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Jack F. Higginbotham

The utilization of ^{77m}Se, half life 17.5 s, and ^{75}Se, half life 119.8 d, for quantification of trace amounts of Se in well water and biological materials by means of instrumental neutron activation analysis (INAA) is described. A Se detection limit of 0.03 ppm was achieved for sheep blood plasma samples which were irradiated for 27 s in a flux of approximately $9x10^{12}$ n $cm^{-2}s^{-1}$, and counted using a Ge(Li) gamma ray spectrometer system. Samples of well water and animal feedstuffs were activated for 13 h at a flux of approximately $3x10^{12}$ n $cm^{-2}s^{-1}$ and were also counted using a Ge(Li) based spectrometer system. Under these conditions, the Se detection limit was found to be 0.02 ppb for well water and 0.03 ppm for animal feedstuffs. Activation analysis of the NBS Standard Reference Material SRM 1577a, bovine liver, demonstrated that this methodology for

determining Se concentrations yielded excellent accuracy and precision. A comparison is made between the results obtained with neutron activation analysis and those achieved with the automated fluorimetric method. The sensitivity and accuracy for both techniques are approximately equal and hence, the choice of which method to use depends on whether a rapid analysis is required.

Selenium Measurement in Ground Water and Biological Material by Instrumental Neutron Activation Analysis

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Samir Yousef

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APPROVED:

Redacted for privacy

Assistant Professor of Nuclear Engineering

Redacted for privacy

Head of Department of Nuclear Engineering

Redacted for privacy

Dean of Graduate School

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Selenium Measurement in Ground Water and Biological Material by Instrumental Neutron Activation Analysis

1. Historical Background

It is possible that Arnold de Villanora was the first person to observe and describe the element which came to be known as Se. In "Rosarius Philosophorum", written around the beginning of the fourteenth century, he described the vaporization of S and the appearance on the container walls of a deposit which he called "sulfur rubeum". However, was not until 1817, that Jon Jakob Berzelius in Gripsholm, Sweden, identified Se as a new chemical element. Because of its chemical similarity to Te (discovered 35 years earlier), it was named Se for the moon (selene in Greek) while Te had been named for the earth (tellus in Latin) [1].

Berzelius conducted no further research with this extremely reactive element. Eventually, Se's unusual physical properties of behaving as a metallic and non-metallic metal were identified. These properties made Se difficult to work with in the laboratory.

Substantial biological research of Se did not occur for many years, due to the lack of a sensitive and reliable method for its detection [2].

Its biological significance was recognized in 1934 when it was identified as the toxic substance causing lameness and death in livestock grazing on certain range plants in Wyoming and the Dakotas [3].

After this discovery, Se was thought to be solely a toxic element. But, in 1957, Schwarz and Foltz demonstrated that a small amount of Se was essential for animals. Se deficiency diseases were found in numerous species and the practical importance of adequate Se nutrition in the economic production of farm livestock was shown to be considerable [4].

Naturally, selenium-induced biological effects in animals raised questions about the potential for similar effects in humans. The importance of Se as a nutritionally essential element was assumed but scientific evidence was not found until Van Rijj demonstrated its significance through reversible clinical and biochemical effects during prolonged intravenous feedings. Biochemical evidence of Se depletion was also identified in severe gastrointestinal disease. Epidemiological studies of children in areas of China also indicated a reversible Se deficiency [4].

Se was thus identified as an essential nutrient but because it exhibits severe toxicity problems, guidelines for limiting Se intake were required. In order to enforce such guidelines, sufficiently sensitive and reliable methods for its measurement need to be available.

Because the concentration of Se in samples of tissue, water, or foodstuffs can cover a wide range, there have developed a number of analytical methods which provide varying degrees of sensitivity for quantifying Se. These methods also vary in the length of time required for each analysis.

2. Introduction

In 1976, the Kuwaiti government established the Radiation Protection Division within the Ministry of Public Health; for the purpose of developing a program to protect occupational workers and the general public from excessive or unnecessary internal or external radiation exposure resulting from the handling, transfer or use of either radioactive materials or machines which produce ionizing radiation. The Radiation Protection Division is divided into three independent sub-units: licensing, inspection and environmental monitoring. The licensing unit examines the operating procedures of radiation generating machines and determines if proper radiation protection safeguards will be used. The inspection unit inspects and tests all licensed equipment and facilities to assure compliance with Kuwaiti regulations. The environmental monitoring unit determines the content of radioactive materials in air, drinking water, and imported foods to ensure compliance with the established radiation level standards. The Kuwaiti health physics program, like other programs in developing countries, is deficient in many of the areas considered essential by western standards, particularly in the areas of training programs, radiation instrumentation, and radioactive waste disposal.

However, in recent years as a result of public concern about radiation protection and increased usage of radiation in health care diagnostics and treatment, the Ministry of Public Health and the

Radiation Protection Division intend to build a Radiation Technology Institute to overcome the current manpower shortage in the areas of health physics and nuclear radiochemistry applications in Kuwait.

The Institute will focus on applied research in radiation protection in hospitals and in radioisotope production, and usage. Procedures and training programs are to be developed covering topics such as handling techniques, shielding requirements, containment and ventilation requirements, packaging and container testing for shipping radioactive material.

To assist with the implementation of this program, the Ministry of Public Health has been encouraging its employees and students to participate of international graduate education in the field of radiation protection.

The Ministry of Public Health is currently attempting to purchase a ^{252}Cf spontaneous fission neutron source for the purpose of radioisotope production and neutron activation analysis. At the same time, the Kuwaiti health physicists will try to develop guidelines containing information on permissible radiation and contamination levels, health physics procedures, shielding requirements, containment and ventilation facilities for the ^{252}Cf source.

