K** **19**	3.69 4.01 **Ca** **20** 0.34	4.09 4.46 **Sc** **21** 0.40	4.51 4.93 **Ti** **22** 0.45 0.46	4.95 5.43 **V** **23** 0.51 0.52	5.41 5.95 **Cr** **24** 0.57 0.58	5.90 6.49 **Mn** **25** 0.64 0.65	6.40 7.06 **Fe** **26** 0.70 0.72	6.93 7.65 **Co** **27** 0.78 0.79	7.48 8.26 **Ni** **28** 0.85 0.87	8.05 8.90 **Cu** **29** 0.93 0.95	8.64 9.57 **Zn** **30** 1.01 1.03	9.25 10.26 **Ga** **31** 1.10 1.12	9.89 10.98 **Ge** **32** 1.19 1.21	10.54 11.73 **As** **33** 1.28 1.32	11.22 12.50 **Se** **34** 1.38 1.42	11.92 13.29 **Br** **35** 1.48 1.53	12.65 14.11 **Kr** **36** 1.59 1.64
13.39 14.96 **Rb** **37** 1.69 1.75	14.16 15.83 **Sr** **38** 1.81 1.87	14.96 16.74 **Y** **39** 1.92 2.00	15.77 17.67 **Zr** **40** 2.04 2.12	16.61 18.62 **Nb** **41** 2.17 2.26	17.48 19.61 **Mo** **42** 2.29 2.40	18.41 19.61 **Tc** **43** 2.42 2.54	19.28 21.66 **Ru** **44** 2.56 2.68	20.21 22.72 **Rh** **45** 2.70 2.83	21.18 23.82 **Pd** **46** 2.84 2.99	22.16 24.94 **Ag** **47** 2.98 3.15	23.17 26.09 **Cd** **48** 3.13 3.32	24.21 27.27 **In** **49** 3.29 3.49	25.27 28.48 **Sn** **50** 3.44 3.66	26.36 29.72 **Sb** **51** 3.61 3.84	27.47 30.99 **Te** **52** 3.77 4.03	28.61 32.29 **I** **53** 3.94 4.22	29.80 33.64 **Xe** **54** 4.11 4.42
30.97 34.98 **Cs** **55** 4.29 4.62	32.19 36.38 **Ba** **56** 4.47 4.83	**57 - 71**	55.76 63.21 **Hf** **72** 7.90 9.02	57.52 65.21 **Ta** **73** 8.15 9.34	59.31 67.23 **W** **74** 8.40 9.67	61.13 69.30 **Re** **75** 8.65 10.01	62.99 71.40 **Os** **76** 8.91 10.35	64.89 73.55 **Ir** **77** 9.19 10.71	66.82 75.74 **Pt** **78** 9.44 11.07	68.79 77.97 **Au** **79** 9.71 11.44	70.82 80.26 **Hg** **80** 9.99 11.82	72.86 82.56 **Tl** **81** 10.27 12.21	74.96 84.92 **Pb** **82** 10.55 12.61	77.10 87.34 **Bi** **83** 10.84 13.02	79.30 89.81 **Po** **84** 11.13 13.44	81.53 92.32 **At** **85** 11.42 13.87	83.80 94.88 **Rn** **86** 11.72 14.32
86.12 97.48 **Fr** **87** 12.03 14.77	88.46 100.14 **Ra** **88** 12.34 15.23	90.89 102.85 **Ac** **89** 12.65 15.71	93.33 105.59 **Th** **90** 12.97 16.20	95.85 108.41 **Pa** **91** 13.29 19.70	98.43 111.29 **U** **92** 13.61 17.22	101.00 114.18 **Np** **93** 13.95 17.74	103.65 117.15 **Pu** **94** 14.28 18.28	106.35 120.16 **Am** **95** 14.62 18.83	109.10 123.24 **Cm** **96** 14.96 19.39	111.90 126.36 **Bk** **97** 15.31 19.97	114.75 129.54 **Cf** **98** 15.66 20.56	117.65 132.78 **Es** **99** 16.02 21.17	120.60 136.08 **Fm** **100** 16.38 21.79	**Md** **101**	**No** **102**	**Lr** **103**	**Actinides** **89-103**
Lanthanides **57-71**		33.44 37.80 **La** **57** 4.65 5.04	34.72 39.26 **Ce** **58** 4.84 5.26	36.02 40.75 **Pr** **59** 5.03 5.49	37.36 42.27 **Nd** **60** 5.23 5.72	38.65 43.96 **Pm** **61** 5.43 5.96	40.12 45.40 **Sm** **62** 5.64 6.21	41.53 47.03 **Eu** **63** 5.85 6.46	42.98 48.72 **Gd** **64** 6.06 6.71	44.47 50.39 **Tb** **65** 6.28 6.98	45.99 52.18 **Dy** **66** 6.50 7.25	47.53 53.93 **Ho** **67** 6.72 7.53	49.10 55.69 **Er** **68** 6.95 7.81	50.73 57.58 **Tm** **69** 7.18 8.10	52.36 59.35 **Yb** **70** 7.41 8.40	54.06 61.28 **Lu** **71** 7.65 8.71	

