

X-Ray Fluorescence

EQUIPMENT NEEDED FROM EG&G ORTEC

Low-energy x-ray calibration sources SK-1X (Table 12.1)
 142PC Preamplifier
 Bin and Power Supply
 480 Pulser
 444 Gated Biased Amplifier
 572 Spectroscopy Amplifier
 556 High Voltage Power Supply
 Si(Li) X-Ray Detector System (SLP-06175); typical specifications, 6 mm diam, 175 eV resolution at 5.9 keV, 1-mil Be window
 459 5 kV Detector Bias Supply

ACE-2K MCA System including suitable IBM PC (other EG&G ORTEC MCAs may be used)
 Oscilloscope
⁵⁷Co excitation source with shield ≥ 5 mCi)
 904-1B Thin-Window Proportional Counter
 Target Kit M-12
 Absorber Kit 3-Z2
 ORC-12 Cable Set
 311 Chamber for X-Ray Fluorescence with a Si(Li) Detector
 312 Chamber for X-Ray Fluorescence with a Proportional Counter

Purpose

The characteristic x rays of several metallic samples will be excited by the x rays or gamma rays from a radioactive source, and a spectrum will be analyzed for each sample.

Introduction

X-ray fluorescence experiments are quite easy to perform. The technique of exciting characteristic x rays of elements has been known and used for many years. Figure 12.1 shows a typical arrangement of the detector and electronics for this experiment.

X rays from the excitation source are allowed to impinge on the sample, and these x rays make photoelectric interactions in the sample. The characteristic x rays that are then produced by the photoelectric interactions are counted by a low-energy x-ray detector. The detector in Fig. 12.1 is a proportional counter. As discussed in Experiment 8, the detector could be a high-resolution Si(Li) X-Ray Detector, which is the type used for Experiment 12.2.

Excitation Sources

The excitation sources to be used in this experiment should have activities of several millicuries, (mCi). Weaker sources can be used, but the counting times required for reasonable statistics are increased. Licenses are required before the sources can be obtained.

A general rule for the selection of an appropriate excitation source is that it should have a gamma, x ray, or Bremsstrahlung continuum slightly above the highest characteristic x ray that is to be excited. The reason is that the photoelectric cross section (Experiments 3 and 7) decreases rapidly as energy increases. The most commonly used sources for x-ray fluorescence measurements and their characteristic x-ray energies are: ⁵⁵Fe, <6 keV; ¹⁰⁹Cd, <9 keV; ⁵⁷Co, between 15 keV and 5 keV; and ²⁴¹Am, for a wide range from 60 keV down. Figure 12.2 shows the decay schemes for ⁵⁵Fe, ¹⁰⁹Cd, and ⁵⁷Co. The decay scheme for ²⁴¹Am was shown in Experiment 4.

Characteristic X Rays

The expected characteristic x rays that are excited by fluorescence are listed in refs. 1, 2, and 9. Unfortunately, not all references use the same nomenclature for binding energies and x-ray energies. (Ref. 2 is a list of binding energies given in the Appendix.) The list includes binding energies for the following energy levels: K, L_I, L_{II}, L_{III}, M_I, M_{II}, M_{III}, M_{IV}, M_V, N_I, N_{II}, . . . P_{III}. The most commonly observed x rays are the K_α and K_β lines, and these are calcu-

Table 12.1. Low-Energy (~1 μCi) X-Ray Calibration Sources

Isotope	X-Ray Energy (keV)	
⁵⁴ Mn	5.414	K _α
	5.946	K _β
⁵⁷ Co	6.40	K _α
	7.06	K _β
	14.41	γ
⁶⁵ Zn	8.04	K _α
	8.90	K _β
⁸⁵ Sr	13.38	K _α
	15.00	K _β
88Y	14.12	K _α
	15.85	K _β
¹⁰⁹ Cd	22.10	K _α
	25.00	K _β
¹¹³ Sn	24.14	K _α
	27.40	K _β
¹³⁷ Cs	32.1	K _α
	36.6	K _β