Dr. Jack Higginbotham and I, as a Kuwaiti employee at the Radiation Protection Division, suggested that the measurement of Se in ground water, and biological materials by neutron activation analysis would help Kuwaitis achieve the goal of making such a facility operational. Such a thesis program would provide the Ministry with

experience in neutron activation analysis techniques, operation of state of the art spectrometers, radiation protection techniques, and a reliable methodology for the determination of Se concentration, since Se deficiency or excesses is newly discovered.

There exist different methods that have been used for the determination of Se concentration in such diverse media as natural water, foodstuffs, hair, blood, etc.. Some of these methods include fluorimetric analysis using diaminonaphthalene (DAN), neutron activation analysis (NAA), X-ray fluorescence spectrometry and atomic absorption spectroscopy (AAS). DAN and NAA have been found applicable to measure Se content in biological materials. The others are not applicable to biological materials due to low sensitivity [5].

The primary goal of this project is to develop a neutron activation methodology which would compare favorably with fluorimetric analysis for the qualitative and quantitative determination of Se. The specific application, includes the accurate determination of the amount of Se in well water, grass, silage, prepared feed, and sheep blood plasma. The results of these analyses will be compared to the results obtained by Dr. P. D. Whanger and Dr. F. Adams of the Oregon State University Department of Agricultural Chemistry using a semi-automated fluorimetric method on similar samples.

The secondary goal of this project is to document the radiation protection practices of the OSU Radiation Center for activation analysis research projects. Since radioactive materials are produced as a result of the neutron activation analysis technique, radiation protection

measures must be implemented. Therefore, the health physicist and the experimenter must utilize protection and precautions to comply with federal, state and local regulations and ensure that any exposure is kept as low as reasonably achievable. The details of the radiation protection procedures will be discussed in the following sections.

3. Neutron Activation Analysis

The first application of neutron activation analysis was in 1936 when Hevesy and Levi used it to determine the concentration of Dy and Eu in a rare-earth mixture [6]. Since then, neutron activation analysis has evolved into an extremely powerful trace-element analysis technique.

In neutron activation analysis a stable isotope, (X), has a certain probability of undergoing a neutron capture reaction when exposed to a field of thermal neutrons for a period of time. The resultant daughter isotope is often radioactive. If it decays by gamma ray emission, a photon of a specific energy will be emitted and a radiation detection system can be used to record the number of gamma ray interactions with the detector. Since the induced activity of the radioisotope is proportional to the amount of its parent isotope in the sample, the method can be used for quantitative analysis.

If a radionuclide (X*) is being produced by neutron activation, and is decaying at the same time, the net number of radioactive atoms present in the sample at any time is the rate of production minus the rate of decay. This may be expressed mathematically by the equation:

rate of change of the radioactive atoms present	=	rate of production	−	rate of decay	(1)

This relation can be written as

$$\frac{dN_{X^*}}{dt} = \varphi\, \bar{\sigma}_a\, n - \lambda_{X^*} N_{X^*} \qquad (2)$$

where

φ = thermal group averaged neutron flux density (n $cm^{-2}s^{-1}$),

$\bar{\sigma}_a$ = thermal group averaged absorption cross-section in cm^2 (1 barn = 10^{-24} cm^2) for stable isotope X,

λ_{X^*} = decay constant of the radionuclide,

N_{X^*} = number of radioactive atoms (X*),

n = number of target atoms (X) and

t = time

and $\bar{\sigma}_a = \frac{\sqrt{\pi}}{2}\, g_a(T)\, \sigma(E_o)\, (\frac{T_o}{T})^{-1/2}$

where

$g_a(T)$ = non-1/v factor,

$\sigma(E_o)$ = microscopic absorption cross-section at 0.0253 eV,

T_o = room temperature and

T = reactor temperature

Equation (2) is a linear differential equation and by assuming that the initial number of radioactive atoms is zero and the product of $\varphi\, \bar{\sigma}_a\, n$ is constant during irradiation, equation (2) can be solved as follows :

Homogeneous solution (N_1)

$$\frac{dN_1}{dt} + \lambda_{X^*} N_1 = 0$$

let $N_1 = a\, e^{mt}$

$$a\, m\, e^{mt} + \lambda_{x^*} a\, e^{mt} = 0$$

$$a\, e^{mt} (m + \lambda_{x^*}) = 0 \longrightarrow m = -\lambda_{x^*}$$

and therefore

$$N_1 = a\, e^{-\lambda x^* t} \qquad (2\text{-a})$$

The particular solution (N_2) can be found by

letting $N_2 = b$

$$\lambda_{x^*} b = \varphi\, \bar{\sigma}_a\, n \longrightarrow N2 = b = \frac{\varphi\, \bar{\sigma}_a\, n}{\lambda x^*}$$

Therefore, the general solution $N_{X^*} = N_1 + N_2$ becomes

$$N_{X^*} = a\, e^{-\lambda x^* t} + \frac{\varphi\, \bar{\sigma}_a\, n}{\lambda x^*}$$

From the initial condition : $N_{X^*}(t = 0) = 0$

$$0 = a + \frac{\varphi\, \bar{\sigma}_a\, n}{\lambda x^*} \qquad \text{which yields} \qquad a = \frac{-\varphi\, \bar{\sigma}_a\, n}{\lambda x^*}$$

Therefore

$$N_{X^*} = \frac{\varphi\, \bar{\sigma}_a\, n}{\lambda_{X^*}} - \frac{\varphi\, \bar{\sigma}_a\, n}{\lambda_{X^*}}\, e^{-\lambda_{X^*} t}$$

and

$$\lambda_{X^*} N_{X^*} = \varphi\, \bar{\sigma}_a\, n\, (1 - e^{-\lambda_{X^*} t}) \qquad (3)$$

where

t = length of activation (λ and t should be in the same units).

