

**ELEMENTAL ANALYSIS OF TELEPHONE
WIRE BY XRF**

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ELEMENTAL ANALYSIS OF TELEPHONE

WIRE BY XRF

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ABSTRACT

X-ray fluorescence was applied to determine the concentrations of elements in telephone wires of different brands. The major constituents found in the telephone wires are Cu and Zn.

CHAPTER I

INTRODUCTION

1.1. Radioisotope X-ray Fluorescence Analysis

Radioisotope x-ray fluorescence is a relatively fast, sensitive, nondestructive and versatile physical method used for elemental analysis of solids, powders, slurries and liquids. This method provides rapid qualitative and semiquantitative analysis. It is one of a number of techniques now available to determine the concentration of elements in different materials. With suitable equipment, analysis for all elements above about atomic number 12 can be done by x-ray fluorescence in a small fraction of the time required by conventional chemical methods. When making accurate quantitative analyses, it is usually necessary to prepare a certain number of reference standards or internal standards as in optical spectroscopy, since absolute measurements cause considerable complications. These standards are used to prepare working calibration curves of x-ray fluorescent intensity as a function of the concentration of the elements. It is generally useful for all major and minor constituents, but for trace elements it is probable that the optical spectrograph method has advantages. The two problems limiting higher accuracy are those of inter-element effects and of particle-size effects.

1.2. ~~Dispersive~~ Methods of X-ray Fluorescence Analysis

~~There~~ there are essentially two methods of x-ray fluorescence analysis.

They ~~are~~

- (1) ~~Wavelength~~ dispersive x-ray fluorescence (WDXRF) method
- (2) ~~Energy~~ dispersive x-ray fluorescence (EDXRF) method

In the WDXRF method, a diffraction grating usually a crystal, is used to separate the various wavelengths by Bragg diffraction. Because much power is lost in diffraction, the primary source must be strong, such as an x-ray tube. Therefore in this technique a crystal diffraction spectrometer is used to indentify the characteristic x-rays from a sample excited by primary x-rays from a high power x-ray machine.

In the EDXRF technique, excitation of characteristic x-rays are accomplished by (a) a primary source of electromagnetic radiation (x-rays from a low-power x-ray tube, x or gamma rays from radioactive sources) or (b) charged particles (alphas or betas from radioactive sources, electrons or photons from accelerators). Thin crystal sodium iodide (Na I) scintillation detectors and lithium drifted silicon Si (Li) or high purity germanium (H P Ge) planar detectors are used in the EDXRF setups to give a distrubution of voltage pulse amplitudes. Electronic separation of the pulse height distribution then gives a photon energy spectrum.

CHAPTER II

EMISSION OF CHARACTERISTIC X-RAY SPECTRA

2.1. X-ray emission

When a sufficiently energetic x-ray photon interacts with an atom, several phenomena take place. One interaction involves the transfer of the photon energy to one of the electrons of the atom (for example, a K shell electron) resulting in its ejection from the atom. Fig (2.1) schematically represents the process. The photoelectron is emitted with an energy $E - \phi$, where E is the original photon energy and ϕ is the binding energy of the electron in its shell. The distribution of electrons in the ionized atom is then out of equilibrium and within an extremely short time returns to the normal state, by transitions of electrons from outer shells to inner shells.

Each such electron transfer, for example from the L shell to the K shell, represents a loss in the potential energy of the atom. The difference in the binding energies of the two shells is given off as a characteristic x-ray photon. One of two processes can then take place, namely (a) the x-ray photon escapes from the atom and contributes to a characteristic radiation of the atom; or (b) the photon is absorbed within the atom itself on its way out and ionizes the atom in an outer shell. For example a K_{α} photon can eject an L, M or N electron; this phenomenon is called the Auger effect. Again, the ionized atom becomes a source of radiation as explained above.

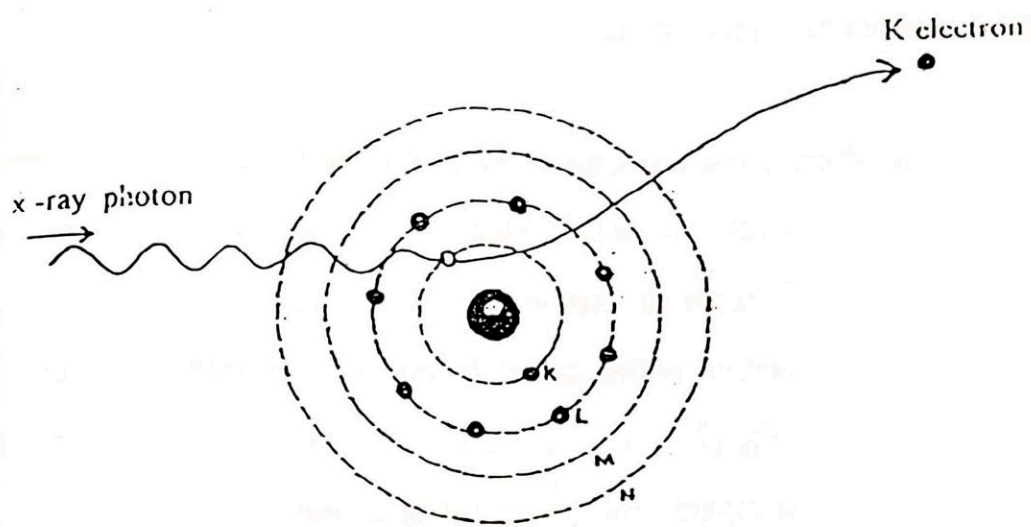


Figure 2.1. Ionization of the K shell by an incident x-ray photon.

