

### EQUIPMENT NEEDED FROM ORTEC

- 4001A/4002D NIM Bin and Power Supply
- 142 PC Preamplifier
- 480 Pulser
- 672 Spectroscopy Amplifier
- 556 High Voltage Power Supply
- 659 0–5kV Detector Bias Supply
- TRUMP-PCI-2K MCA System including PC (other ORTEC MCAs may be used)
- Si(Li) X-Ray Detector System (SLP-06175); typical specifications: 6 mm diameter, 175 eV resolution at 5.9 keV, 1-mi Be window
- C-36-12 Cable
- C-36-2 Cable
- C-24-12 Cable (2 ea.)
- C-24-1 Cable
- C-29 BNC Tee Connector

### OTHER NEEDED EQUIPMENT

- Chamber for X-Ray Fluorescence: vacuum chamber fitted to a vertical Si(Li) detector endcap with dimensions of 8-in. diameter x 3-in. deep. The chamber should have four sample positions which can be indexed while under vacuum.
- Chamber for X-Ray Fluorescence with a Proportional Counter: vacuum chamber with dimensions of 8-in. diameter x 3-in. deep. The chamber should have four sample positions which can be indexed while under vacuum.
- Target Sample Set for X-Ray Fluorescence, should include: Fe, Ni, Cu, Zn, Mo, Cd, Ag, Ge, and Zr plus 3 composite samples.
- Multiple Metal Foil Set, should include 3 each: Al, Fe, Cu, Mo, Sn, Ta, and Pb. Thicknesses range from 400 mg/cm<sup>2</sup> to 1500 mg/cm<sup>2</sup>.
- Sealed X-Ray Sources (disk type) 1–5 μCi, <sup>57</sup>Co, <sup>55</sup>Fe, <sup>65</sup>Zn (substitute alternate sources with similar energies).
- <sup>57</sup>Co excitation source with shield (≥5 mCi)
- Thin-Window Proportional Counter
- Oscilloscope

### Purpose

The characteristic x-rays of several metallic samples will be excited by 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 used for many years. Fig. 12.1 shows a typical arrangement of the detector and electronics for this experiment.

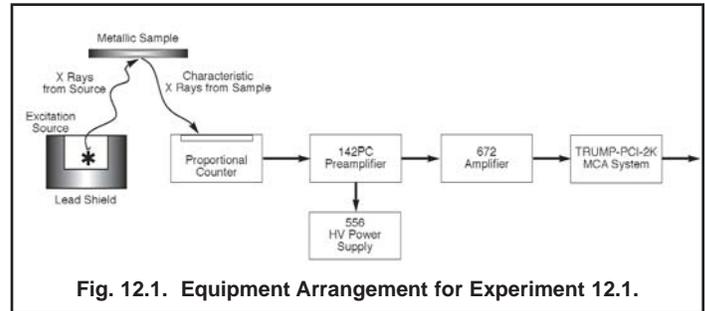


Fig. 12.1. Equipment Arrangement for Experiment 12.1.

X-rays from the excitation source are allowed to impinge on the sample and create photoelectric interactions in the sample. The characteristic x-rays produced by these photoelectric interactions are then counted by a low-energy x-ray detector. The detector shown in Fig. 12.1 is a proportional counter; however, 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.

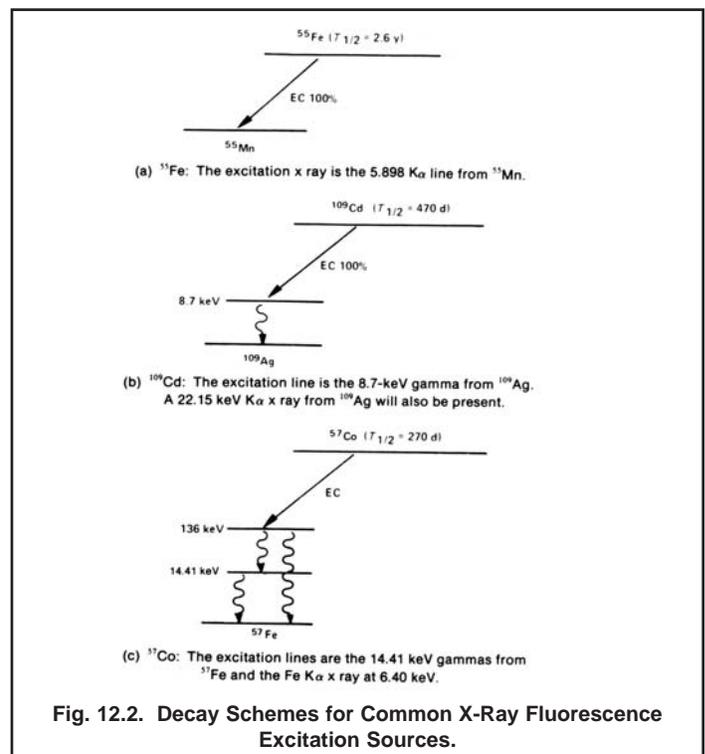


Fig. 12.2. Decay Schemes for Common X-Ray Fluorescence Excitation Sources.