A4.2 Selected Spectral Overlaps

The following table presents selected spectral overlaps of relevance in cultural heritage objects. In these examples, one line of an element series overlaps with one line of another element series; this may make it difficult to determine which element is present. The user should always look at *all* the lines in each element series to confirm whether that element is present.

Peak A		**Peak B**		**Potential Overlap Sources**
Line	**Energy (keV)**	**Line**	**Energy (keV)**	
Mg K_α	1.25	As L_α	1.28	Cobalt violet pigments containing Mg and As
Si K_α	1.74	Rb L_α Sr L_α	1.69 1.81	Low amounts of silicon-based compounds (e.g., quartz) with high amounts of calcium- or barium-containing compounds, which often contain Sr
P K_α	2.01	Ca K_α escape peak	1.95	Low amounts of phosphorus-containing pigment (bone black, cobalt phosphate violet) in the presence of large amounts of calcium compounds
S K_α	2.31	Pb M_α	2.34	Lead-based pigment layers over calcium sulfate–based ground; mixtures of lead-based pigments with sulfides (HgS, vermilion; ZnS, zinc sulfide in lithopone; CdS and CdS(Se)) and sulfates ($CaSO_4$, $BaSO_4$, etc.)
Cl K_α	2.62	Pb Mγ	2.65	Co-occurrence of chlorine-containing synthetic pigment (phthalocyanine green) and lead white; co-occurrence of chlorinated salts and leaded pigments; lead chloride containing salts
Cl K_α	2.62	Rh L_α	2.70	Chlorine-containing compound analyzed with Rh anode X-ray source
Ag L_α	2.98	Ar K_α	2.96	Silver-based photographs and silver-containing alloys analyzed in air, which contains argon
Sb L_α	3.60	Sn L_β	3.66	Alloys containing both antimony and tin. Glasses or glazes containing Naples yellow, tin-based opacifier, or lead-tin yellow colorant. Co-occurrence of Naples yellow and lead tin yellow in paint layer
Sb L_α	3.60	Ca K_α	3.69	Co-occurrence of small amounts of Naples yellow and calcium-based white or black in paint layers
Ti K_α	4.51	Ba L_α	4.47	Co-occurrence of barium sulfate and titanium white
Cr K_α	5.41	Ba Lγ	5.53	Small amounts of chromium-containing pigment (chrome yellow, chrome green, viridian) in the presence of barium sulfate
Mn K_α	5.90	Cr K_β	5.95	Small amounts of manganese-containing pigment in the presence of large amounts of chromium-containing pigment in paint layers or glass or glaze layers
Fe K_α	6.40	Cu K_α escape peak	6.31	Copper alloy with trace amounts of iron. Co-occurrence of iron-containing pigment (iron oxide, Prussian blue, etc.) with copper pigment (azurite, malachite, verdigris, emerald green, etc.)