2.2. Emission from X-ray Tubes

Modern x-ray generators are still built around the Coolidge type (1913), i.e. a vacuum tube in which electrons are emitted by an incandescent filament (negative electrode or cathode), accelerated by a high voltage V and focused on a water-cooled metal target (positive electrode or anode). A typical spectrum is shown in Fig (2.2); it consists of a continuous x-ray Spectrum or white radiation on which are superposed a few characteristic lines of the target element in this case W. The characteristic spectrum results from the direct ionization of the atoms by the impinging electrons and is only observed if the voltage V is high than the critical voltage V_K in the case of the K lines.

The critical excitation voltage of W is 69.5 kV for the K spectrum and 10-12 kV for the L spectrum. Consequently, the emission spectrum of a W target tube operated at 50 kV consists of white radiation and L lines of W as shown in fig(2.2), but at 100 kV both the K and L spectra are observed. On account of the monochromatic character, it is relatively easy to measure the intensity of the characteristic lines as a function of applied voltage. It is found that the intensity varies as

$$I = A i (V - V_K)^n \quad (2.1)$$

Where A is a constant, I is the current through the tube and the exponent n is a constant that has a value between 1.5 and 2 depending on the emission line. The rapid increase in intensity predicted by eqn (2.1) does not materialize when V exceeds three or four times the critical voltage V_K or V_L .

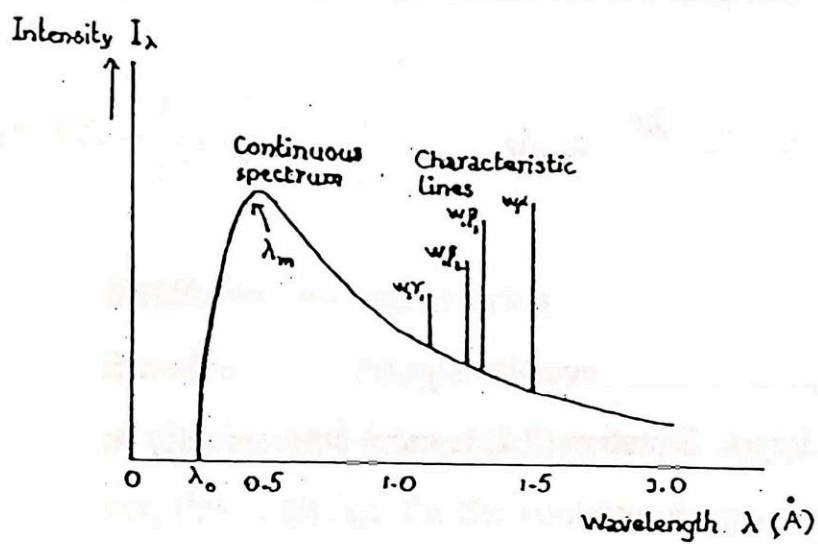


Figure 2.2 Typical emission spectrum from a W target x-ray tube at 50 KV.

The continuous spectrum is the result of loss of energy by the electrons as they collide at random with the loosely bound electrons of the target, hence the name of Bremsstrahlung also given to this radiation. The properties of the continuum that concern the analyst can be expressed by three criteria;

(1) The short wavelength limit is given by λ_0 ; i.e. the spectrum starts abruptly at wavelength that does not depend on the target material but follows the Duane-Hunt relation

$$h \nu_0 = \frac{hc}{\lambda_0} = eV \quad (2.2)$$

This expression signifies that the energy of any electromagnetic radiation in the emission spectrum can never be higher than the kinetic energy of the electron striking the target. Equation (2.2) is more conveniently written.

$$\lambda_0 = \frac{12.398}{V} \quad (2.3)$$

Where λ_0 is in Å and V in kV. The fact that the short wavelength limit varies as the reciprocal of the applied voltage is clearly shown in fig 2.3.

(2) The total or integrated intensity, the area under the curve in fig (2.3), is an increasing function of applied voltage V and atomic number Z of the target. Ultra found the experimental relation

$$I = KZ V^2 \quad (2.4)$$

Where K is a constant that includes the electron current I in the tube.

(3) The spectral distribution of the continuum was investigated by Kulenkampff who derived the approximate empirical relation

$$I_{\lambda} = CZ \frac{1}{\lambda^2} \left(\frac{1}{\lambda_0} - \frac{1}{\lambda} \right) \quad (2.5)$$

Where C is a constant that includes the current I. This is a remarkable equation because it describes the intensity distribution rather well, it predicts the observed maximum at $\lambda_m = 1.5 \lambda_0$ and it is in agreement with eqn (2.4) for the integrated intensity. However, this analytical for the continuous spectrum is not sufficiently accurate for present requirements in spectrochemical analysis, and so led to newer developments along both theoretical and experimental lines.