### 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 higher energy sources can be obtained.

A general rule for selecting 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. This is because (as determined in Experiments 3 and 7) the photoelectric cross section rapidly decreases as energy increases. The most commonly used sources for x-ray fluorescence measurements and their characteristic x-ray energies are:  $^{55}\text{Fe}$ , <6 keV;  $^{109}\text{Cd}$ , <9 keV;  $^{57}\text{Co}$ , between 15 and 5 keV; and  $^{241}\text{Am}$ , with its wide range of energies from 60 keV down. Fig. 12.2 shows the decay schemes for  $^{55}\text{Fe}$ ,  $^{109}\text{Cd}$ , and  $^{57}\text{Co}$ . The decay scheme for  $^{241}\text{Am}$  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<sub>I</sub>, L<sub>II</sub>, L<sub>III</sub>, M<sub>I</sub>, M<sub>II</sub>, M<sub>III</sub>, M<sub>IV</sub>, M<sub>V</sub>, N<sub>I</sub>, N<sub>II</sub>, . . . P<sub>III</sub>. The most commonly observed x-rays are the K<sub>α1</sub> and K<sub>β1</sub> lines, and these are calculated from the binding energies (BE), in the following manner:

$$K_{\alpha 1}(\text{energy}) = \text{BE}(\text{K}) - \text{BE}(\text{L}_{\text{III}}), \quad (1)$$

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

$$K_{\beta 1}(\text{energy}) = \text{BE}(\text{K}) - \text{BE}(\text{M}_{\text{III}}). \quad (2)$$

The method for calculating other characteristic x-ray energies is listed in ref. 9.

## Experiment 12.1 X-Ray Fluorescence with a Proportional Counter

### Procedure

1. Set up the equipment as shown in Fig. 12.1. Adjust the 556 to the voltage level required for the proportional counter and calibrate the system as in Experiment 11 so that the 32.2 keV x-ray from  $^{137}\text{Cs}$  is being stored in the upper channels of the MCA when set for 1024 channels. Use as many sources from Table 12.1 as are necessary

Isotope	X-Ray Energy (keV)	
$^{54}\text{Mn}$	5.414	K <sub>α</sub>
	5.946	
$^{57}\text{Co}$	6.40	K <sub>α</sub>
	7.06	K <sub>β</sub>
	14.41	γ
$^{65}\text{Zn}$	8.04	K <sub>α</sub>
	8.90	K <sub>β</sub>
$^{85}\text{Sr}$	13.38	K <sub>α</sub>
	15.00	K <sub>β</sub>
$^{88}\text{Y}$	14.12	K <sub>α</sub>
	15.85	K <sub>β</sub>
$^{109}\text{Cd}$	22.10	K <sub>α</sub>
	25.00	K <sub>β</sub>
$^{113}\text{Sn}$	24.14	K <sub>α</sub>
	27.40	K <sub>β</sub>
$^{137}\text{Cs}$	32.1	K <sub>α</sub>
	36.6	K <sub>β</sub>

to calibrate the system. Determine the slope of the calibration line and the resolution of the 32.2 keV line of  $^{137}\text{Cs}$ .

2. Remove the calibration sources and place a cadmium sample and the  $^{57}\text{Co}$  fluorescence source in position in the chamber for x-ray fluorescence with a proportional counter. Acquire a spectrum for a period of time sufficient to identify the characteristic x-rays from the cadmium sample. Read the data from the MCA and plot the spectrum. Fig. 12.3 shows a typical cadmium spectrum

