

EXPERIMENT # 5

NEUTRON ACTIVATION ANALYSIS (NAA)

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Location: SSC14

NEUTRON ACTIVATION ANALYSIS

1. Introduction

Neutron activation analysis (NAA) is an extremely sensitive and versatile method of analyzing samples for their content of trace and major elements. The many fields of application include geology, environmental science, medicine, archeology and forensic science. Because the method is nuclear based rather than chemically based, it is truly element specific; that is, it identifies elements by isotope irrespective of their chemical or biological form. This isotopic composition can be used to deduce the concentration of the element in the unknown sample.

In this laboratory you will apply the method of NAA to determine the potassium concentration in $\mu\text{g/g}$ or parts per million (ppm) in bananas and cashews. You will also determine the range of error for these concentration measurements. You will also determine which other isotopes are present in the banana and cashew samples. Finally you will present your findings in a complete and professional written laboratory report.

2. Theory

2.1 Activation

When matter is irradiated with neutrons, one of the most common reactions to occur is the capture of a thermal neutron by the nucleus of one of the atoms of the material. Having absorbed a neutron, the resulting atom is often made radioactive and will eventually decay by emitting radiation in the form of beta particles (e^- or e^+) and gamma rays. For example, if a sample containing sodium is irradiated in a neutron field, a very small fraction of the naturally occurring Na-23 absorbs neutrons to become radioactive Na-24. The radioisotope Na-24 decays with a half-life of 15 hours to stable magnesium-24, emitting a beta particle and two gamma rays with energies 1369 keV and 2754 keV. A schematic of this process is illustrated in Figure 1.

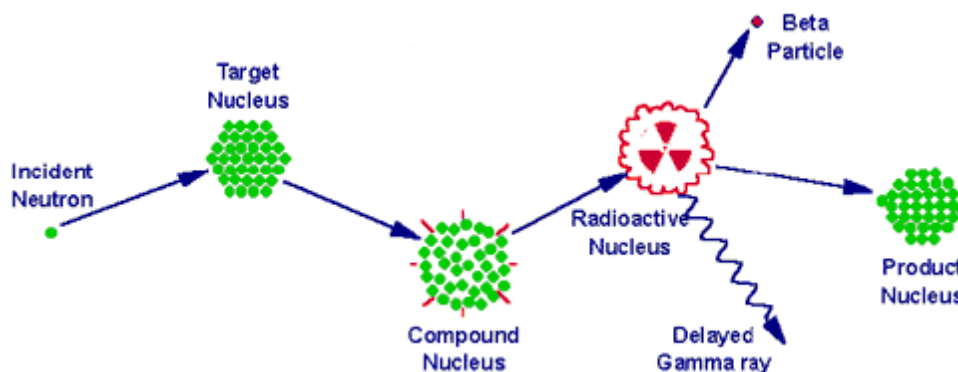


Figure 1. Schematic of the activation of Na-23 to Na-24 and eventual decay to Mg-24.

The transformation processes are summarized below:

Activation: $\text{Na-23} + n \rightarrow \text{Na-24}$

Decay: $\text{Na-24} \rightarrow \text{Mg-24} + \beta + \gamma$ (half-life: 15 hours)

In NAA, the gamma rays from the decay process are detected and counted, and their energy is accurately measured. The gamma ray emission spectrum is unique to the particular radioisotope, and hence serves as a signature of that isotope (hence element). Moreover, the rate of gamma emission is directly proportional to the quantity of the radioisotope and can be related to the concentration of the original stable isotope or element.

2.2 Basic Activation Equations

When a sample is irradiated with neutrons, the equation describing the net buildup of activity during the irradiation process is:

$$A_i = N_T \phi \sigma (1 - e^{-\lambda t_i}) \quad (1)$$

where: A_i is the activity after irradiation time t_i ,

N_T is the number of atoms of the target isotope in the sample,

ϕ is the neutron flux ($\text{m}^{-2}\text{s}^{-1}$),

σ is the activation cross-section (m^2),

λ is the radioactive decay constant of the radioisotope, and

t_i is the irradiation time

The rate of buildup of activity depends on the half-life of the radioisotope; isotopes with short half-lives build up quickly, isotopes with long half-lives slowly. As a rule of thumb, it takes about five half-lives for saturation to be attained. For example, if Na-24 ($t_{1/2} = 15.031$ hr) were being activated, it would take about 75 hours for saturation to be reached. This growth and decay of activity is shown graphically in Figure 2. Except in the case of very short-lived radioisotopes, the irradiation period (t_i) is rarely long enough for saturation to occur.