The activity is defined as

$$D_{X^*} = \lambda_{X^*} N_X \qquad (4)$$

and the number of target atoms is given by

$$n = \frac{W_X\, Ave\, F}{M} \qquad (5)$$

where

D_{X^*}= disintegration s^{-1} of a radionuclide X^* at the end of bombardment,

W_X = weight of an element X irradiated , in grams,

Ave = Avogadro's number, 6.02×10^{23} atoms $mole^{-1}$,

F = fractional isotopic abundance of target element and

M = atomic weight of the element X (g $mole^{-1}$).

By substituting Eq. (4) and Eq. (5) in Eq. (3), the following equation is obtained :

$$D_{X^*} = \frac{W_X\, Ave\, F}{M} \varphi\, \bar{\sigma}_a\, (1 - e^{-\lambda_{X^*} t}) \qquad (6)$$

The activity of a radionuclide X^* at some time T after the end of irradiation would be

$$A_{x^*} = D_{x^*} \; e^{-\lambda x^* T} \qquad (7)$$

where

A_{x^*}= activity (disintegration s^{-1}) of a radionuclide X^* at some time T after the end of irradiation, or the length of time from the end of irradiation to the start of counting.

The number of gamma rays emitted by the radionuclide X^* during the counting interval is the number of atoms that decay multiplied by the gamma-ray yield, Y, (fraction of radionuclide disintegrations producing the gamma-ray of interest). The number of counts observed by the detector system is the number of gamma-rays emitted multiplied by the absolute efficiency, ε, of the detector. Thus, the total number of counts (photopeak area, P_a) observed during the time interval is [7]

$$P_a = A_{x^*} \; Y \; \varepsilon \qquad (8)$$

Substitution of Eq. (6) into Eq. (7) yields

$$A_{x^*} = \frac{W_x \, Ave \, F}{M} \varphi \bar{\sigma}_a \; (1 - e^{-\lambda x^* t}) \; e^{-\lambda x^* T} \qquad (9)$$

And by substituting Eq. (9) into Eq. (8), the following equation for the photopeak area is obtained :

$$P_a = \frac{W_x \, Ave \, F}{M} Y \varepsilon \varphi \bar{\sigma}_a \; (1 - e^{-\lambda x^* t}) \; e^{-\lambda x^* T} \qquad (10)$$

It is clear from the above equation that the measured activity induced is not only dependent on the amount of the parent isotope present in the sample but also on : (1) neutron flux, (2) the neutron reaction cross-section, (3) the decay constant of the nuclide measured, (4) the irradiation time and (5) the detector efficiency (ε). Therefore, these parameters affect the accuracy of determining the amount of the element (X) in the sample [8]. However, a comparative method, in which both unknown and standard sample are irradiated simultaneously for the same length of time (i.e., $\varphi_{un} = \varphi_{std}$) and counted under exactly the same conditions (i.e., counting system, geometry, etc.), eliminates any uncertainly in the parameters φ, $\bar{\sigma}_a$, and ε. This can be shown by rewriting Eq. (6), Eq. (7) and Eq. (8) respectively as follows

$$W_x = \frac{M\ D_{x^*}}{A_{ve}\ F\ \varphi\ \bar{\sigma}_a\ (1-e^{-\lambda t})}$$

$$D_{x^*} = \frac{A_{x^*}}{e^{-\lambda x^* T}} \qquad (12)$$

$$A_{x^*} = \frac{P_a}{Y\ \varepsilon} \qquad (13)$$

Substituting Eq. (13) into Eq. (12), and Eq. (12) into Eq. (11) for the unknown and the standard samples gives the following equations.

$$W_{xun} = \frac{M\ P_{un}}{A_{ve}\ F\ Y\ \varepsilon\ \varphi\ \bar{\sigma}_a\ (1-e^{-\lambda t})e^{-\lambda T un}} \qquad (14)$$

$$W_{xstd} = \frac{M\ P_{std}}{A_{ve}\ F\ Y\ \varepsilon\ \varphi\ \bar{\sigma}_a\ (1-e^{-\lambda t})e^{-\lambda T std}} \qquad (15)$$

where

P_{un} = peak area of an unknown sample,

P_{std} = peak area of a standard sample,

T_{un} = decay time after the end of irradiation of an unknown sample and

T_{std} = decay time after the end of irradiation of a standard sample.

Dividing Eq. (14) by Eq. (15) gives

$$\frac{W_{xun}}{W_{xstd}} = \frac{P_{un}\ e^{\lambda x * Tun}}{P_{std}\ e^{\lambda x * Tstd}} \qquad (16)$$

What becomes apparent is that the greater the activity, the better the detection sensitivity (i.e., the smaller quantity of element X that may be measured) for a given element. The sensitivity can be increased by optimizing the following parameters regarding the amount of an element of interest in the sample. These parameters are the detector resolution and efficiency, the irradiation time, the decay interval before counting, the neutron flux in the reactor, the half-life and γ-ray energy of a radioisotope.

Since other nuclides may also produce the radioisotope X^* during irradiation or produce radionuclides which have gamma-ray energies approximately equal to the energies emitted by X^*, the resulting interference should be eliminated. This can be done by specific chemical or radiochemical separation in which the interfering elements are removed from the sample, or interference from another radioisotopes can be subtracted from the photopeak of interest [6].