Peak A		Peak B		Potential Overlap Sources
Line	**Energy (keV)**	**Line**	**Energy (keV)**	
Co K_α	6.93	Fe K_β	7.05	Co-occurrence of cobalt-containing pigment (smalt, cobalt blue, Cerulean blue, cobalt violet) and iron-containing pigment (iron oxide, Prussian blue, etc.)
As K_α	10.54	Pb L_α	10.55	Copper alloys with As and Pb content; presence of orpiment (or other As-containing pigment) along with lead white or other lead-based pigment. Look for As K_β peak to confirm presence of As.
As K_β	11.72	Au L_β	11.61	Presence of orpiment (or other As-containing pigment) along with gilding
As K_β	11.72	Hg L_β	11.82	Presence of orpiment (or other As-containing pigment) along with vermilion
Pd K_α	21.18	Pb L_α + Pb L_α sum peak	21.10	Palladium-containing photographic print mounted on paper board with lead-based white
Cd K_α	23.17	Pb L_α + Pb L_β sum peak	23.16	Co-occurrence of cadmium yellow or cadmium red along with lead white or other lead-containing pigments
Sn K_α	25.27	Pb L_β + Pb L_β sum peak	25.22	Alloys with both Pb and Sn (bronzes, pewter, etc.); mixture of lead-tin yellow and other lead-containing pigments

A4.3 Spectral Interpretation Guide

1. Identify elements associated with the instrument (see chapter 2):
    - Identify the anode Rayleigh (elastic) and Compton (inelastic) scatter peaks:
        - The Rayleigh peaks will lie on the XRF emission lines for the anode element.
        - The Compton peaks will be broader, at lower energy than their corresponding Rayleigh line.
    - Identify any elements associated with the instrument (these should have previously been determined by examining a spectrum acquired from polyethylene foam).
2. Identify elements in the sample/area of interest (see chapter 3):
    - Begin with the most intense peaks, working toward the smallest peaks.
    - Look for the elements you suspect might be present.
    - Identify *all* the peaks in a series (i.e., K, L, M) to be present for secure identification. Within the K series, the relative Kα/Kβ ratio intensity is nominally 5:1; within the L series, the ratio of the Lα and Lβ peaks is typically 3:2 (but this can be affected by mixing or layering).
    - Look for the lower-energy series for each element (L and M series for K and L, respectively).
3. Identify any spectral artifacts (see chapter 3):
    - Sum peaks will occur at twice the intensity of a large peak or may occur at the sum of two peaks (e.g., Lα + Lβ, Kα + Kβ).
    - Escape peaks will occur at 1.74 keV less than the large peak from which it arises.
4. Interpret the results (see chapter 4):
    - Once the analysis is completed, ask yourself, do the results make sense?
    - Have you identified *all* the peaks?
    - Are the elements identified consistent with your expectations?

Glossary

Accelerating voltage/potential. See *Operating voltage/potential.*

Acquisition time. Acquisition time, or accumulation time, is defined differently for analog and digital pulse processor multichannel analyzer systems relative to "live time." In both types of systems, acquisition time is shorter than real time. In analog multichannel analyzers, live time, rather than acquisition time, is used to represent the total time used for the measurement of valid events. In digital pulse processor multichannel analyzers, the acquisition time is the actual elapsed time during which counts are measured.[1] Acquisition time excludes periods during which data acquisition stops, such as during preamplification and data transfer for systems with digital multichannel analyzers. For digital multichannel analyzers, acquisition time is longer than live time, because it includes the dead time per pulse, or the time necessary to correct for overlapping pulses. See also *Dead time*, *Live time*, and *Real time*.