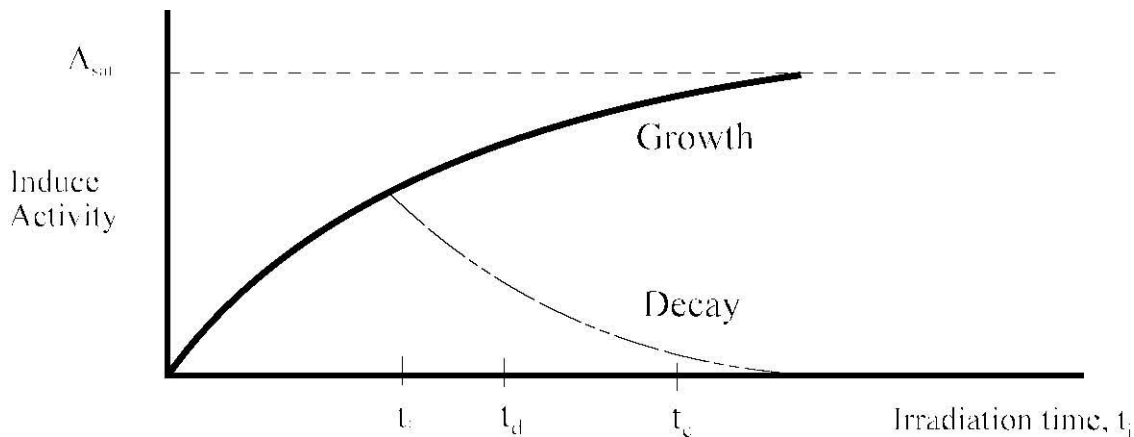


Figure 2. Induced activity as a function of time during irradiation.

Once the sample is removed from the reactor after an irradiation time t_i , no more radioisotope production occurs and the sample will only decay. Therefore, the time, or decay time, t_d , between removing the sample from the irradiation site and placing the sample in front of the detector is important, and must be recorded for use in the analysis (t_d). The general decay law for radioactivity is, for any time t :

$$A_t = A_0 e^{-\lambda t} \quad (2)$$

Where A_0 is the activity at time $t = 0$.

After irradiation, to determine the area under the decay curve, Figure 2, between the time of decay t_d and the time of count t_c , integrate equation 2 where $A_0 = A_{\text{irradiation}} (A_i)$

$$\int_{t_d}^{t_d+t_c} A_t dt = A_i \int_{t_d}^{t_d+t_c} e^{-\lambda t} dt \quad (3)$$

Which results in:

$$\text{Area} = \frac{A_i}{\lambda} \cdot e^{-\lambda t_d} \cdot (1 - e^{-\lambda t_c}) \quad (4)$$

Combining equations 1 and 4:

$$\text{Area} = \frac{N_T \phi \sigma \cdot (1 - e^{-\lambda t_i}) \cdot e^{-\lambda t_d} \cdot (1 - e^{-\lambda t_c})}{\lambda} \quad (5)$$

The number of target atoms N_T is related to concentration by the following:

$$N_T = \frac{C W N_A \theta}{M} \quad (6)$$

Where: C is the concentration of the element of interest

W is the weight of the sample in g

N_A is Avogadro's number

θ is the isotopic abundance of an isotope M is the atomic mass of the element

Physical Constraints:

The gamma ray detector is used to determine the *counts* under the peak of interest for the element under investigation. The detection efficiency is the ratio of gamma rays detected (counted) for a given radioisotope at a given energy, to the total number of gamma rays emitted from the sample for a given radioisotope at a given energy. Because the detector is not 100% efficient, the counts seen by the detector system are too small and have to be adjusted by detector efficiency and branching ratio of the decaying radioisotope as in equation 7.

$$\text{Area} = \text{counts}/(\varepsilon \cdot I) \quad (7)$$

Where: ε is the efficiency of the detector at a specific energy
 I is the branching ratio for a given radioisotope