For cases where there is significant radionuclide decay during counting then a correction for instrumentation losses must be included. This is the case when samples are irradiated in the pneumatic transfer facility. The following equations were used to calculate the activity of a radionuclide in this case for unknown and standard samples [9] :

$$A_{std} = \frac{N_{std}\,[e^{-\lambda x\,\Delta T_{std}} - 1]}{[1 - e^{-\lambda x(LT_{std})}]\,[\Delta T_{std}]} \qquad (17)$$

and

$$A_{un} = \frac{N_{un}\,[e^{-\lambda x\,\Delta T_{un}} - 1]}{[1 - e^{-\lambda x(LT_{un})}]\,[\Delta T_{un}]} \qquad (18)$$

where

A_{std}= counting rate of the standard photopeak at the start of the counting interval,

A_{un}= counting rate of the unknown photopeak at the start of the counting interval,

N_{std}= net counts in the photopeak for standard sample,

N_{un} = net counts in the photopeak for unknown sample,

λx = decay constant of the radionuclide,

CT_{std}= clock time for counting interval for standard sample,

CT_{un}= clock time for counting interval for unknown sample,

LT_{std}= live time for counting interval for standard sample,

LT_{un} = live time for counting interval for unknown sample,

ΔT_{std}= CT_{std} - LT_{std} = dead time of the detector for standard sample and

ΔT_{un} = CT_{un} - LT_{un} = dead time of the detector for unknown sample.

The next important step in neutron activation analysis is the choice of a method of isolating the activity of the interested element (X*) in order to measure it. The two methods of isolating X* commonly used are instrumental activation analysis (IAA) and radiochemical activation analysis (RAA). The major difference between these two methods is that IAA is a nondestructive method, allowing further use of the sample. The short activation application of the IAA technique allows for the identification of various elements which would not be possible if a lengthy chemical separation were to precede the counting [10].

Se has six stable isotopes that exist in nature and only seven of its radioisotopes can be produced by neutron activation. The isotopes which undergo neutron- gamma ray (n,γ) reaction and their nuclear data

are summarized in Table 1. The radioisotopes ^{75}Se (T1/2 =120 d) and ^{77m}Se (T1/2 =17.5 s) were used to analyze the amount of Se in the activated samples. The choice of the two isotopes was based on the length of their half-lives and the magnitude of their thermal neutron cross-sections. ^{75}Se was chosen because it has the longest half-life of Se isotopes, giving enough time to allow short half life radioisotopes to decay and also allows for a complete chemical separation. The shortest half-life of the ^{77m}Se radioisotope allows for rapid sample analysis with high sensitivity which is desirable for biological samples [11, 12]. This technique was applied to the determination of Se in blood plasma samples.

Table 1. Nuclear Decay Data for Selenium Isotopes [13]

Target nuclide	^{74}Se	^{76}Se	^{78}Se	^{80}Se	^{80}Se	^{82}Se	^{82}Se
Abundance (%)	0.9	9.0	23.5	49.6	49.6	9.4	9.4
$\sigma(E_0)$(barns)	51.8	22.0	0.38	0.08	0.53	0.039	0.005
Isotope produced	^{75}Se	^{77m}Se	^{79m}Se	^{81m}Se	^{81}Se	^{83m}Se	^{83}Se
Half-life	119.8 d	17.5 s	3.91m	57.3m	18.5 m	70.4 s	22.5 m
$E\gamma$ (keV)	264.6	162.0	95.9	103.1	275.9	1030	510.0
$E\gamma$ intensity (%)	59.1	52.1	9.47	9.79	0.87	20.9	44.3

4. Sample Description and Preparation

Since the accuracy of neutron activation analysis can be affected by incorrect preparation of samples and reference standards, it is important that sample preparation be performed with care to avoid the risk of loss, or contamination. Also, the unknown and standard samples should have the same size, composition and homogeneity insofar as possible, to ensure that attenuation effects are similar for all samples [10].

Since the Se content in animals is greatly influenced by the Se concentration in local water and the feedstuffs; ground water, silage, grass hay and prepared feed samples were selected for analysis. Also, since the estimation of the Se intakes of animals can be made by blood analysis, thirty samples of sheep blood plasma were analyzed.

4.1. Decontamination of Polyethylene Vials

Since all samples were required to be sealed in polyethylene vials for irradiation and analysis, contamination must be controlled and minimized.

The possibility of contamination was minimized by cleaning all flasks by two normal nitric acid (2 N HCL) and distilled water. Also, all polyethylene vials, commonly refered to as polyvials, were placed in a large beaker filled with ethyl alcohol and then placed in an ultrasound

bath for fifteen minutes. Then, the vials were rinsed with distilled water and washed with normal nitric acid in the ultrasound.

4.2. Water Sample

The water samples were collected from a well located south of Philomath in Benton County, Oregon. The sampled location is shown in the map of Fig. 1.

Three, 2l samples were taken from a depth of 24 m. To prevent Se volatization, the pH of the three, two liter samples was adjusted to alkaline with sodium hydroxides and evaporated on a hot plate to almost dryness.

Following this concentration, two of these samples were set aside for individual chemical separation to remove elements which produce radionuclides which interfere with the detection of the element of interest. In this manner, the good sensitivity and precision needed for Se level determination could be achieved (Details of the chemical separation are given below). From the remaining samples, three 1/2 ml aliquots of water were pipetted and placed into individual 1/2-dram polyvials. Each polyvial was weighed before and after filling with water to obtain the sample weights. Each of the polyvials were then heat sealed and placed into separate 2 dram polyvials which were also heat sealed. The vials were always handled with gloves and placed on clean surfaces, to avoid further contamination.