2.3. Radioisotope Sources

Radioisotopes (Table 2.1) are commonly used because of their stability and small size when continuous and monochromatic sources are required. Safety regulations require that x-ray emission from these sources is limited to about 10^7

photons $\text{s}^{-1} \text{steradian}^{-1}$ compared with 10^{12} or 10^{13} for x-ray tubes, the difference is only partly compensated for by the small size of the source, which allows very compact source-specimen-detector assemblies to be constructed that are very convenient due to their portability. On the other hand, the low intensities preclude crystal dispersion so that these sources are used almost exclusively in energy dispersion techniques. Separation of analytical lines is sometimes done with selective filters but more often with pulse height analysers in combination with high resolution Si (Li) semiconductor detectors.

The fluoresced analyte line intensity in a radioisotope excited fluorescence spectrometer is proportional to the activity yielding the excitation line.

If the spectrometer is operated over a time period significant with respect to the source half-life, the concentration calibration curves must be corrected for the decrease in source activity.

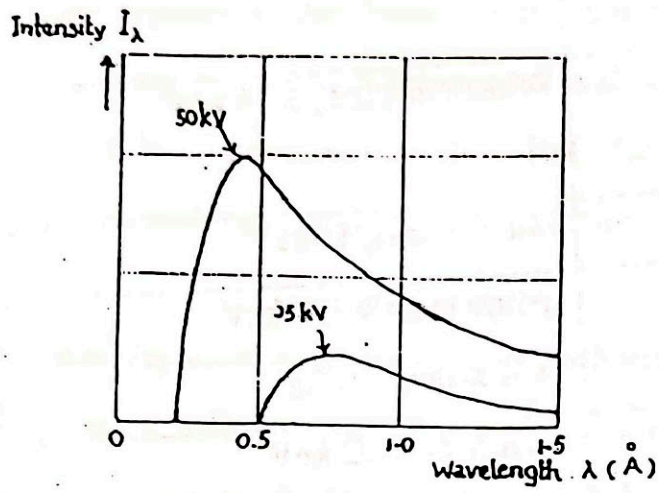


Figure 2.3 Effect of voltage on the continuous spectrum

Table 2.1 Radioisotope X-ray and γ -ray Sources

Isotope	Half-life (years)	Type and energy emitted	Efficient for
^{57}Fe	12.3	White radiation, 3-10 keV	Ca(K), Cr(K) Mn(K), Fe(K)
^{59}Fe	2.7	Mn K x-rays, 5.9 keV	Ca(K), V(K)
^{57}Co	0.74	γ -rays mainly 122 keV Fe K x-rays, 6.4 keV	W(K)
^{109}Cd	1.3	Ag K x-rays, 22 keV	Fe(K), Cu(K) W(L), Mo(K)
^{135}Cd	0.65	γ -rays, 100 keV Eu K x-rays, 42 keV	W(K)
^{147}Pm	2.6	White radiation, 10-100 keV	Mo(K), Ag(K) W(K)
^{241}Am	460	γ -rays 60 keV Np L x-rays 11-22 keV	Mo(K), Ag(K)

CHAPTER III

EXPERIMENTAL SET UP

3.1. Sample Preparation

This experiment has been worked out using Japan and China made telephone wires. First, the cover was removed and wound the wire in the form of circle or coil which has a diameter of 1 inch. But, due to inflexibility of the wire so many gaps were formed between them. In this form, the wires were not usable as samples.

Thus, Japanese made wire of length 5 inches was cut and heated until it was melt by using bellows with a mixture of air and petrol to produce blue flames. Then, it was cooled in water which was at the room temperature (30°C) for one minute. After cooling, it was hammered and pressed with rollers. The copper sheet produced was then cut into disc-shaped sample of diameter 1 inch.

Similarly, the second wire, made in China, was made into a circular disc of 1 inch diameter.

3.2. X-ray Tube

The tube stand type S, Siemens C 79298 is used as a holder for air insulated FK 60-04 x-ray tube. The tube stand is mounted horizontally and is connected to the x-ray generator via the high-voltage cable, the connection cable

and the cooling water hoses. The tube windows are controlled by the timer unit of the X-ray generator, Kristalloflex 710.

X-ray tube has a Mo target and works at 60 kV, 20 kW. The X-ray generator is a powerful device for supplying highly stable HT voltage to X-ray tubes. It has a maximum power of 2000 W.

3.3. High Resolution X-ray Spectrometer

A high resolution semiconductor x-ray detector, lithium drifted silicon semiconductor detector, Canberra Model SL 30180, with an operating voltage of negative 500 volts was used in the present work. The detector can be stored at room temperature but the working temperature of the detector must be kept at liquid nitrogen (77 K).

The x-ray fluorescence analysis system consists of a Canberra Si (Li) detector, Canberra Model 2008 (U.S.A) spectroscopy amplifier, Personal Computer Analyzer (PCA) card, Nucleus compatible computer Yale system. The detector has an area of 30 mm^2 and thickness of 5 mm. The cryostat is equipped with a thin beryllium (Be) window to minimise absorption of low energy x-rays. The window thickness is 10 mil (0.025 mm). The resolution FWHM of the Si (Li) detector system was 172 eV at an x-ray energy of 5.9 keV.