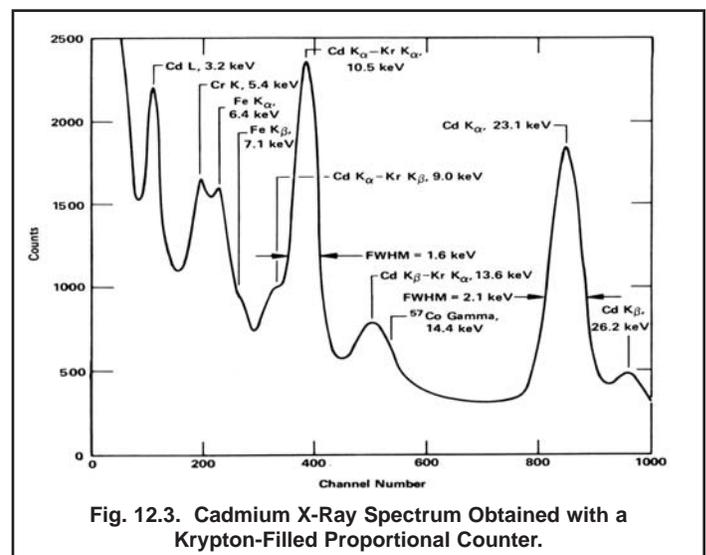
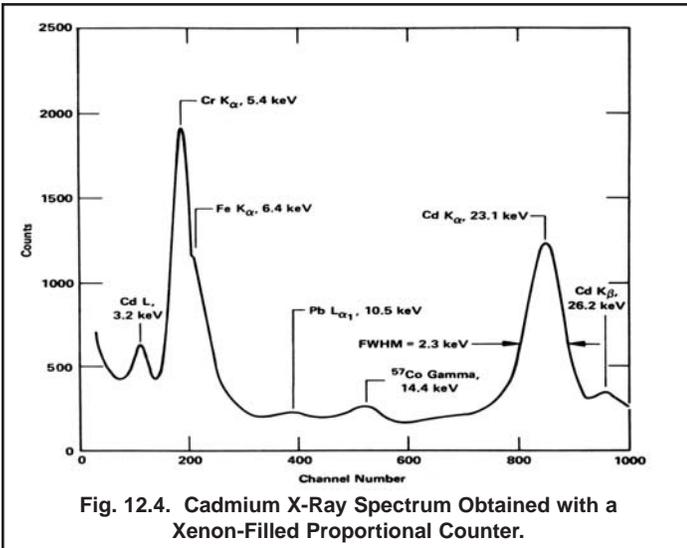


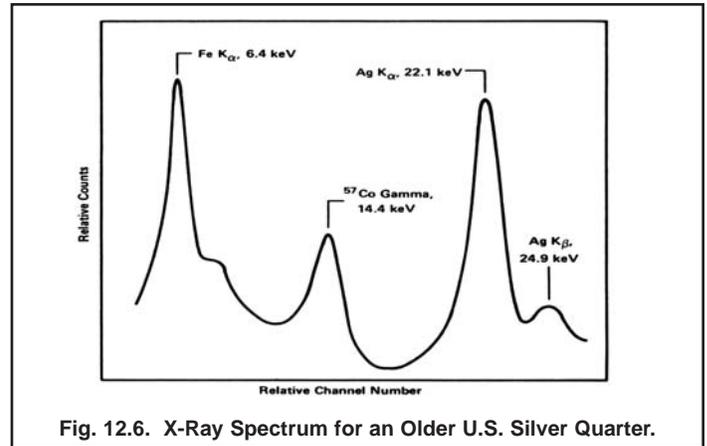
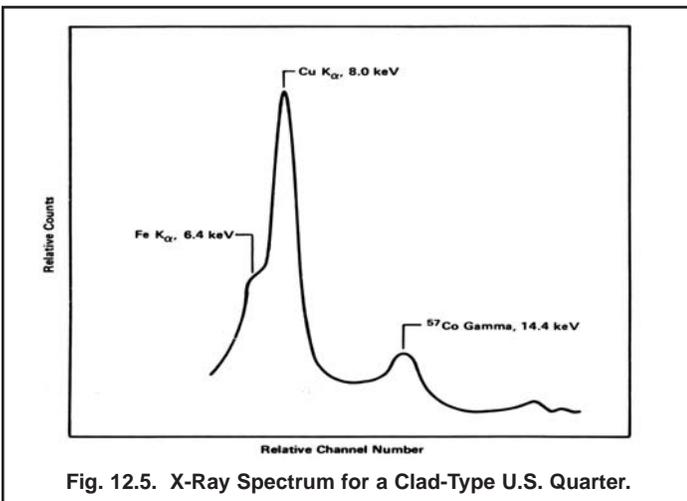
Fig. 12.3. Cadmium X-Ray Spectrum Obtained with a Krypton-Filled Proportional Counter.



using a krypton-filled proportional counter. In this device, the krypton  $K_{\alpha 1}$  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  $K_{\alpha 1}$  minus the krypton  $K_{\alpha 1}$  escape peak, etc.

