Nuclear Science 346-2
LAB MANUAL

EXPERIMENT 8.

X-RAY ENERGY SPECTROSCOPY

(The report for this experiment is due 1 week after the completion of the experiment)

X-ray energy spectroscopy (XES) or, as it has also been called, energy dispersive X-ray fluorescence, has become an invaluable instrumental method for obtaining qualitative and quantitative elemental analyses of many different types of samples. Using experimental techniques and detection systems originally developed for nuclear science research, XES can provide multi-elemental analyses for elements of $Z > 11$, rapidly and accurately for widely varying concentrations (from 100% to $\approx$ ppm) and for samples in many different forms. It uses small samples, is non-destructive and has found applications in a wide variety of fields; e.g., clinical chemistry, archaeology, criminology, soil analysis for environmental studies or for mining, etc. This versatility and sensitivity provides a complementary system to these instrumental techniques, e.g., NAA (Neutron Activation Analysis), AAS (Atomic Absorption Spectroscopy), etc., which are more sensitive but also much more time-consuming or limited to single element determinations. The detection range of XES is ideally suited for trace element analyses of biological samples.

In the present experiment, a response curve for cobalt will be obtained to determine the cobalt content in an unknown sample.

8.1 Principle of the Technique

The principle is based on the identification of an element from its characteristic X-ray energy emission. Vacancies are created within the inner atomic electron core (K, L shells) of elements in samples using incident radiation, usually photons, protons or alpha particles. Following electron rearrangement within the shell, X-rays are emitted whose energy is characteristic of that element. The total number of such X-rays depends upon the concentration of that element in the sample.

All of the emitted X-rays are detected using a high resolution ($\Delta E \approx 200$ eV) Si(Li) X-ray spectrometer which is an integral-type of detector, providing the energies of all observed X-rays in a single determination. The SFU system is a secondary target, photon excitation system in which usually a silver secondary target is used from which Ag K X-rays ($K_\alpha = 22.104$ and $K_\beta = 24.942$ keV) are generated. These, in turn, are used to excite the elements in the sample. A schematic diagram of the set-up is shown on Fig. 1. Table 1 lists energies (keV) of the K_{absopt}, K_α and K_β lines for various elements of $Z < 42$ and of the L_{absopt}, L_α, L_β, and L_γ lines for some elements of $Z > 42$. In general, the relative intensities of the K_α to K_β emissions are in the ratio 10:1, while those of the L_α, L_β, and L_γ lines are 5:4:2.

Table 1. X-ray energies (keV) of the K and L lines for selected elements.

Element(Z)	K_{absorp}	$\langle K_\alpha \rangle$	$\langle K_\beta \rangle$	Element(Z)	L_{absorp}	$\langle L_\alpha \rangle$	$\langle L_\beta \rangle$	$\langle L_\gamma \rangle$
Na(11)	1.08	1.04	–	Cd(48)	3.538	3.13	3.44	3.72
K(19)	3.607	3.312	3.589	Ta(73)	9.876	8.11	9.50	10.89
Fe(26)	7.111	6.40	7.059	Au(79)	11.919	9.66	11.50	13.38
Cu(29)	8.980	8.041	8.907	Hg(80)	–	9.99	11.82	13.83
Zn(34)	9.66	8.63	9.65	Pb(92)	13.044	10.50	12.61	14.76
As(33)	11.863	10.532	11.729	–	–	–	–	–
Sr(38)	16.016	14.142	15.849	–	–	–	–	–

Clearly, while an answer to the question, "What elements are present (above limits of detection) in the sample?", is relatively easy to determine (from the energies and relative intensities of observed X-rays), it is more difficult to answer the question, "How much?", accurately.

The intensity I_x of emitted X-rays of a particular line (e.g., K_α) from a trace element with concentration C_x present in a thick sample is given by

$$I_x = I_o \, \sigma \, g \, A \, C_x \tag{1}$$

where I_o = intensity of incident radiation

g = detection efficiency of system (including geometry source-detector)

σ = total cross-section for production of a particular line for the element considered

A = self-absorption factor, depending on the sample matrix

In general, some of these various quantities are difficult to estimate with any accuracy, especially for a thick sample.

In order to minimize inter-elemental effects, such as enhancement, and to reduce absorption losses, it is useful to study very thin samples.