ALARA (As Low As Reasonably Achievable). A radiation safety principle based on minimizing radiation exposure based on three factors: minimizing exposure time, maximizing distance from radiation, and maximizing shielding.

Anode. Part of an X-ray tube that, along with the cathode, forms an electric circuit. A current of electrons is accelerated from the cathode toward the anode at an energy controlled by the potential (voltage) difference between the cathode and anode, and upon hitting the anode produces X-rays. A continuum (bremsstrahlung) of radiation is thus produced, as well as characteristic lines corresponding to the elemental composition of the anode. Also called *target.*

Atomic number (Z). Number of protons in the nucleus of an atom that uniquely identifies each chemical element. The periodic table is arranged in order of increasing atomic number.

Bremsstrahlung. From the German, meaning "braking radiation." Radiation produced by rapid deceleration of electrons at the anode of an X-ray tube. Bremsstrahlung is produced in a continuum spectrum of energies, from a maximum energy corresponding to the accelerating potential applied to the tube.

Characteristic radiation. Series of fluorescence spectral emission lines associated with a specific chemical element (e.g., K, L, or M series). The energies at which the emission lines occur are unique for each element. See also *Electron shell / principal energy level*.

Counts. The number recorded each time a photon strikes the detector. "Raw counts" describes the total number of X-ray photons hitting the detector; "valid counts" refers to the number of counts that the detector can accurately record. See also *Dead time.*

Current (I). A flow of electric charge measured in amps (A) or microamps (μA); 10^{-6} A = 1 μA. In XRF spectrometers, current controls the number of electrons flowing from the cathode to the anode, and thus controls the total amount of generated X-rays.

Dead time. The time after a recording event during which the detector is not actively recording. The percentage of dead time is the ratio of the difference between the raw and valid counts to the raw counts:

$$\%DT = \frac{raw - valid}{raw} \times 100$$

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[1] http://www.amptek.com/wp-content/uploads/2015/07/Application-Note-Acquisition-Time-Live-Time-Dead-Time.pdf

Dead time should be kept as low as possible to avoid saturation. Dead time can typically be lowered by reducing the current through the X-ray tube.

Detector. Instrument component for energy-dispersive spectroscopy (EDS) that records the intensity of X-radiation as a function of its energy. Handheld XRF spectrometers usually employ solid-state detectors, either silicon PIN (Si-PIN) detectors or silicon drift detectors (SDDs), which can handle higher count rates without deterioration of energy resolution compared to Si-PIN detectors.

Electron binding energy / ionization potential / absorption edge. Terms used to indicate the minimum energy required to cause an electron to be ejected from a specific shell (K, L, or M) of an atom.

Electron shell / principal energy level. Model used to describe the energy of the electrons orbiting an atomic nucleus. The shell closest to the nucleus is called the K shell, the next closest is known as the L shell, next is the M shell, and so on. The shells also can be referred to by their principal quantum numbers (K=1, L=2, M=3, etc.); X-ray notation generally uses Siegbahn notation (K, L, M, etc.). See also *Siegbahn notation.*

Escape peak. Peak that occurs when a fluorescent X-ray hits the detector and causes ionization (and subsequent X-ray fluorescence) from the silicon in the detector. The resulting loss of energy from the silicon fluorescence causes a peak to appear at an energy equal to that of the initial fluorescent X-ray minus the silicon fluorescence (1.74 keV).

$$E_{\text{escape}} = E_{\text{element}} - 1.74$$

Electric power (P). The rate of doing work in an electric circuit, expressed in watts (W), which is equal to one joule per second (J/sec). Power is related to current (I) and voltage (V) through the equation $P = I \times V$.

Filter. A material placed between the X-ray source and sample to preferentially enhance excitation of certain elements and/or to attenuate the background in a region of interest for improved signal-to-noise ratio. Filters can be single materials or layers of different materials with various thicknesses.