Combining equations (5), (6) and (7) and isolating for concentration gives:

$$C = \frac{\lambda \cdot \text{counts} \cdot M}{W \phi \sigma N_A \theta I \varepsilon (1 - e^{-\lambda t_i}) \cdot e^{-\lambda t_d} \cdot (1 - e^{-\lambda t_c})} \quad (8)$$

For equation 8 a constant “B” is defined as:

$$B = \frac{N_A \theta \sigma I \varepsilon}{M} \quad (9)$$

Combining equations 8 and 9 gives the final equation for concentration used in the relative method:

$$C = \frac{\lambda \cdot \text{counts}}{W \phi B (1 - e^{-\lambda t_i}) \cdot e^{-\lambda t_d} \cdot (1 - e^{-\lambda t_c})} \quad (10)$$

2.3 Measurement of Induced Activity by Gamma Spectroscopy

A block diagram of the equipment used to detect, measure, and count gamma rays from a radioactive sample is shown below. The detector is a high purity germanium crystal cooled to liquid nitrogen temperature. Gamma rays entering the detector generate electrical pulses, the amplitudes of which are proportional to the energy deposited in the detector.

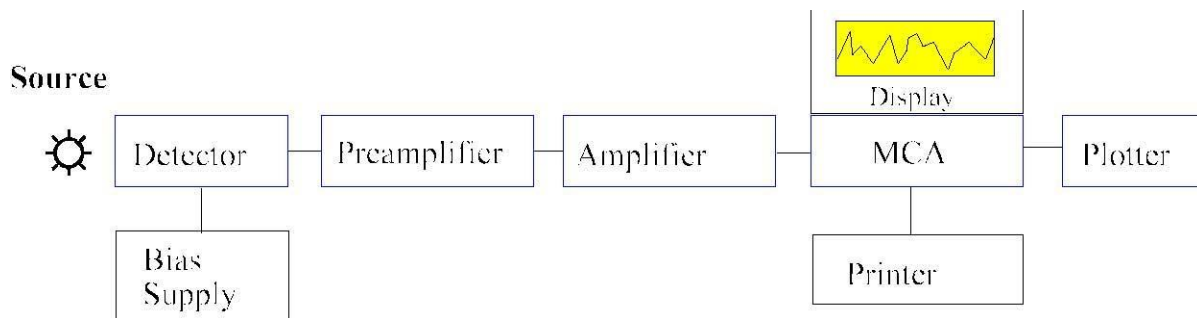


Figure 3. Block diagram of analysis equipment.

The pulses are amplified in a linear amplifier and passed to a multichannel analyser (MCA). The MCA is essentially a pulse height analyser; that is, it measures the amplitude of each pulse and assigns the value to a particular channel (usually 4096 channels spanning the range 0–10 V). Using gamma ray sources of known energy (calibration standards) the relationship between channel number on the MCA and energy is easily established. Once calibrated, the horizontal scale of the MCA reads gamma ray energy in keV. Since gamma rays have discrete energies, when viewed on a high purity germanium detector (HPGe) they give rise to narrow peaks

(photo peaks) appearing at some location in the spectrum. A sketch of spectrum from activated Na-24 is shown below in Figure 4. The photo peaks at 1.369 MeV and 2.754 MeV (1369 keV and 2754 keV) are clear peaks above the background spectrum in Figure 4.