In this case, equation (1) simplifies to

$$I_x = I_o\, \sigma\, g\, m_x \tag{2}$$

where m_x is the mass (or number of atoms) of element x in the sample.
This assumes that the sample is completely irradiated by the incident beam, *ie*, the beam area is larger than the sample area.
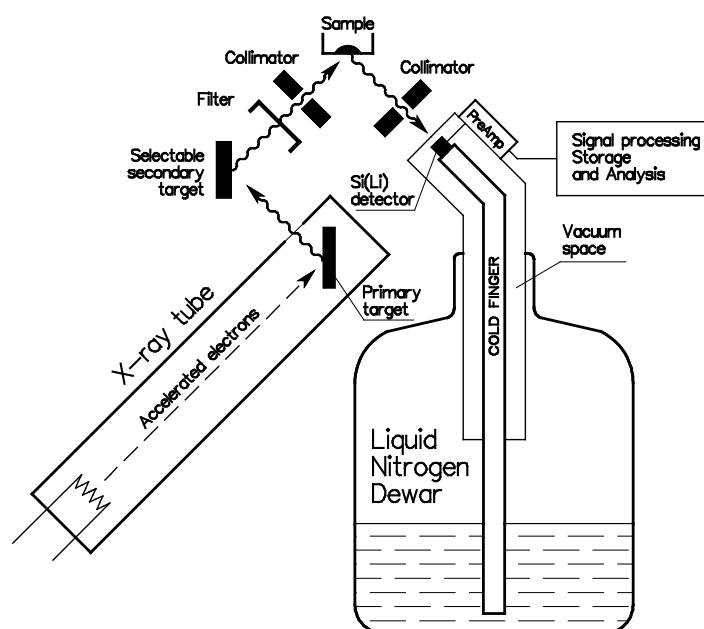

Fig. 1. Schematic diagram of the XRF set-up used at SFU. The production target (primary target) is gold while the choice of secondary target depends on the X-ray energy required to excite the elements of interest in a particular sample.

Equation (2) is valid only if absorption of the incident and emitted beam by the sample matrix is negligible; i.e., $I_x > 0.9\ I_o$, which translates in terms of the thickness of the sample, m_x (expressed in mg cm^{-2})

$$m_x \le \frac{0.1}{\mu(E_0) + \mu(E_i)} \tag{3}$$

where $\mu(E_o)$ and $\mu(E_i)$ are the mass absorption coefficients (cm^2 mg^{-1}) of the sample matrix materials for incident (E_o) and emitted (E_i) X-ray energies.

Even with this simplification, the absolute magnitude of the various terms in equation (2) is difficult to estimate.

One way to circumvent this problem is to perform measurements relative to some internal standard. This also should take care of electronic instability.

An internal standard must satisfy the following conditions: 1) the energy of the corresponding X–ray line must not interfere with other X–ray energies of interest, 2) the corresponding element should have a high X–ray cross–section in order to produce intense lines, and 3) one must be able to spike conveniently the samples with the standard. For the present study Yttrium – as $Y(NO_3)_3$ – satisfies all these conditions. Using equation (2) for yttrium, and for element x and taking the ratio, one obtains:

$$\frac{I_x}{I_y} = \frac{I_0 \sigma_x g_x}{I_0 \sigma_y g_y m_y} m_x = K_x m_x \tag{5}$$

or in terms of peak areas:

$$\frac{A_x}{A_y} = K_x m_x + c_x \tag{6}$$

where A_x and A_Y are the areas of the peak of interest and of the yttrium K_α line, respectively, while c_x is an empirical constant which reflect some small contribution from the background to the measured ratio. The constant K_x (system response constant for element x) and c_x can be determined for each element from a series of measurements on thin standard samples with known m_x.

For the present experiment, students will prepare a series of calibration standard samples of known concentration of a particular element, all spiked with the same amount of $Y(NO_3)_3$, and will determine the system response constant, K_x, for this element. This information can then be used to analyze quantitatively for the corresponding elements in an unknown sample.

8.2 Experimental

The X-ray spectra are generated with a Multi Channel Analyzer (MCA) integrated into a desktop computer. The instructor will demonstrate the operation of the system.

8.2.1 ENERGY CALIBRATION

The energy corresponding to different channels of the MCA must be determined. Four or five samples of known elemental composition must be analysed ranging from one with an element near the minimum detectable (Z = 16) to one with an atomic number just below that of the target. Overlay the spectra of a series of known elements and perform an energy calibration (Channel# versus keV) of the MCA using the built-in calibration feature. Record the slope and the intercept corresponding to this internal calibration.

Finally, in order to gain some insight into the ability of the technique to resolve different elements, estimate the widths of some of the observed lines. In general, the resolution will be limited by the detector resolution.