Live time. Live time is shorter than real time for a measurement (the amount of time elapsed between the start and end of a measurement). In general, it can be considered the total time during which valid events are recorded by the detector system. For analog signal processors, the total live time represents the time during which counts are measured and live time is used to estimate input count rate (counts per second). In the case of digital pulse processor (DPP) multichannel analyzer (MCA) systems, live time is computed rather than measured and is an estimate of the total time of count acquisition by the DPP.

Matrix effects. General term used to refer to the decrease or increase of secondary (fluorescent) X-rays from an element of interest due to interaction with other elements in the sample. If X-ray fluorescence from an element of interest is absorbed by another element in the sample matrix, the signal will decrease (absorption); if X-ray fluorescence from other elements in the matrix is of sufficient energy (i.e., above the electron binding energy/ionization potential/absorption edge) to induce fluorescence from the element of interest, the signal will be increased (enhancement).

Noise. Any unwanted random addition to a signal that may be introduced by the various electronic components in the spectrometer. Since noise is an intrinsic function of the spectrometer, the signal-to-noise ratio (S/N) can be improved by increasing the signal or decreasing the variation in the noise either by averaging or by using longer acquisition time. See also *Signal-to-noise ratio.*

Normalization. The scaling of one spectrum to another so that they have the same intensity at one selected point. Typically, a point somewhere on the continuum background is selected as the normalization point to allow comparison of the relative intensities of the emission lines.

Operating voltage/potential. The amount of voltage (or electric potential difference) applied to the cathode of the X-ray tube to accelerate electrons toward the anode, thus generating X-radiation. It is measured in volts (V) or kilovolts (kV); 1000 V = 1 kV. Also called *accelerating voltage/potential.*

Photoelectric effect. Emission of electrons from a material following the absorption of a photon of sufficient energy (i.e., X-rays) to eject an electron from an atom and cause ionization.

Photon energy (E). Energy of X-ray photons, typically expressed in units of electron volts (eV); this is *not* the same as an electric potential (V), expressed in volts. An eV is the amount of energy necessary to move a single electron across a potential difference of one volt. Therefore, in XRF spectrometers the maximum energy of X-ray photons that can be produced is governed by the accelerating/operating voltage (e.g., if the tube is operating at 40 kV, the maximum energy of X-rays that can be produced is 40 keV). Photon energy can also be expressed as the wavelength (λ) or frequency (ν) of radiation through the relation:

$$E = \frac{hc}{\lambda} = h\nu, \text{ where } h = 4.136 \times 10^{-15}\,\text{eV} \bullet \text{s}; c = 3 \times \frac{10^8\,\text{m}}{\text{s}}$$

The relation between energy and wavelength reduces to

$$E\left(\text{keV}\right) = \frac{1.24}{\lambda\left(\text{nm}\right)}$$

Thus, XRF spectra presented as a function of wavelength will appear reversed along the x-axis compared to those presented as a function of energy.

Real time. The actual time that has passed between the start and end of a measurement, equaling the time interval as it could be measured by the instrument operator using a watch or other chronometer. Detector systems containing multichannel analyzers do not acquire data (measure counts) for the full time period of a measurement, so the actual amount of time during which counts are measured is shorter than the real time.

Resolution. Term used to describe the energy, or spectral, resolution of a spectrometer, which is a measure of how well it can resolve individual features in the spectrum (i.e., how well it can resolve closely spaced peaks). Theoretically, XRF emission lines are monochromatic—that is, they have a single, well-defined energy/wavelength—but in reality they appear as a peak with a width that is a function of the detector and other components of the spectrometer. For XRF the energy resolution is typically measured as the full width at half maximum (FWHM) of the Mn Kα emission line. ***Note:*** Resolution can also refer to the spatial resolution, which is a measure of how well the instrument can resolve two closely spaced features; spatial resolution largely depends on the spot size of the primary X-ray beam.