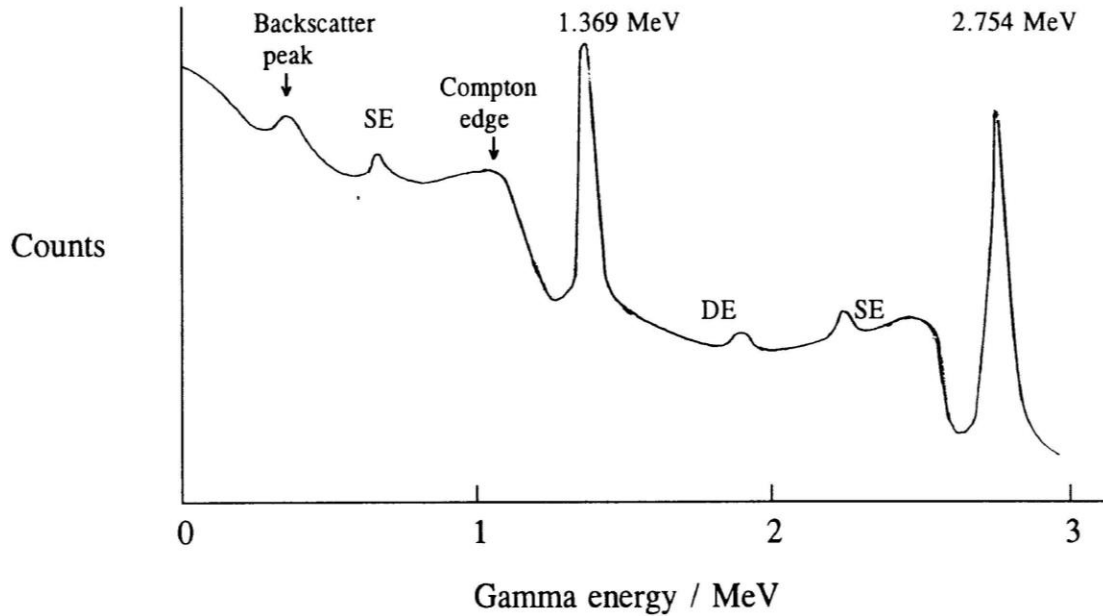


Figure 4. Gamma emission spectrum for Na-24.

Returning to equation (10) the number of counts produced under a specific energy for each element is proportional to the amount of element present, if all other parameters are constant (e.g., t_i , t_d , t_c , etc.). If a known amount of element (standard) is irradiated, its counts-to-mass ratio can be compared to the same element in the unknown sample. With this information the amount of element in the unknown sample can be determined by a simple ratio.

Isolating the constants for two equations for the standard (known) and unknown

$$\frac{\phi B}{\lambda} = \frac{\text{count } s_{std}}{C_{std} W_{std} (1 - e^{-\lambda t_i}) \cdot e^{-\lambda t_d} \cdot (1 - e^{-\lambda t_c})} \quad (11)$$

and

$$\frac{\phi B}{\lambda} = \frac{\text{counts}_{unk}}{C_{ukd} W_{unk} (1 - e^{-\lambda t_i}) \cdot e^{-\lambda t_d} \cdot (1 - e^{-\lambda t_c})} \quad (12)$$

Equating the right-hand side of both equations gives:

$$\frac{\text{count } s_{std}}{C_{std} W_{std} (1 - e^{-\lambda t_i}) \cdot e^{-\lambda t_d} \cdot (1 - e^{-\lambda t_c})} = \frac{\text{count } s_{unk}}{C_{ukd} W_{unk} (1 - e^{-\lambda t_i}) \cdot e^{-\lambda t_d} \cdot (1 - e^{-\lambda t_c})} \quad (13)$$

Isolating the concentration of the unknown, and if possible further cancellation of terms if all of the irradiation parameters are the same, results in the equation

$$C_{\text{unk}} = C_{\text{std}} \cdot \left(\frac{W_{\text{std}} \cdot \text{counts}_{\text{unk}}}{W_{\text{unk}} \cdot \text{counts}_{\text{std}}} \right) \quad (14)$$

Note that if any of the irradiation, decay or count time is not identical for both the known and the standard then equation (13) has to be used.

To determine the activity of a particular radioisotope, one first locates the appropriate photo peak. A table of gamma ray peaks will be provided. Next one measures the area of the photo peak; that is, the total number of counts appearing in the photo peak region. Usually, the photo peak is superimposed on a continuous underlying background, and it is necessary to subtract this background from the total count to get the net count due to gamma rays from the radioisotope in question. Most MCAs have a facility whereby the user can perform this background subtraction.

2.4 Automating the Analysis Procedure by the EPAA Programme

In this experiment, a specially adapted computer programme, EPAA Java, is used for analysis. This programme essentially calculates the mass of the element in the sample by comparison to a standard and then calculates the concentration of the element in its sample. The programme is specifically designed to analyse standard solutions (i.e., of known activity) to determine a sensitivity constant the constant B. Once the sensitivity constant, B is known, the concentration of the element in the unknown solution can be determined. A detailed user guide for the EPAA Java programme will be available in the laboratory. The following is only a brief outline of the method employed by the programme.