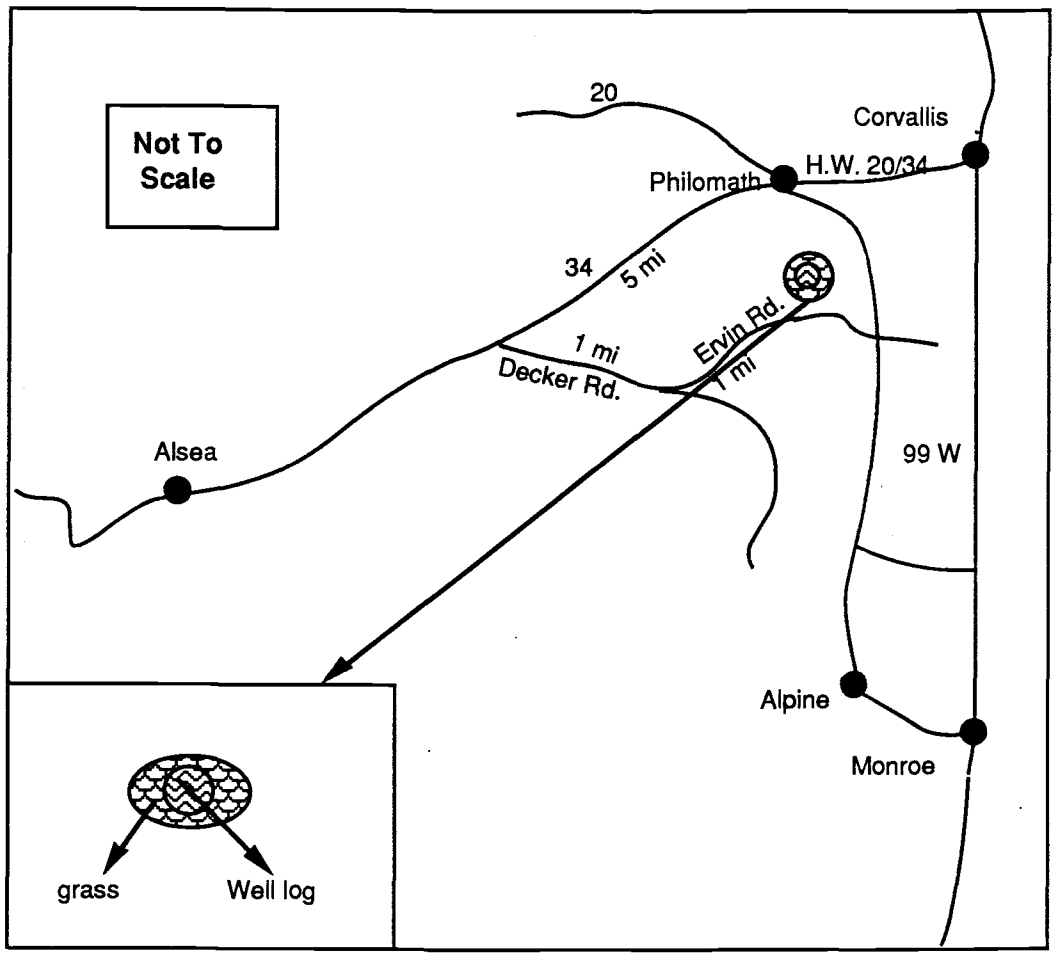

Fig.1. Location of Well Log and Grass Samples in Western Oregon.

4.3. Individual Chemical Separation Procedures

Individual chemical separation is sometimes necessary when the concentration of an element in a sample is very low. Since the Se concentration in ground water was expected to be low and the water samples contain many elements which could interfere with the detection of ^{75}Se, it was thought that chemical separation would be necessary for better sensitivity and precision.

The water samples set aside after concentration and designated for chemical separation were transferred to smaller containers (125 ml erlenmeyer flasks) as a result of the reduced volume. They were then treated with 10 ml of concentrated nitric acid and 6 ml concentrated perchloric acid to remove the organic matter by oxidation.

The samples were heated until white fumes were generated from the volatilization of perchloric acid at approximately 205 $^{\circ}C$. The heating was continued for 15 min after the first appearance of fumes, then removed from the hot plate and cooled to room temperature. To complete the perchloric acid digestion, the flask was never allowed to dry out during heating.

To reduce selenate (SeO_4) to selenite (SeO_3), 3 ml of concentrated hydrochloric acid was added to the sample once it cooled. The sample was then returned to the hot plate and heated an additional 15 min.

After cooling, 20 ml of 0.009 mole ethyiene diamine tetra acetic (EDTA) acid solution was added as well as 0.2 ml of pH indicator solution (0.1 g cresol red and 0.1 g bromocresol green per 250 ml). The samples were titrated with ammonium hydroxide and HCl to achieve a pH between 2 and 3. Then each sample was mixed with 20 ml of 2 mg/ml 2,3 diaminonaphthalene (DAN) in 0.1 M HCL. The DAN solution was washed three times with cyclohexane prior to use to remove impurities. This was done by combining 100 ml DAN with 30 ml cyclohexane in an extraction funnel, mixing it thoroughly and setting it aside allowing the two phases to separate. The upper organic phase which contains the DAN-selenite complex was removed and saved. The cyclohexane extraction was repeated two more times for each sample. The aqueous phase was discarded at each step. The extracted samples were concentrated by evaporating them under a stream of air until the volume was small enough to fill 1/2 dram polyvial. The cyclohexane extractions were transferred to a one half dram polyvial which was heat sealed.

Each water sample was then placed in 2-dram polyvial. The outer container was also heat sealed in order to avoid leakage during and after activation.

4.4. Animal Feedstuff Samples

In some areas of the United States, animal feedstuffs contain sufficiently high Se concentrations to cause Se toxicity in livestock; in other regions the Se concentrations are extremely low and cause deficiency problems. At the same time, there are many regions where the Se concentrations in feedstuffs are sufficient to meet livestock requirements [3]. To demonstrate that the methods developed in this work can quantify this wide range of Se concentration, silage samples were selected from Washington, grass hay samples from Montana, and prepared feed samples from Nevada. These samples were obtained from Dr. Frank Adams of the Agricultural Chemistry Department at Oregon State University.