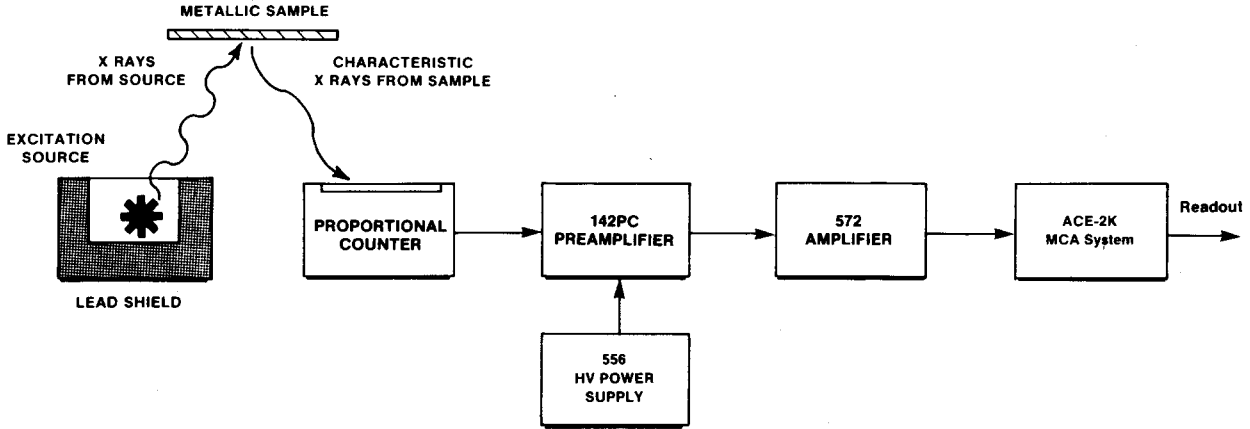


Fig. 12.1. Equipment Arrangement for Experiment 12.1.

lated from the binding energies, (BE), in the following manner:

$$K_{\alpha_1} \text{ (energy)} = BE(K) - BE(L_{III}), \quad (1)$$

where BE(K) is the binding energy of the K level, etc.,

$$K_{\beta_1} \text{ (energy)} = BE(K) - BE(M_{III}). \quad (2)$$

The method for calculating other characteristic x-ray energies is listed on page 570 of ref. 9.

EXPERIMENT 12.1 X-Ray Fluorescence with a Proportional Counter

Procedure

1. Set up the equipment shown in Fig. 12.1. Adjust the 556 to the high-voltage level required for the proportional counter. Calibrate the system as in Experiment 11 so that the 32.2-keV x ray from ¹³⁷Cs is being stored in the upper channels of the analyzer. Use as many sources from Table 12.1 as are necessary to establish the calibration for the system. Determine the slope of the calibration line and the resolution of the 32.2-keV line of ¹³⁷Cs.

2. Remove the calibration sources and place a cadmium sample and the ⁵⁷Co fluorescence source in position in the Model 312 Chamber. Accumulate a spectrum for a period of time sufficient to identify the characteristic x rays from the cadmium sample. Read the data out of the MCA and plot the spectrum. Figure 12.3 shows a typical cadmium spectrum using a krypton-filled proportional counter. In this device the krypton K_α at 12.651 keV can escape from the proportional counter before it makes a photoelectric interaction in the gas. The second pronounced peak in Fig. 12.3 is therefore the cadmium K_α minus the krypton K_α escape peak, etc.

Figure 12.4 shows the cadmium characteristic x rays measured with a xenon-filled proportional counter. The xenon K_α escape peak is not present in this spectrum because its energy is 29.78 keV and thus it is not energetically possible to produce this peak with the cadmium sample and the ⁵⁷Co source.