The PCA card contains a 100 MHz Wilkinson Analog to Digital Converter, (ADC), Single Channel Analyzer (SCA), Multichannel Scaler (MCS), and a dual ported memory. The dual ported memory allows the operator to exist the PCA program through DOS without interrupting the analysis and storage of

data input to the PCA card. The card, along with the standard software, transforms the personal computer into a very powerful Multichannel Analyzer. An input of 0 to 8 volts from a shaping amplifier is the only external signal necessary for pulse height analysis (PHA) operation.

The software utilizes the personal computer functions to transfer data to a printer or to store and load data to the floppy or hard disk. The operating procedures are menu intensive and important parameters are displayed on the monitor with the spectral data.

3.4. AXIL X-ray Analysis Software

The Analysis of x-ray spectra by Iterative least squares fitting (AXIL) software package is an integrated system for energy dispersive x-ray spectrometric analysis. It runs on an IBM-PC or compatible computer and performs such tasks as:

- Communication with external multi-channel analyzers
- Conversion of spectral data, stored in various formats
- Analysis spectra using non-linear least-squares fitting
- Calculation of quantitative analysis results
- Plotting and printing of data

Provision is made for the processing of:

- X-ray fluorescence Analysis (XRF)
- Particle Induced X-ray Emission (PIXE)
- Analytical Electron Microscopy (EM)

The characteristics of the software are:

- Easy to use, due to a convenient user-interface
- Powerful non-linear least squares fitting algorithm
- Can be installed and tailored to your needs
- Provides a consistent environment for further developments

The peak areas are calculated first by the spectrum fitting procedure and then the concentrations of the elements contained in the sample were calculated.