Fig. 12.4 shows the cadmium characteristic x-rays measured with a xenon-filled proportional counter. The xenon  $K_{\alpha 1}$  escape peak is not present in this spectrum because its energy is 29.78 keV; thus it is not energetically possible to produce this peak with the cadmium sample and the  $^{57}\text{Co}$  source.

3. Remove the cadmium and replace it with one of the other samples in the target kit. Acquire 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. Acquire a spectrum and identify all peaks. Fig. 12.5 shows a composite spectrum taken for a clad-type U.S. quarter. This can be contrasted with Fig. 12.6 which shows one of the older U.S. silver quarters.

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

#### Introduction

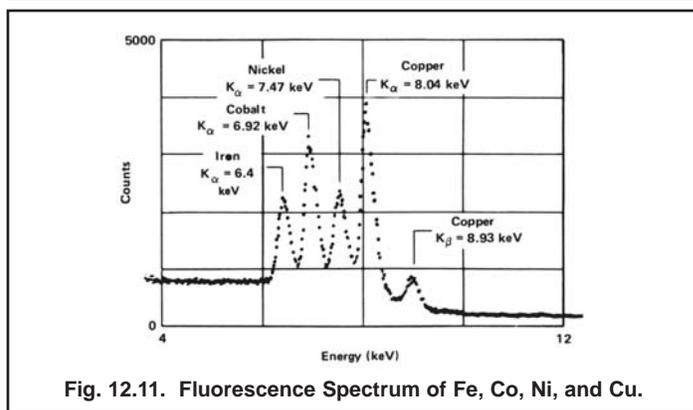
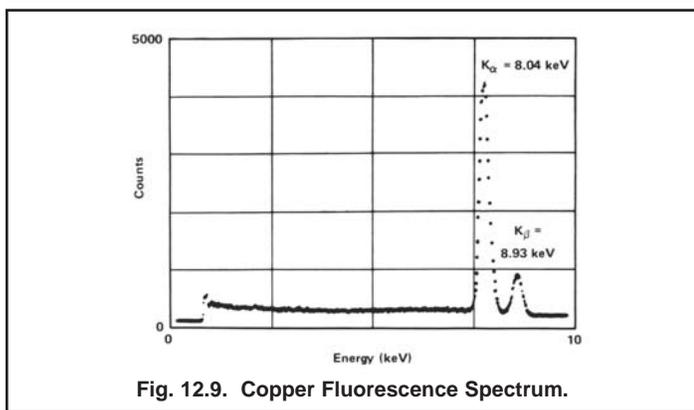
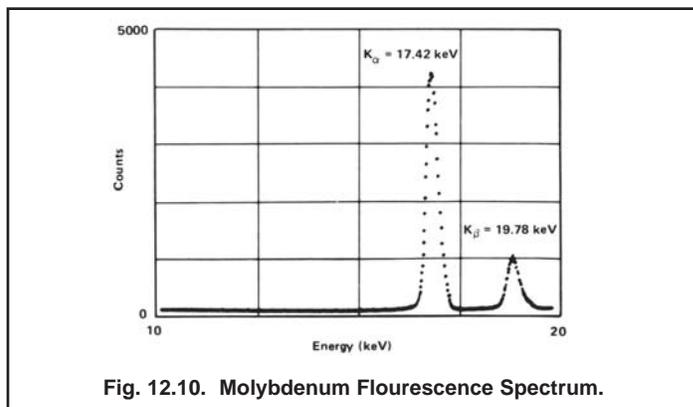
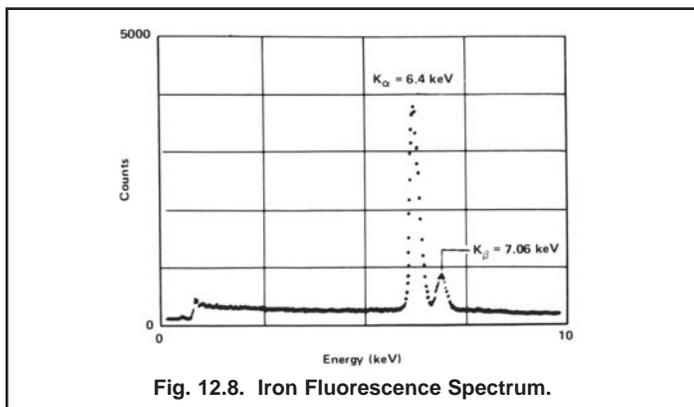
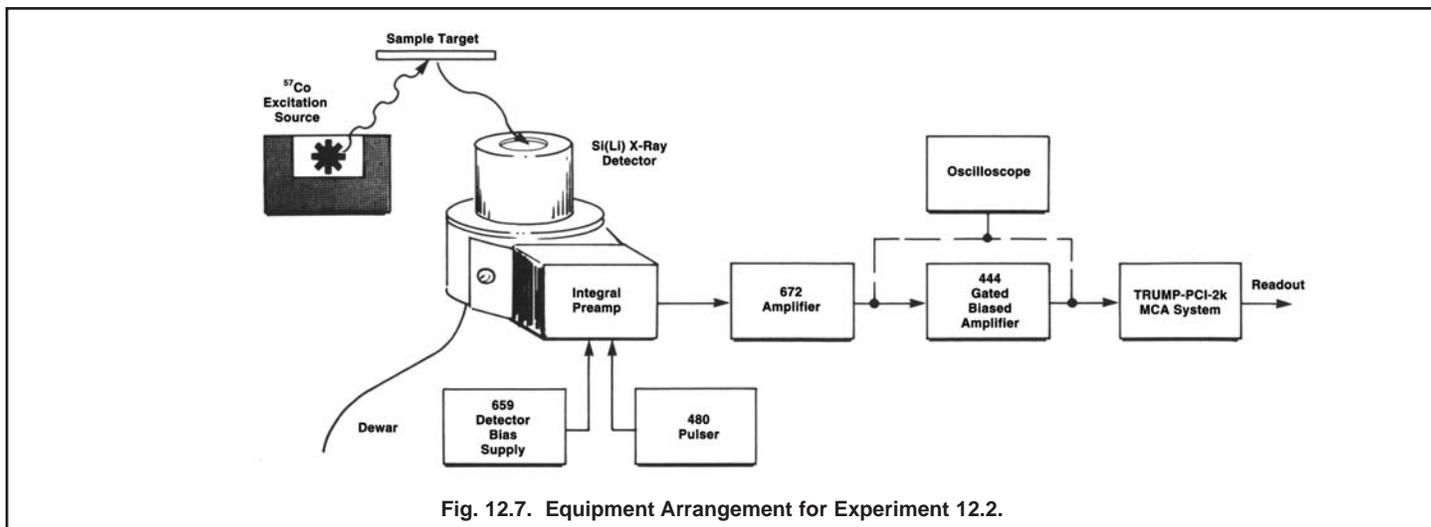
As discussed in Experiment 8, Si(Li) x-ray detectors have been developed that have a resolution of 150 eV or better for the 6.4 keV line of  $^{57}\text{Co}$ . With resolutions of this order, it is possible to distinguish between adjacent energy lines that can come from various metallic elements in a sample. In other words, if the  $K_{\alpha 1}$  lines of the elements in the sample are resolvable from each other, the elemental constituents of the targets can be determined. Experiment 8 should be completed before this experiment is started.