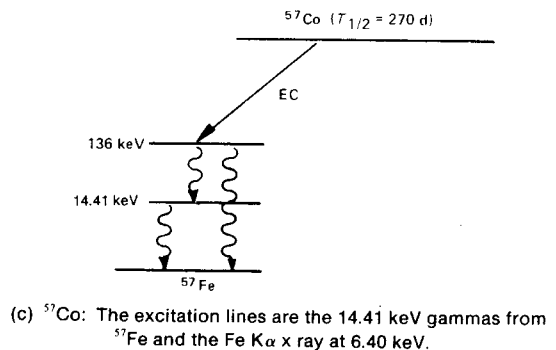
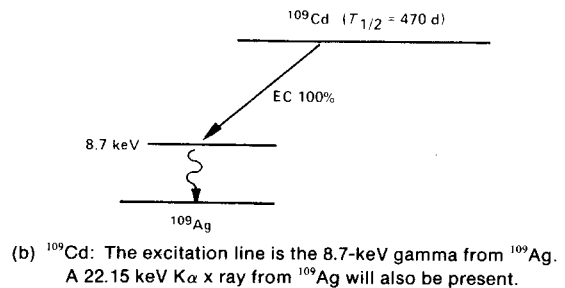
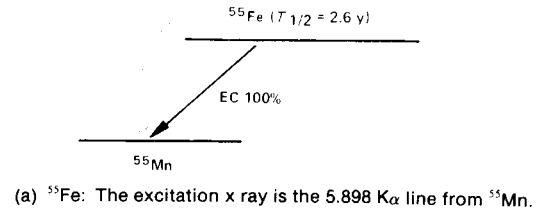


Fig. 12.2. Decay Schemes for Common X-Ray Fluorescence Excitation Sources.

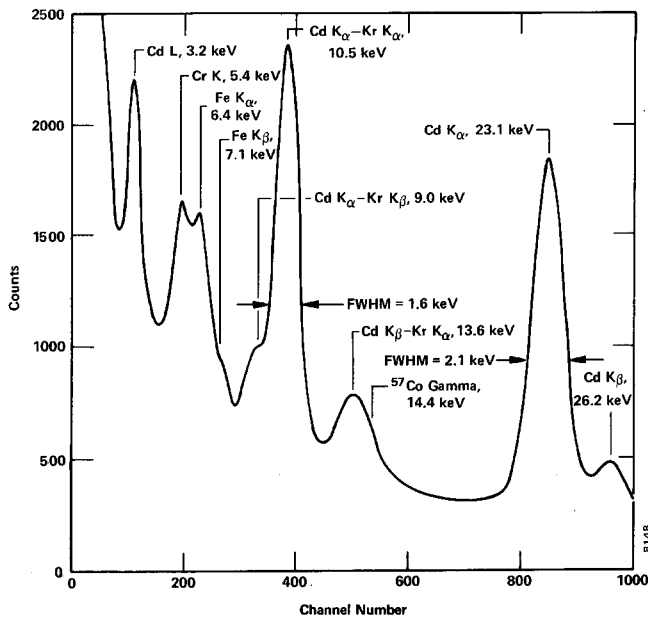


Fig. 12.3. Cadmium X-Ray Spectrum Obtained with a Krypton-Filled Proportional Counter.

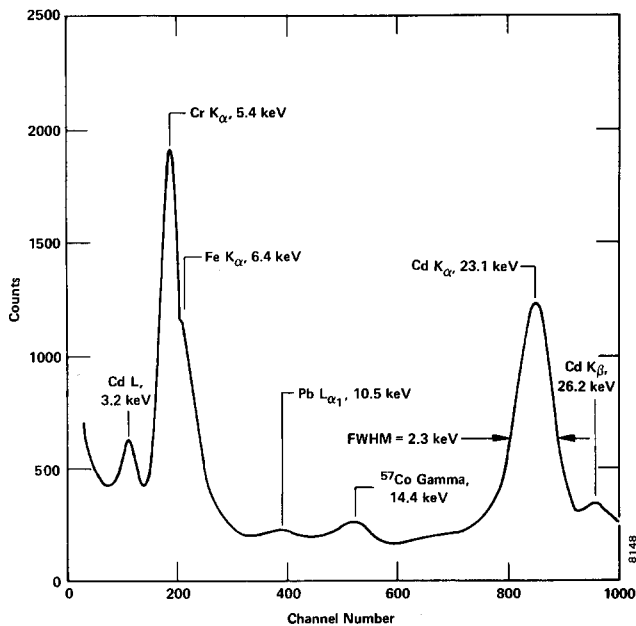


Fig. 12.4. Cadmium X-Ray Spectrum Obtained with a Xenon-Filled Proportional Counter.