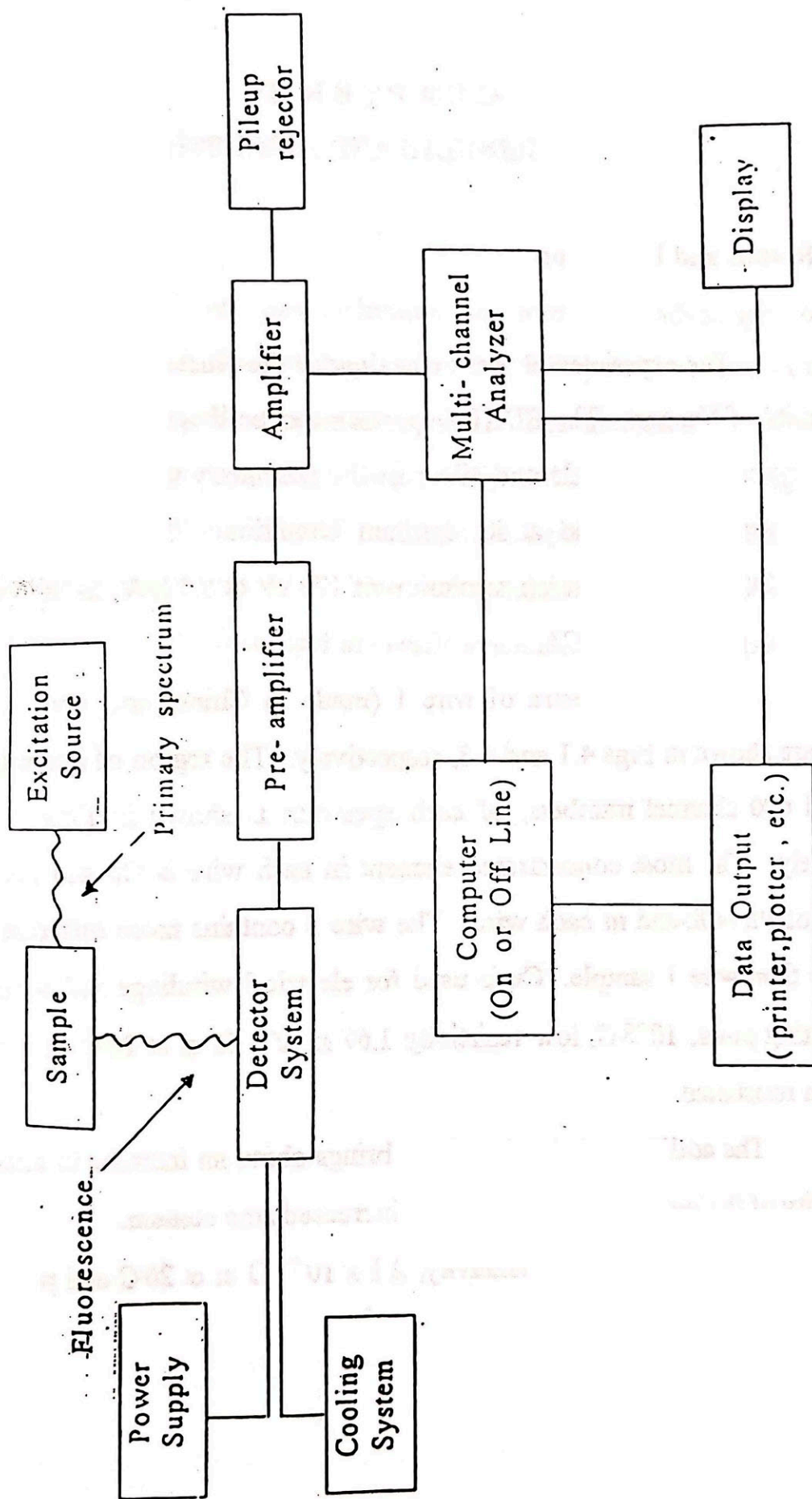


Figure 3.1 Basic Components for energy dispersion x-ray fluorescence system

CHAPTER IV

RESULTS AND DISCUSSION

4.1. Results and Discussion

The experimental work was done at the Nuclear Research Laboratory, University of Yangon. The EDXRF spectrometer used was a tube excited system with molybdenum as anode and silver in the secondary target arrangement. The spectrometer was operated at its optimum condition. The detection unit is Canberra Si(Li) detector with a resolution of 170 eV at 5.9 keV, x-ray spectra were acquired on a PC based MCA.

The x-ray spectra of wire 1 (made in China) and wire 3 (made in Japan) are shown in Figs 4.1 and 4.3, respectively. The region of interest, between 200 and 600 channel numbers, of each spectrum is shown in Figs 4.2 and 4.4 respectively. The most concentrated element in each wire is Cu and nearly equal amount of Pb is found in each wire. The wire 3 contains more different kinds of elements than wire 1 sample. Cu is used for electrical windings and wiring for its high melting point, 1083°C, low resistivity $1.67 \times 10^{-8} \Omega \text{ m}$ at 20°C and very good corrosion resistance.

The addition of zinc in wire 1 brings about an increase in strength and the ductility of the wire also increases with increased zinc content.

Lead also has low resistivity, $2.1 \times 10^{-7} \Omega \text{ m}$ at 20°C and possesses excellent resistance to corrosion.

4.2. Conclusion

The XRF analysis technique has numerous advantages over other methods while the only disadvantage is that the Si (Li) detector used in the system must be operated at liquid nitrogen temperature. This method is time saving and rapid. Repeatability and accuracy are generally limited by the sampling error. The analytical versatility of the EDXRF method is due primarily to the ability of the Si (Li) detector to detect most of the elements simultaneously and to the fact that the data are stored in digital form and are easily available for computer treatment.

Spectrum WIRE1.SPE Iteration 20: ChiSquare = 7.9; Dif = .3
WIRE1 MAR 21 1995 10:45:36 AM