#### Procedure

1. Set up the equipment as shown in Fig. 12.7. The chamber for x-ray fluorescence with a Si(Li) detector is used for this experiment. As outlined in Experiment 8, use the 480 Pulser and any of the sources listed in Table 12.1 to calibrate the system from 2 keV to 25 keV. Plot the calibration line, determine the slope in eV/channel, and measure the resolution for the 6.4 keV line of  $^{57}\text{Co}$ .

2. Using a piece of copper from the target kit as the first target, position it as shown in Fig. 12.7. Determine the energies of the Cu  $K_{\alpha 1}$  and  $K_{\beta 1}$  lines from your calibration curve. Compare these with the calculated values for Cu shown in the Appendix.

3. Repeat for the other elements in the target kit. For comparison, Figs. 12.8, 12.9, and 12.10 show x-rays from iron, copper, and molybdenum samples.



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. Fig. 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 widely accepted in industry as a method by which surface elemental analysis can be quickly performed.

**References**

1. X-Ray Critical Absorption and Emission Energies Chart, (Slide Rule)
2. X-Ray Critical-Absorption and Emission Energies in keV (Appendix).
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.
4. R.D. Giaque and J.M. Jaklevic, "Rapid Quantitative Analysis by X-Ray Spectrometry", Adv. In X-Ray Analysis 15, Plenum Press, New York (1972).
5. J.M. Jaklevic and F.S. Goulding, "Semiconductor Detector X-Ray Fluorescence Spectrometry Applied to Environmental and Biological Analysis", IEEE Trans. Nucl. Sci. NS-19 (1972).
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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8. J.L. Campbell and L.A. McNelles, "An Intercomparison of Efficiency Calibration Techniques for Semiconductor X-Ray Detectors", Nucl. Instrum. Methods 125, 205–223 (1975).
9. C.M. Lederer and V.S. Shirley, Eds., Table of Isotopes, 7th Edition, John Wiley and Sons, Inc., New York (1978).