3. Remove the cadmium and replace it with one of the other samples in Target Kit M-12. Accumulate a spectrum and read out the MCA. Identify the groups in the spectrum. Repeat for the other elements in the kit.

4. Place the composite sample from the target kit in the irradiation position. Accumulate a spectrum and identify all peaks. Figure 12.5 shows a composite spectrum that was taken for a clad-type U.S. quarter. This can be contrasted with Fig. 12.6 which shows one of the older type U.S. silver quarters.

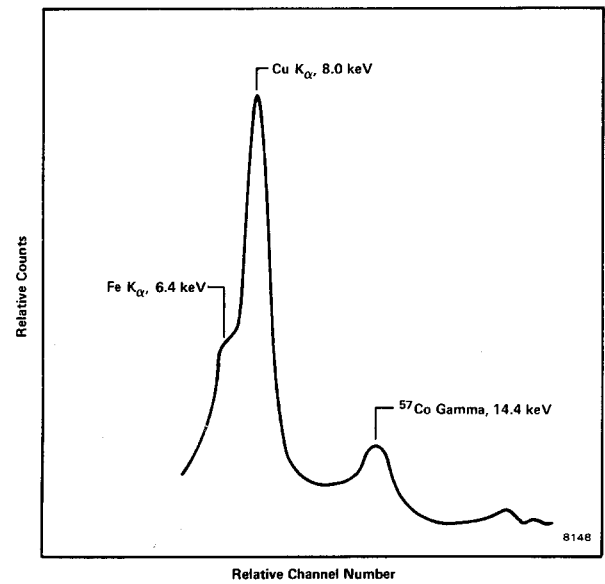


Fig. 12.5. X-Ray Spectrum for a Clad-Type U.S. Quarter.

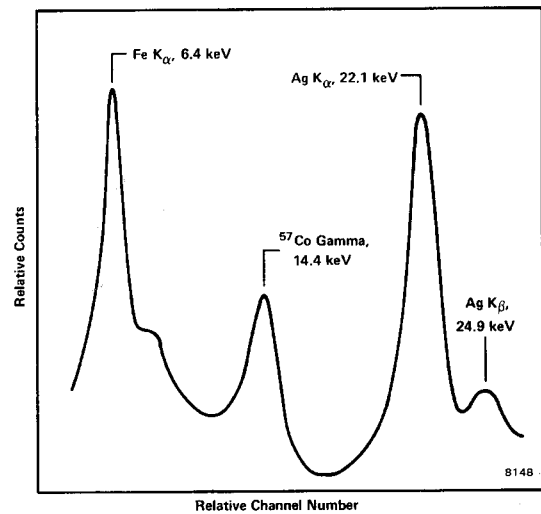


Fig. 12.6. X-Ray Spectrum for an Older U.S. Silver Quarter.

EXPERIMENT 12.2 X-Ray Fluorescence with a Si(Li) Detector

Introduction

Si(Li) x-ray detectors have been developed that will have a resolution of 150 eV for the 6.4-keV line of ⁵⁷Co, as discussed in Experiment 8. It is possible, with resolutions of this order, to distinguish between adjacent energy lines that can come from various metallic elements in a sample. In other words, if the K_α lines of the elements in the sample are resolvable from each other, the elemental constituents of the target can be determined.

Experiment 8 should be completed before this experiment is started.