Oregon grass samples were also collected from the location which provided the water samples (see Fig.1). These grass samples were chosen to investigate if the grass accumulates Se from either the water or the soil around the well and to investigate if the grass contains Se at levels which would be toxic to farm animals. There are three different sets of samples categorized by radial distance from the well: 20 m, 40 m, and 60 m. Each set contains 5 samples of approximately equal weight .

The Oregon grass samples were placed in an oven at 100°C for 24 h. After each batch of grass was removed from the oven it was ground to a 20 mesh grind in a Wiley Mill and packed into 2-dram polyvials.

Each 2-dram polyvial was weighed before and after the grass was transferred to obtain net weights. In this project, the weight of samples range from 1.3-1.7 g. The polyvials were heat sealed, placed in a plastic bag which was then heat sealed.

Extraction of Se from organic tissue can not be conducted by the dry ashing procedure because Se will volatilize at 600 °C. In chemical analysis Se is extracted from organic matter by a wet ashing method which involves using strong mineral acid digestion such as nitric and perchloric acids. The individual chemical separation procedures discussed in section 4.2 were applied to grass samples to measure Se concentration by the fluorimetric method.

4.5. Blood Sample

The blood plasma is not only an accessible tissue for determination of Se concentration, but also it can be helpful in the diagnosis of animal disease [3]. The blood plasma samples were chosen to be analyzed by short neutron activation analysis because it can provide a rapid and reliable result.

Thirty samples of sheep plasma were obtained from Dr. P.D. Whanger of the Agricultural Chemistry Department at Oregon State University. Dr. Whanger categorized the samples into three groups, of ten each, depending on their Se content. The samples were from an experiment to investigate the metabolism of organic and inorganic Se by sheep [14]. In that experiment, the sheep began with a low Se

concentration in their blood and blood samples were taken after the sheep were fed diets containing 1.0 μg Se g^{-1} diet.

The low Se containing samples were taken from the sheep prior to the start of the study. The sheep were killed after 16 weeks and the medium and the high Se containing samples were obtained.

The plasma samples were prepared by digestion with nitric and perchloric acids, then Se levels were determined by a semi-automated fluorimetric method using an autoanalyzer.

The samples used for activation analysis consisted of 1/2 ml blood plasma pipetted to a half dram polyvial and sealed. Each polyvial was weighed before and after filling with plasma to obtain the net weight. Then, each 1/2-dram polyvial was placed in a 2-dram polyvial and heat sealed.

4.6. Standard Solution

For a standard solution of the element investigated, sodium selenite (Na_2SeO_3, 45.66% Se) was used. The concentration of the solution used for the standard was 1.726 μg ml^{-1}. The 1.726 μg ml^{-1} solution was prepared by dissolving 7.56 mg of Na_2SeO_3 in 2000 ml distilled water. Then, ten 1/2 ml amounts of water were pipetted and placed into individual 1/2-dram polyvials. The remaining amount of the solution was evaporated almost for dryness. Then two 1/2 ml amounts of sodium selenite solution were pipetted and placed into individual 1/2-dram polyvials. Each of all these 1/2-dram polyvials were then

heat sealed and placed into separate 2-dram polyvials which were also heat sealed.

The bovine liver, National Bureau of Standards (NBS)-standard was used to evaluate the reliability of the determination of Se in standard samples. The Se concentration in the bovine liver is certified as 0.71±0.07 μg Se g^{-1} liver. The certified values for the constituent elements of bovine liver are listed in appendix A.

5. Sample Activation Facilities and Handling Procedures

The Oregon State University TRIGA reactor, OSTR, was used to perform all the sample irradiations required for this work. The OSTR is housed at the University's Radiation Center and it is a light water cooled and moderated reactor which utilizes 70% enriched fuel. For sample irradiation it contains a rotating rack which is composed of 40 tube locations for positioning samples and during irradiation the rack revolves around the core at one revolution per minute. Also, the OSTR has a pneumatic transfer system (rabbit) which is used for rapid insertion and removal of samples from the reactor.

For executing the neutron activation analysis experiment, there are some important radiation protection procedures that were followed by the experimenter to minimize radiation exposure and to prevent the spread of radioactive material (contamination). Some of these radiation protection procedures are be discussed in this section.

5.1. Pneumatic Transfer Facility

In order to quantify the concentration of Se using the short-lived isotope ^{77m}Se, the blood samples were irradiated in the OSTR's pneumatic transfer facility (rabbit system). In the rabbit schematic of Fig. 2, it can be seen that the sample is loaded into the transfer system then is drawn by air suction into an irradiation terminus located in one of the reactor-core grid positions. The valving of the rabbit system is then altered so that at the end of the irradiation the sample is drawn back to the loading terminus. For this work the unknown and standard samples were placed one at a time in polyethylene "rabbit" polyvial, which was loaded in the rabbit system, fired into the irradiation terminus and irradiated in flux of 9×10^{12} n $cm^{-2}s^{-1}$ (reactor operating at a power level of 1 megawatt) for a period of 27 s. This activation time was found to be optimum (i.e., the gamma peak at 162 keV was observed) after several runs in which the activation time was increased from 5 s in increments of 5 s. These runs showed a 30 s interval to be optimum. However, since the sample needs 3 s for the transfer from the core to the loading terminus, the actual activation time is 27 s. The irradiation time was limited to a maximum of 27 s to avoid raising the background count rate and losing the accuracy and sensitivity of the technique. After each irradiation, the sample exposure rate at one foot was immediately checked by a remote area monitor to ensure it was not