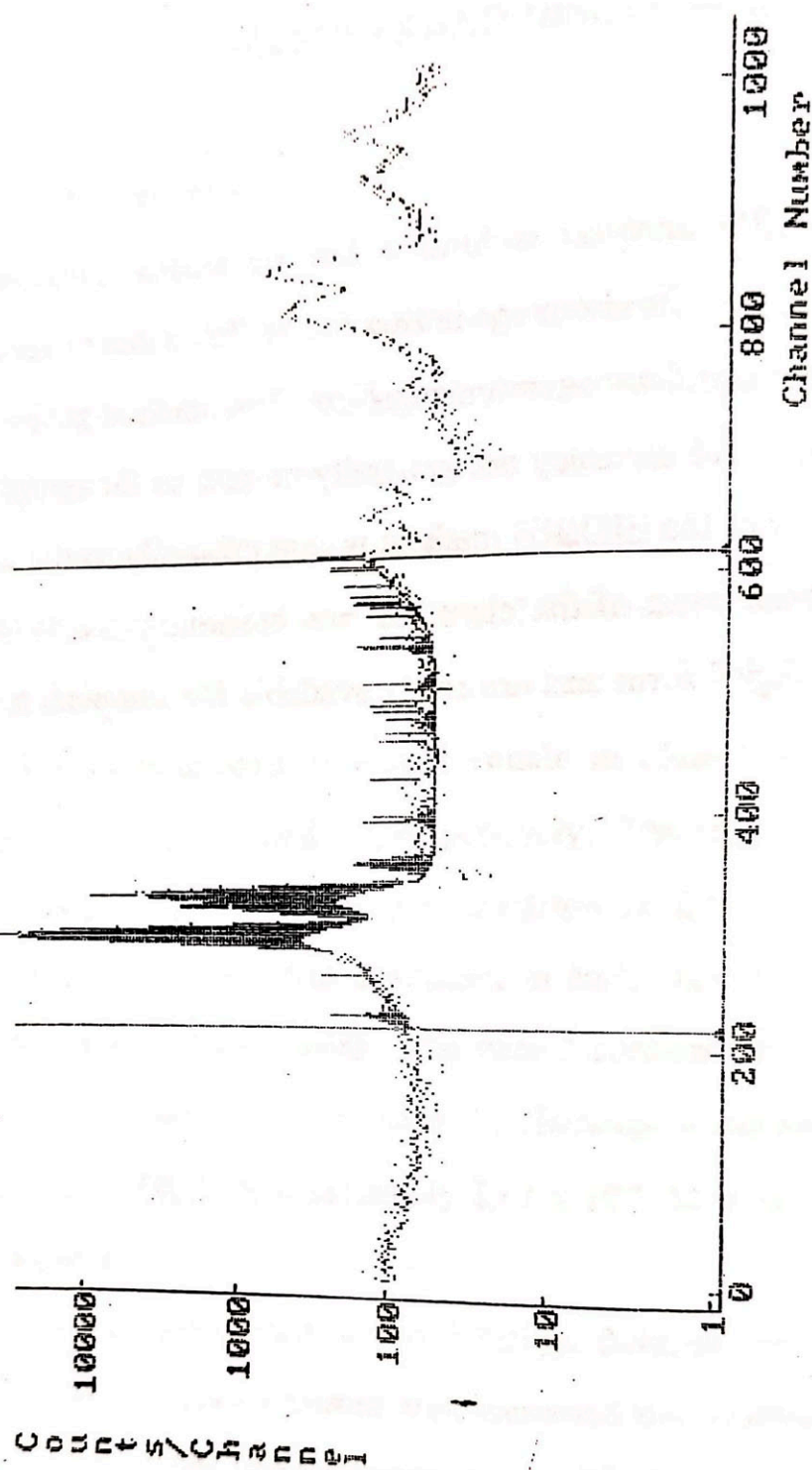


Figure 4.1 Full x-ray spectrum of wire 1 (China)

7.9; Dif = .3

Spectrum WIRE1.SPE Iteration 20: ChiSquare =

MAR 21 1995 10:45:36 AM

WIRE1

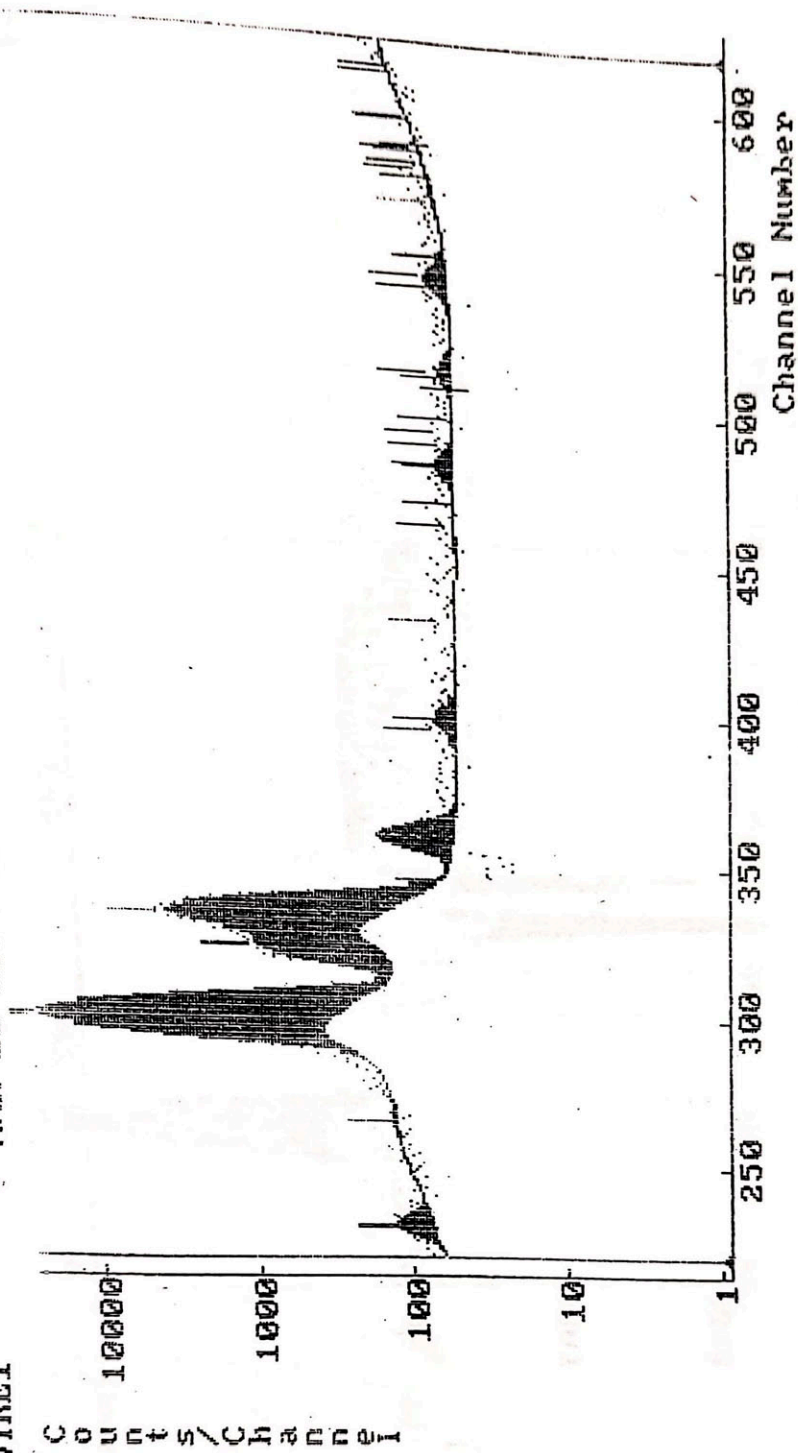


Figure 4.2 Region of interest x-ray spectrum of wire 1

Spectrum WIRE3.SPE Iteration 38: ChiSquare = 5.9; Dif = 1
 WIRE3 MAR 21 1995 10:53:50 AM