When a standard is analysed, the user enters C_{std} in $\mu\text{g/g}$ (the known concentration of the element), the various times and the flux. The user selects the appropriate photo peak, defines the peak region and identifies regions to be used for background subtraction. The programme then measures the total counts in the peak and counts and determines the value of B from the equation:

$$B = \frac{\lambda \cdot \text{counts}}{W\phi C(1 - e^{-\lambda t_i}) \cdot e^{-\lambda t_d} \cdot (1 - e^{-\lambda t_c})} \quad (15)$$

The value of B is entered into a library file on the computer by the user. The programme can now analyse the spectrum for the unknown. The parameters supplied by the user are the same as those for the standard analysis (except C_{unk}) and the same photo peak and background regions are selected. The programme again calculates counts, and then determines C_{unk} using equation (10). The concentration is usually expressed in parts per million (ppm) weight/weight.

The irradiation conditions need not be identical for the "standard" and "unknown" analyses; the EPAA programme will take care of the arithmetic by computing the correct value of ϕ , t_i , t_d , t_c using data provided by the user. Since B depends on the detector efficiency, the source–detector geometry must be identical for both the standard and the unknown measurements. If the geometry is changed (for example, by changing the distance between the detector and the source), a new value of B must be determined for that location using a standard. Also, since the efficiency (hence

B) depends on gamma ray energy, a new value of B is calculated for each gamma ray included in the analysis.

3. Safety Measures

Work in the nuclear facilities including SLOWPOKE-2 reactor is accompanied by an inherent radiation hazard; normal laboratory safety procedures must be followed. Laboratory coats, safety glasses and disposable gloves must be worn when handling solutions. A technician must be consulted immediately in the event of a spillage or other incident.

All personnel working in the SLOWPOKE-2 Facility must pass a Workplace Hazardous Material Information System (WHMIS) and Radiation Safety Trainings provided on site and work safely in accordance with acquired trainings. Officer cadets receive radiation protection training from the RMC Radiation Safety Officer (RadSO) as part of the safety orientation before they start experiments in the laboratory.

Before any project is permitted to be conducted in the SLOWPOKE-2 facility, the proposed project is assessed for physical, radiological and chemical hazards by the Director of the SLOWPOKE-2 facility and the RadSO. Other specialists are consulted for advice, and calculations of the dose rate of the sample after irradiation are performed as necessary. In general, all proposed projects should follow as low as reasonably achievable (ALARA) principles. If the safety hazards are considered to be under control and risk minimized, the project/experiment form is signed by a project supervisor, the Director of the SLOWPOKE-2 facility and the RadSO before the project is allowed to proceed. Experimental work cannot commence until appropriate MSDS safety sheets have been consulted.

Samples of unknown composition should be irradiated for no more than 30 seconds initially. The neutron flux level should also be chosen in accordance with the sample matrix and expected sample composition to minimize radioactivity.

To monitor radiation levels in the area several stationary gamma and neutron meters are installed in various locations of the SLOWPOKE-2 facility. Readings from the meters installed in close proximity to the irradiation site controllers show how long the irradiated sample should stay inside the shielded compartment before it can be safely removed for further analysis or use. A wide collection of portable detectors is also available for this purpose. Other meters installed next to the reactor provide operational status signals directly to the Military Police Station at Canadian Force Base Kingston to increase radiation safety awareness.

To monitor personnel exposure to radiation, regular users of the SLOWPOKE-2 facility must wear a thermoluminescent dosimeter with X ray and gamma capability, a separate dosimeter for neutrons (both provided by Health Canada's National Dosimetry Service), as well as a personal alarming device (SOR R/F) that is monitored internally by the RMC RadSO.

Occasional workers and visitors are always accompanied by certified reactor operators or authorised users and must wear a personal alarming device, with their use and dose recorded in the appropriate dosimeter log and monitored by the RadSO.

All abnormal levels of radiation recorded by the personal dosimeters or stationary detectors are investigated internally and reported to the Canadian Nuclear Safety Commission.

Specific safety issues related to radiation and work within the SLOWPOKE-2 facility will be identified by the member of staff involved.