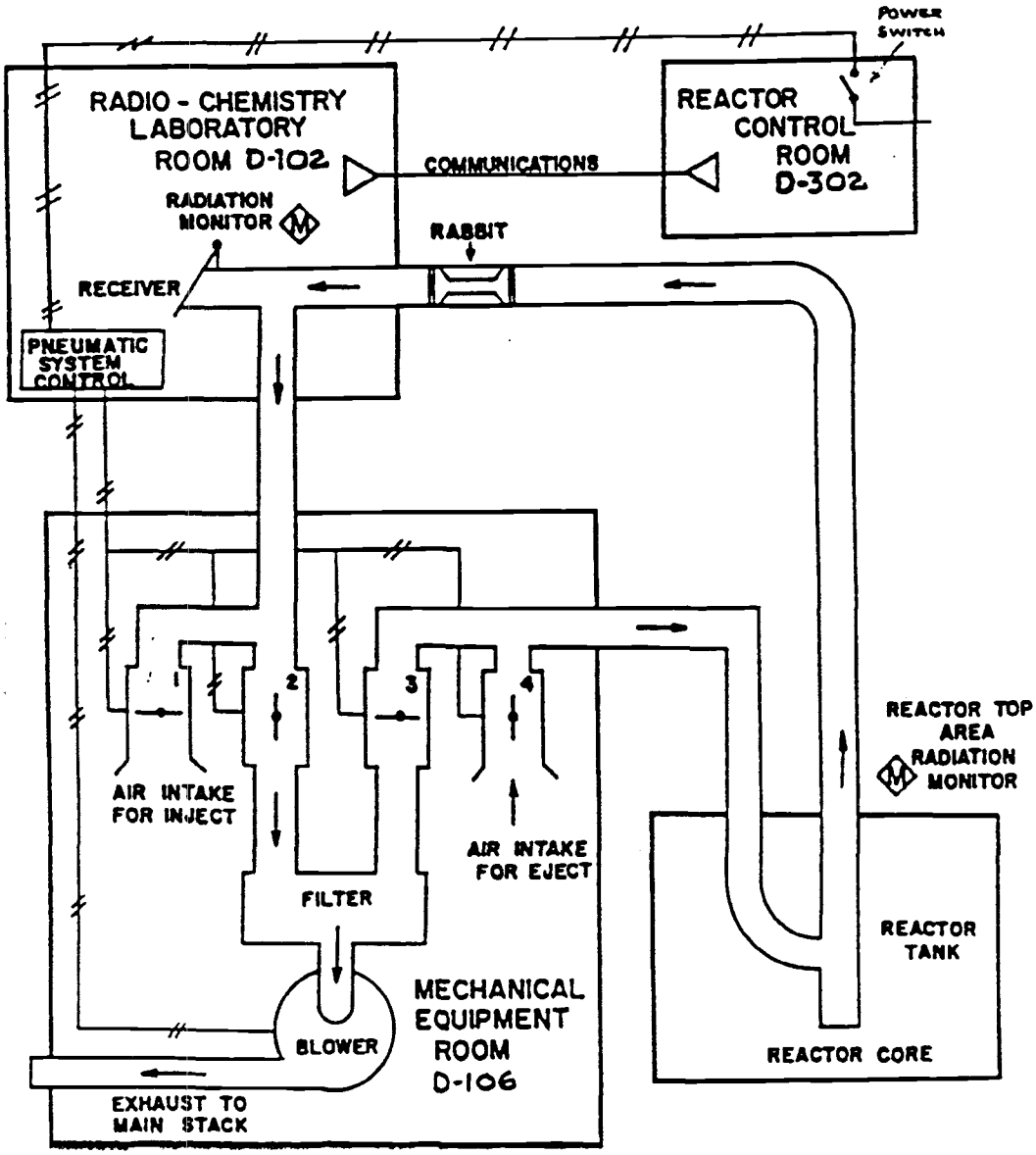

Fig.2. Standard Rabbit System Schematic.

greater than the OSTR radiation protection procedural limit of 50 mR h^{-1}. The sample was then removed from the rabbit system and its exposure rate with the ion chamber, window open at contact (WO), was monitored by the Cutie Pie, ion chamber, to ensure it was not greater than the OSTR's radiation protection procedural limit of 500 mR h^{-1}. Also, the exposure rate was checked with the ion chamber, window closed, at one foot from the Cutie Pie chamber centerline (WC_2) to ensure it was not greater than 500 mR h^{-1}.

Each sample was then transferred to a clean polyvial to prevent the spread of contamination. Due to radiation protection procedures, the decay time was approximately 25 s. Then the sample was moved to the Ge(Li) spectrometer system where it was counted for 40 s.

The protective clothing requirements for the experimenter included wearing latex gloves and a laboratory coat during rabbit operation. The samples were picked up by 15 to 23 cm long tongs to minimize extermity radiation exposure. To measure the radiation dose received by the whole body and extremities a film badge, finger rings and a 0-200 mR gamma-sensitive pocket ion chamber were worn.

From a radiation protection standpoint, there are also many different pre-irradiation and post-irradiation technical procedures and precautions which were followed during the handling of irradiated samples. Some of the pre-irradiation procedures include:

1- completing an Irradiation Request (IR) form approved by the Reactor Supervisor and the Senior Health Physicist, to predict post-irradiation radioactivity levels;

2- wearing the dosimeters in a position where they would measure the highest dose to the areas of interest, usually the upper chest above the level of the lead shield in the rabbit terminal hood;

3- having the rabbit terminal hoods organized and spacious to reduce exposure time and to prevent spread of contamination;

4- performing an operational test of the cutie pie ion chamber to be used; and

5- making the clean vials and the lead cask for sample transfer available before the rabbit activations are performed.

After each sample was irradiated and placed in the transfer container, the post irradiation radiation protection procedures which were followed included:

1- checking the experimenter's gloves for contamination using a GM tube based survey meter during sample handling, and replacing them if they were contaminated;

2- disposing all radioactive waste in the radioactive waste container; and

3- surveying the experimenter's lab coat, clip board, and ion chamber for contamination before removing them from the rabbit laboratory.