Saturation. The condition wherein the number of photons hitting the detector exceeds its capacity to count them. The saturation limit depends on the type of detector, but in most XRF spectrometers it can be observed as an asymmetrical broadening of the emission peak to lower energies.

Scattering. One of the ways that X-rays, along with photoelectric absorption, can interact with matter. The interaction can be either elastic (with no change in energy, also called *Rayleigh scattering*) or inelastic (with loss of energy, also called *Compton scattering*).

Shielding. In terms of radiation safety, a physical barrier placed between the user and the source to block some or all the radiation. To ensure safety, the amount and type of barrier material needed is dependent on the energy of the X-ray source. In a layered system, shielding is used to refer to the absorption of X-radiation by the upper layers, attenuating the amount of primary radiation reaching the lower layers, and, similarly, the amount of fluorescence radiation that reaches the detector.

Siegbahn notation. System used to denote the individual spectral emission lines produced by an electronic transition between electron shells. For XRF emission lines, the letters K, L, and M refer to the electron shell at which the transition terminates, and the notation α, β, γ, etc., indicates the specific sub-levels.

Signal-to-noise ratio (S/N or SNR). The measure of the desirable signal relative to the level of background noise. In general, a S/N of at least 3 is considered sufficient to confidently distinguish a peak from noise, although strictly speaking, a S/N of at least 5 is required to distinguish features with 100% certainty.

Sum peak. Occurs when two photons hit the detector simultaneously and are recorded as a single event; the photons may be of the same or different energies. Typically, sum peaks are observed only for the most intense emission lines.

X-radiation. A form of electromagnetic radiation. X-rays have a wavelength in the range of 0.01 to 10 nanometers, corresponding to frequencies in the range of 30 petahertz to 30 exahertz (3×10^{16} Hz to 3×10^{19} Hz) and energies in the range of 100 eV to 100 keV. X-rays are a form of ionizing radiation: they can ionize atoms and disrupt molecular bonds.

X-ray fluorescence (XRF). Emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by high-energy X-rays ("primary" radiation). Analogous to UV fluorescence, the emitted X-ray fluorescence photons have less energy (longer wavelength) than the excitation source.

X-rays. Classified as either primary or secondary in XRF: primary (or incident) X-ray photons (those emitted from the tube) create photoelectrons from the target atoms; secondary (or fluorescent) X-ray photons are emitted upon filling of the electron vacancy.

X-ray tube. A vacuum tube that creates X-rays. The basic principle involves the application of a high voltage (known as accelerating voltage/potential, or operating voltage/potential, typically 15–50 kV for handheld spectrometers) and current (the rate at which electrons flow, typically 1–30 μA for handheld spectrometers) to a cathode. The electrons are accelerated toward the anode—usually made of rhodium (Rh), rhenium (Re), or silver (Ag) for handheld spectrometers—according to the accelerating potential. Upon colliding with the anode, the rapid deceleration of the electrons produces X-rays; this is called *bremsstrahlung*. X-rays are also produced when a cathode electron knocks out an inner-shell electron from the anode to create a vacancy that is subsequently filled by higher orbital electrons; this is called fluorescence. The energy of X-rays thus produced is governed by the applied accelerating voltage, and the intensity is governed by the current.

About the Authors

Anikó Bezur is the Wallace S. Wilson director of scientific research of the Technical Studies Laboratory at Yale's Institute for the Preservation of Cultural Heritage. She and her team employ a variety of nondestructive and sample-based approaches to decode the materiality of objects in Yale's collections to inform scholarship on their making, use, and change with time; and to aid their preservation. Over the past two decades of using X-ray fluorescense to study a broad range of cultural heritage objects, she has shared her expertise through courses, workshops, and mentoring. She holds a PhD in materials science and engineering from the University of Arizona. Prior to joining Yale in 2012, Dr. Bezur held positions at the Museum of Fine Arts, Houston, the Menil Collection, the Art Institute of Chicago, and the Art Conservation Department at Buffalo State College.

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