4. Experimental Section

4.1 Procedure

4.1.1 Preparation of Samples

- i. All aliquots of the standard, control, and unknown required for the short irradiations will be prepared in the sample preparation room (Rm. 2507).
- ii. Details of samples and labelling are provided in Appendix A. Results should be noted in Appendix B.
- iii. For the standard, the elements may be combined into one vial and should include only those elements being sought during a short irradiation.
- iv. For quality control, accurately make up approximately the same concentration as that of the standard.

4.1.2 Energy Calibration of the MCA

Note: The MCA should already be calibrated; an understanding of the process of calibration will be described.

4.1.3 Activation Constants for the Standard

- i. For the short-lived elements being sought, irradiate the prepared aqueous standards for a given t_i as recommended by the instructor in the SLOWPOKE-2 reactor (neutron flux is $5 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$). After a decay period of 1 minute (t_d), measure the γ spectrum of the sample for a time of 5 minutes (t_c). Note the shelf on which the samples are measured. Transfer the spectrum to the microcomputer for storage. If desired, repeat this procedure for one or two further aliquots of the prepared standard.
- ii. Analyse the two or three standard spectra using the computer programme EPAA to obtain the activation constants (B values). Average the B values for each element, and enter these constants into the library file used by the EPAA programme.

4.1.4 Analysis of a Control

Activate and analyse the control sample using the same conditions as used for the prepared standard ($t_i = 5 \text{ min.}$, $t_d = 1 \text{ min.}$, $t_c = 600 \text{ s}$). Transfer the spectrum to the computer and calculate the concentration of the elements under study using the EPAA programme. Compare the measured concentration to the expected value.

4.1.5 Analysis of Unknowns

- i. Analyse the unknowns using the same conditions as used for the prepared standards and control sample ($t_i = 5$ min., $t_d = 1$ min., $t_c = 600$ s). Repeat this procedure for one further sample of each unknown.
- ii. Using the computer programme EPAA, calculate the concentrations of the elements under study.

4.1.6 Analysis of a Blank

Prepare a blank irradiation capsule with an equivalent amount of pen markings as were used for the standards/control/unknown. Irradiate and analyse this blank in a similar manner to that used above. Repeat this procedure for one or two other blanks.

5. Discussion

The following should be addressed as part of the discussion section:

1. What are the stable isotopes of potassium?
2. What is the radioactive isotope of K used in your NAA experiment, and from which stable isotope is it formed?
3. What is the natural abundance of this stable isotope of K?
4. Given a 100 g banana and your NAA results, how much K does the NAA experiment find present? How does the experimental result compare to the reported elemental concentration of K present in bananas?
5. How much K do you estimate is present in cashews? How does the experimental result compare to the reported elemental concentration of K present in cashews?
6. After irradiation, in addition to the radioisotopes of potassium, which other radioisotopes were seen in the banana and cashew samples?
7. After irradiation, which radioisotopes were seen in the blank/empty vials?
8. Do the NAA vials affect the gamma ray spectrum? If yes, how so (which radioisotopes)?

6. Reporting

One formal report is required per group. Consult the Department Writing Guide for information regarding the structure and content of this report. Error should be considered as part of the report, but errors derived from weighing, etc., can be considered negligible. Error calculations should be

based on the counting statistics of the Poisson distribution for both calibration standards and samples. Where the error is defined by the square root of the total activity, as defined by:

$$\begin{aligned} \text{error} &= \sqrt{\text{gross counts} + \text{background counts}} \\ \text{error} &= \sqrt{\text{net counts} + 2 \text{ background counts}} \end{aligned} \quad (16)$$

The formal report will represent 70% of the final mark for this experiment. The formal report must be a professional document which includes the following sections:

Abstract	Provide a clear and concise paragraph that reviews the experiment, your methods, your results and error ranges of these results. Also a statement of the importance of this work should be included.
Introduction	Provide a review of the relevant theory important to this laboratory. Also, define the important equations used in your calculations. Note, this section is <u>not</u> a verbatim repeat of the notes found within the laboratory manual. To obtain full marks in this section, the writer should attempt to demonstrate their understanding of the subject matter and apply their knowledge to the report and analysis at hand.
Materials and Methodology	A list of the equipment and solutions used should be included. Also a list of the procedure used should be included. Any deviations from the procedure listed in the laboratory manual should be noted. Some procedural subsections to be included are: 1) preparation procedure, 2) irradiation and counting procedure, and 3) analysis procedure.
Results	Tables and figures should be included that clearly and concisely demonstrate your results. A table listing the concentrations of K in your standards, controls and unknowns should be included with the appropriate error range. Also a table listing the energy peaks seen in the banana and cashew sample spectra should be included. Also, the isotopes corresponding to the energy pecks should be listed. Sample calculations should be included in appendices but referenced in the results section.
Discussion	This section should provide an interpretation of your results and answers to the questions listed in section 5 of this laboratory manual. As this is a formal report, the answers to these questions should <u>not</u> be answered numerically, but included in the body of your discussion section.
Conclusion and Recommendations	This section should summarize your findings and offer some concluding remarks along with any recommendations to be considered for the improvement of your results or the experiment.
References	References should be included. Full marks will only be considered for additions references not listed in the laboratory manual that are relevant to your report.

All figures plots should be labelled correctly below the image or plot. All tables should be clearly labelled above the intended table. Equations should be also numbered sequentially. Sample calculations and error analysis are to be included in the report appendices and references in the text of the report.

7. Mark Scheme

The experiment will be marked from a total of 100. Marks will be distributed as follows.

70% will be awarded from the formal report, 15% to calculations, and 15% will be based on answers to the separate questions.

i. Formal Report

70 Marks in Total

The following criteria will be used in assessment of the formal report:

- Quality of laboratory data (15 Marks)
- Manipulation of data to present accurate and scientifically valid results (10 Marks)
- Adherence to formal report structure (10 Marks)
- Evaluation of QA/QC data (10 Marks)
- Interpretation of results (15 Marks)
- Examination of error (10 Marks)
- General style and presentation (10 Marks)

ii. Sample Calculation

15 Marks in Total

The following criteria will be used in assessment of the sample calculation:

- Presentation of appropriate data, and data manipulation (5 Marks)
- Use of appropriate units and significant correctly labelled figures and tables (5 Marks)
- Additional references (5 Marks)

iii. Questions

15 Marks in Total

8. References

- 1 D. Skoog, F. Holler and T. Nieman, "Principles of Instrumental Analysis", 5th Edition, Thomson learning Inc., USA, 1998.
- 2 H. Willard, L. Merritt and J. Dean, "Instrumental Methods of Analysis", 5th Edition, D. Van Nostrand Company, USA, 1974.
- 3 G. Knoll, "Radiation Detection and Measurement", 3rd Edition, John Wiley and Sons, USA, 2000

Appendix A. Sample Preparation and Labelling

Element / Sample	Designation	Solution	Vial label*
K	Standard	1000 μ L of 1000 ppm K	S-XXI
K	Control	1000 μ L of standard of 1000 ppm K	C-XXI
Blank	Blank	Empty vial	B-XXI
1000 mg of Banana	Unknown	1000 μ L of mashed banana	BN-XXI
1000 mg of Banana	Unknown	1000 μ L of mashed banana	BN-XXD
1000 mg of Cashew	Unknown	1000 μ L of crushed cashew	CW-XXI
1000 mg of Cashew	Unknown	1000 μ L of crushed cashew	CW-XXD

* Replace XX with your initials.

Appendix B. Data Sheet

Date of experiment: _____

Name: _____

Partners: _____

1. Elements analysed: K

2. Analysis of the standard: (Attach printed results from computer)

Standard concentration: _____ / _____ / _____ ppm

Peak(s): _____ / _____ / _____ keV

B VALUE

Element	
1	
2	
3	
Mean	

3. Analysis of control sample (Attach printed results from computer.)

Element	
Measured concentration / ppm	
Expected concentration / ppm	

4. Analysis of unknown sample (Attach printed results from computer.)

CONCENTRATION / ppm

ELEMENT	K
1000 μ L of banana	
1000 μ L of banana	
1000 mL of cashew	
1000 μ L of cashew	

5. Other isotopes present in the γ ray spectrum:

Empty vial (Note the isotope and the peak energy):

Banana sample (Note the isotope and the peak energy):

Cashew sample vial (Note the isotope and the peak energy):