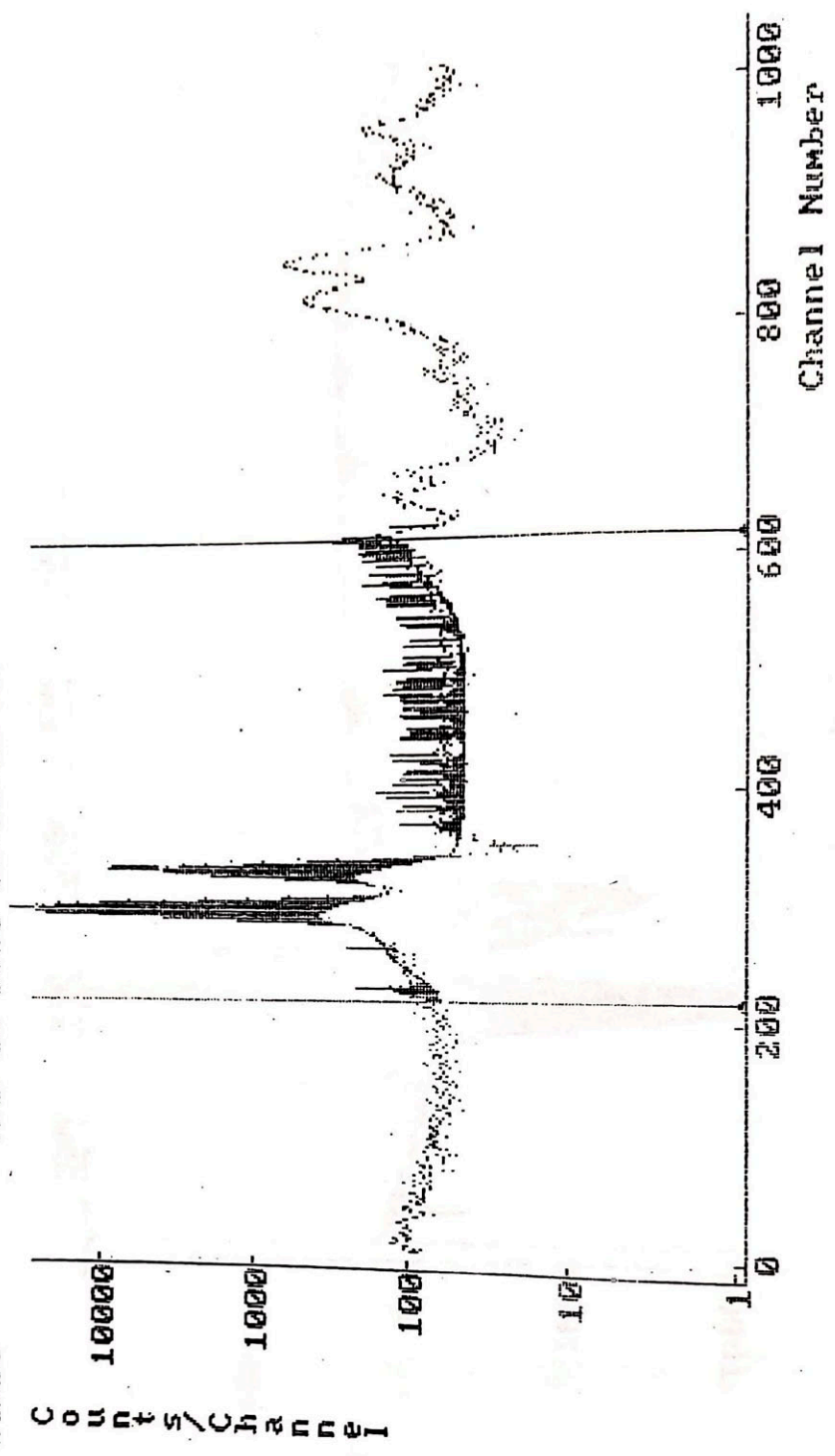


Figure 43 Full x-ray spectrum of wire 3 (Japan)

Spectrum WIRE3.SPE Iteration 38: ChiSquare = 5.9; Dif = .1
WIRE3 MAR 21 1995 10:53:50 AM