8.2.2 SAMPLE PREPARATION

8.2.2.1 Thin Samples

Stock solutions of the relevant elements are provided. Record the concentrations in your book. For calibration purposes, prepare a series of Co solutions in the range 20 to 500 ppm[1] Co using the Co stock solution provided; the stock is in the range ~3000 ppm Co (record ex-

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[1] ppm stands for "part per million"; 1 ppm is 1 mg per kg (or 1µg per g).

act composition). A set of 5 ml volumetric flasks is provided, and recommended dilutions of the stock solution are 1/5, 0.5/5, 0.2/5, 0.1/5, 0.05/5 using an adjustable automatic pipette.

Using a 10 µl GC syringe, spot 5 µl of each solution on special XRF mylar, dry, then spot 5 µl of the yttrium solution provided as internal standard on top of the previous dried spot and let dry; in each case record the exact volume spotted. The positioning of the drop is critical. It is also important that the drop does not spread greater than ≈3 mm in diameter (active region of the system) for the X-ray beam to analyze *all* of the atoms in the sample. Mount the pre-pared samples on the special plastic holders provided.

Prepare, in the same fashion (including the internal standard), three replicate samples of the unknown solution.

8.2.2.2 *Thick samples*

Alternatively, the sample may be prepared to be of infinite thickness in the form of con-stant geometry pellets. For calibration purpose these pellets may be doped with a known amount of the element of interest. This technique will be demonstrated during the laboratory session.

8.2.2.3 *For demo and fun*

Collect spectra of various materials available for qualitative identification of elements pre-sent (personal jewelry, hair, old paint sample, suspicious dirt, etc…).

8.2.3 DATA COLLECTION

The operations and the procedure to collect the various spectra will be demonstrated during the session. Collect and save an XRF spectrum for each of the calibration sample. Record the area of the Co-K_α and the Y-K_α peaks as well as the duration of counting. Collect and save spectra for the unknown and as before, record the peak areas for Co-K_α and Y-K_α.

8.3 Data Analysis and Discussion

8.3.1 ENERGY CALIBRATION

For the various elements used during the PHA energy calibration, plot the known X-ray energy versus the channel at which the corresponding peak appeared; verify that the energy calibration is linear, and check that slope and intercept agree with the MCA parameters.

Table 2. Recommended format to tabulate results for the XRF experiment.

			XRF sample	Yttrium soln
Calibration solutions				
Soln #	Volume stock used/ml	Volumetric flask/ml	Vol. spotted/μl	Vol. spotted/μl
1				
2				
3				
4				
5				
Unknown		**ID**	Vol. spotted/μl	Vol. spotted/μl
Trial 1				
Trial 2				
Trial 3				

	Kα Co			Calibration		Kα Y		
XRF measurements								
Duration/s	Gross	+/-	Net	+/-	Gross	+/-	Net	+/-
	Kα Co			Unknown		Kα Y		
Duration/s	Gross	+/-	Net	+/-	Gross	+/-	Net	+/-

8.3.2 COBALT RESPONSE CALIBRATION

For each calibration sample, calculate first the mass of cobalt present in the spot, and then prepare a calibration graph of $A_x/A_{\alpha Y}$ *versus* mass of cobalt in the irradiated spot (eqn. 6). Use the slope and the intercept of this graph to obtain the mass of cobalt present in the spot containing the unknown sample; the masses are usually expressed in μg or ng and concentrations in ppm (mg/kg). Next calculate the %Co in this unknown sample knowing that it was prepared by dissolving x mg in 25 ml (For unknown labeled S97*nn*, $x = 22.9$mg, for S01*nn*, $x = 35.3$mg). Combine the results from the replicates to report one final result along with the uncertainty. Tabulate your results in the format recommended in Table. 2. When submitting your report, provide also a digital version of your data tabulated in the spreadsheet XRF_results.xls available from *www.sfu.ca/~brodovit/files/nusc346/templates/*.

In your report, in addition to the description of the experiment and the experimental results, include an analysis of source of errors, potential interference between elements as well as suggestions for the application of this technique.

References

1. Bertin, *Principles and Practise of X-Ray Spectrometric Analysis* (Plenum Press, N.Y.; 1975) QD 96 X2 B47.

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3. Willard, L.L. Merritt and J.A. Dean, *Instrumental Methods of Analysis*, 5th Edition (Van Nostrand Co., Toronto; 1974) Chapter 10.

4. Ewing, *Instrumental Methods of Chemical Analysis*, 4th Edition (McGraw-Hill Co., Toronto; 1975) Chapter 10.