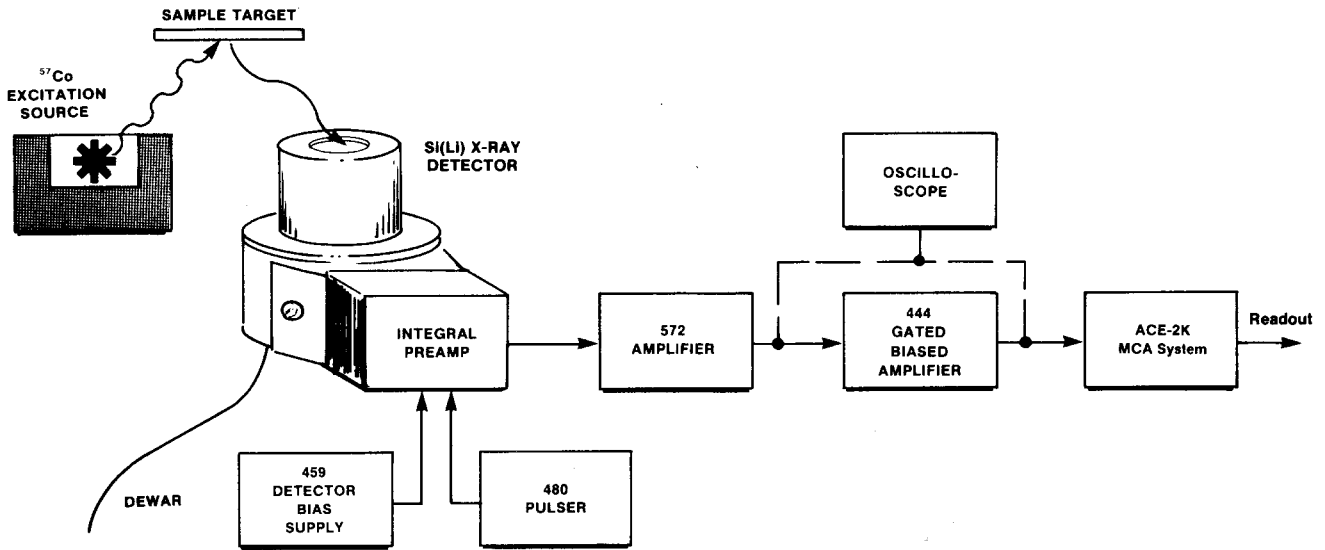


Fig. 12.7. Equipment Arrangement for Experiment 12.2.

Procedure

1. Set up the equipment as shown in Fig. 12.7. The Model 311 Chamber is used for this experiment. Use the pulse generator and any of the sources listed in Table 12.1 to calibrate the system from 2 keV to 25 keV, as outlined in Experiment 8. Plot the calibration line, determine the slope in eV/channel, and measure the resolution for the 6.4-keV line of ⁵⁷Co.
2. Use a piece of copper from the target kit as the first target and position it as shown in Fig. 12.7. Determine the energies of the Cu K_α and K_β lines from your calibration curve. Compare these with the calculated values for Cu shown in the Appendix.
3. Repeat for the other elements in Target Kit M-12. For comparison, Figs. 12.8, 12.9, and 12.10 show x rays from iron, copper, and molybdenum samples.

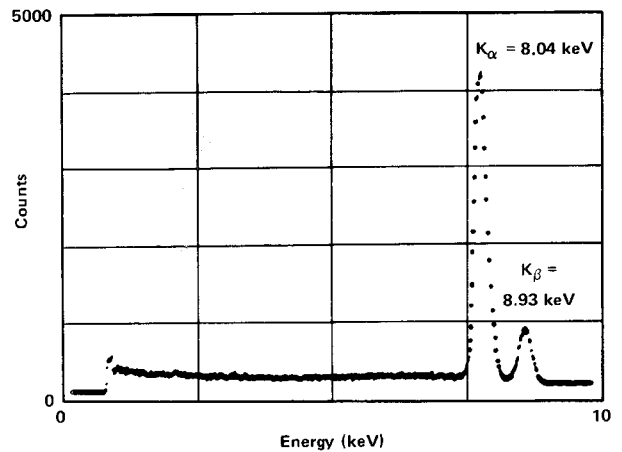


Fig. 12.9. Copper Fluorescence Spectrum.