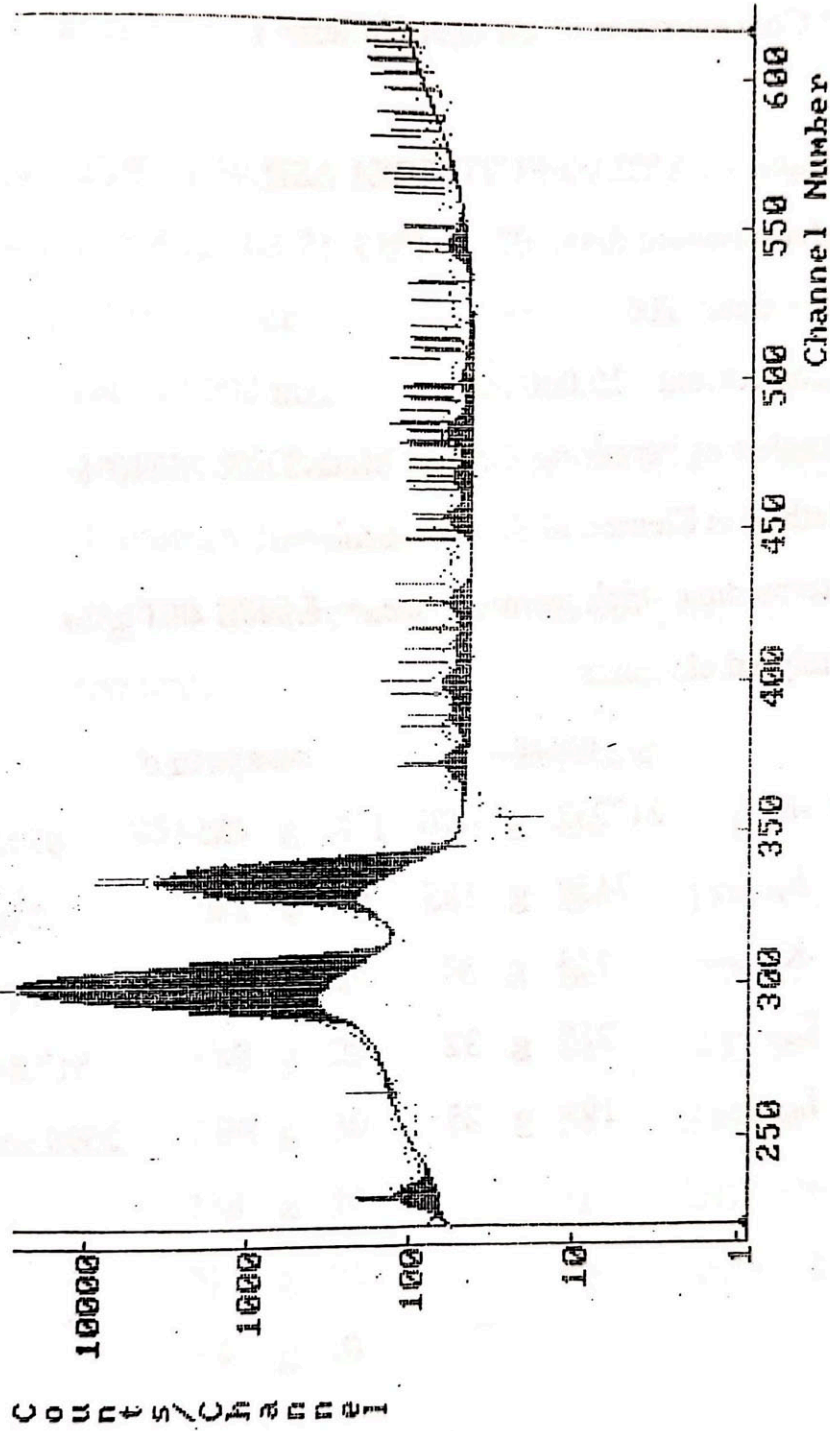


Figure 4.4 Region of interest x-ray spectrum of wire 3

Table 4.1 Concentration of elements in wire 1

Sample: C:\AXIL\SPECT\WIRE1.ASR

Measurement date: 03-21-1995

Live time: 200 sec

Tube current: 10.000 mA

Number of iterations: 20 Last Mean Diff: 0.310% Max Diff: 0.544%

Method is Elemental Sensitivities

Intermediate thick sample, mass = 1.500E-001 g/cm²

Analysed elements:

El	counts	compound	conc
Cu K _α	247232 g 476	Cu	87.870 g 3.341 %w
Zn K _α	7458 g 105	Zn	2.015 g 0.148 %w
Rb K _α	113 g 30	Rb	<338.028
Sr K _α	215 g 32	Sr	517.845 g 99.710 ppm
Pb L _α	193 g 25	Pb	2598.956 g 346.831 ppm

Table 4.2 Concentration of elements in wire 3

Sample: C:\AXIL\SPECT\WIRE3.ASR

Measurement date: 03-21-1995

Live time: 200 sec

Tube current: 10.000 mA

Number of iterations: 38 Last Mean Diff: 0.009% Max Diff: 0.032%

Method is Elemental Sensitivities

Intermediate thick sample, mass = 2.013E-001 g/cm²

Analysed elements:

El	counts			compound	conc		
Cu K _α	253058	g	481	Cu	91.312	g	3.476 %w
Ge K _α	185	g	29	Ge	1537.179	g	272.437 ppm
Se K _α	156	g	29	Se	798.557	g	205.739 ppm
Br K _α	153	g	29	Br	633.608	g	13.6892 ppm
Sr K _α	139	g	30	Sr	336.820	g	73.786 ppm
Tl L _α	138	g	24	Tl	2013.779	g	362.403 ppm
Pb L _α	211	g	25	Pb	2825.318	g	308.906 ppm
Bi L _α	94	g	24	Bi	1164.018	g	308.906 ppm

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