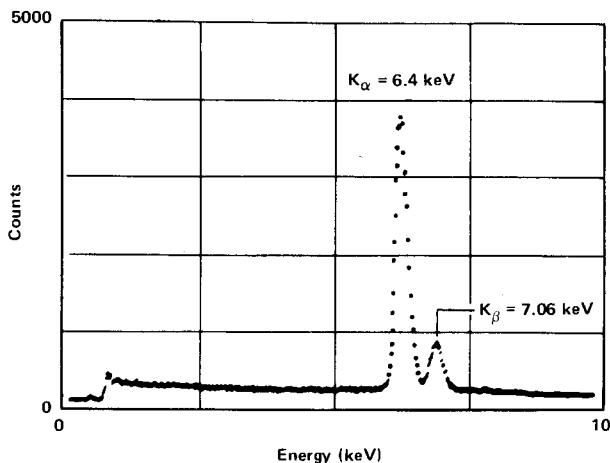


Fig. 12.8. Iron Fluorescence Spectrum.

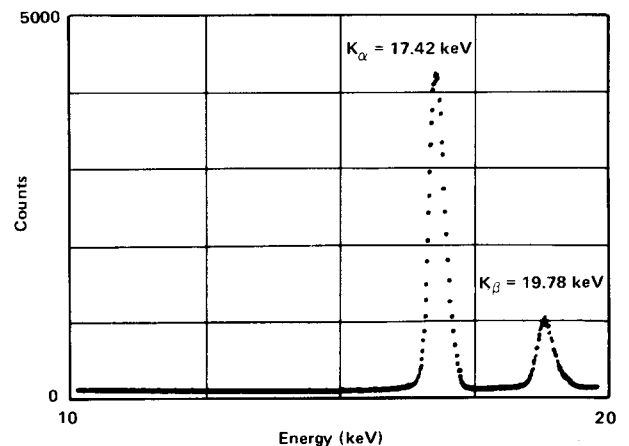


Fig. 12.10. Molybdenum Fluorescence Spectrum.

4. Place the composite sample from the target kit as the target. Determine the elements present in the sample by identifying each set of characteristic x rays. Figure 12.11 shows a spectrum for a composite metallic sample of Fe, Co, Ni, and Cu. Adjacent elements of the heavier metals can easily be identified by x-ray fluorescence as shown in Fig. 12.11. This technique is being widely accepted in industry as a method by which surface elemental analysis can be performed quickly.

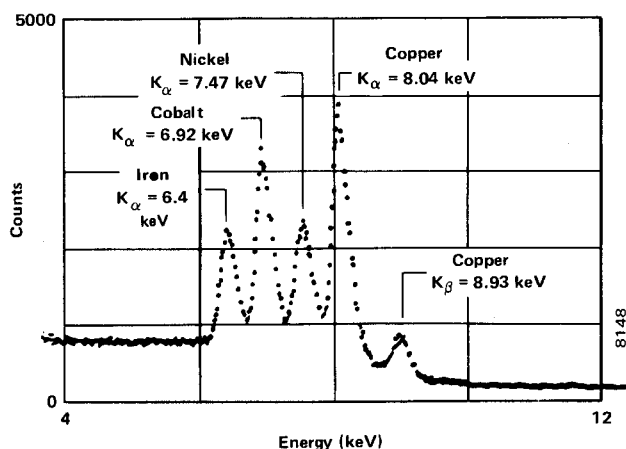


Fig. 12.11. Fluorescence Spectrum of Fe, Co, Ni, and Cu.

References

1. X-Ray Critical-Absorption and Emission Energies Chart, available from EG&G ORTEC (Slide Rule).
2. X-Ray Critical-Absorption and Emission Energies in keV (Appendix in this manual).
3. J. C. Russ, Coordinator, *Energy Dispersion X-Ray Analysis, X-Ray and Electron Probe Analysis*, available from ASTM Special Technical Publication 485, 1970, 04-485000-39 from American Society for Testing and Materials, Philadelphia, Pennsylvania.
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6. J. S. Hansen, et al., "Accurate Efficiency Calibration and Properties of Semiconductor Detectors for Low Energy Photons," *Nucl. Instrum. Methods* **106**, 365 (1973).
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9. C. M. Lederer and V. S. Shirley, Eds., *Table of Isotopes*, 7th Edition, John Wiley and Sons, Inc., New York (1978).