The radioactivity produced was estimated from the exposure rate measurements at one foot from each sample using the expression [13]

$$\dot{X} = 6\,C\,E\,n \qquad (19)$$

where

$\dot{X}$= Gamma exposure rate (mR h^{-1}), WC_2

C= Source activity (mCi).

E= Average energy of the gamma emitted from the source (MeV).

n= Number of gamma rays emitted per disintegration.

And finally the irradiation request form was completed and transferred to the Reactor Supervisor.

5.2. Rotating Rack

After collecting and preparing the water, silage, prepared feed, and the grass samples, they were irradiated in the rotating rack facility. The unknown and standard samples were placed in the bottom of the irradiation positions in the rotating rack and to ensure each sample received the same neutron fluence the rack was rotated during all irradiations. Fig. 3 shows the rotary specimen rack. The samples were activated in a flux of approximately 3×10^{12} n $cm^{-2}s^{-1}$ when the reactor was operated at a power level at 1MW. The feedstuffs and water samples were activated for 13 h which is the maximum time allowed for polyethylene vials to be irradiated in the OSTR.

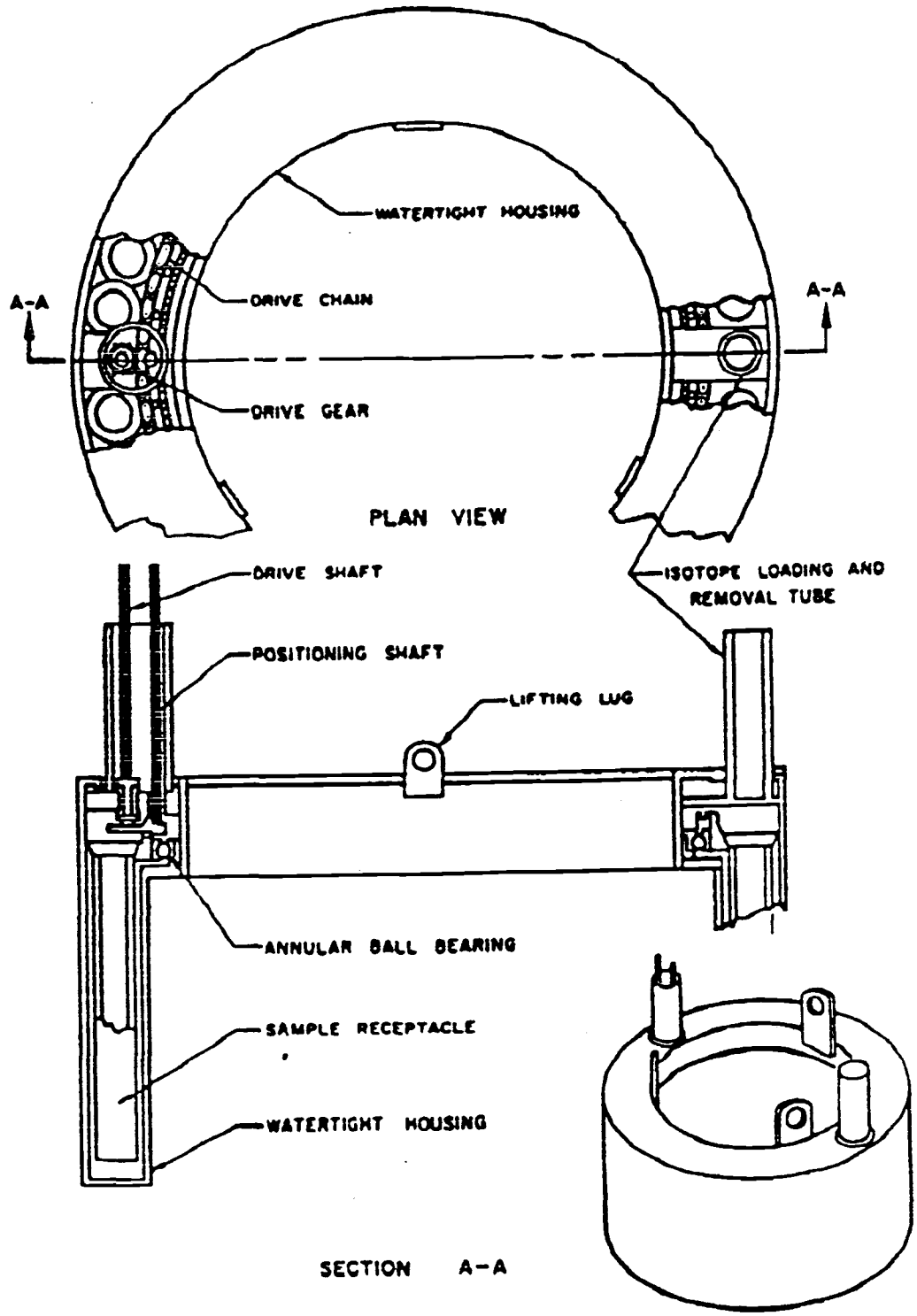

Fig.3. The Rotary Specimen Rack.

The radiation protection procedures followed during the unloading and counting of these samples are similar to those used during rabbit operation. After irradiation, the exposure rate (mR h^{-1}) of the activated samples was checked by Cutie Pie meter as follows :

WO = Window Open at contact reading ($\beta + \gamma$)

WC_1= Window Closed at one foot reading (γ only)

WC_2= Window Closed at one foot from centerline, reading true γ radiation.

From the above readings, the dose equivalent rate (mrem/hr) for beta particles and gamma rays can be calculated by using the following equations [15].

$$\text{Dose equivalent rate of contact } \left(\frac{\text{mrem}}{\text{h}}\right) = (\text{contact WO})\,(\text{BSCF})\left(\frac{\text{Area of CP Window}}{\text{Area of Source}}\right) \quad (20)$$

$$\text{Dose equivalent rate at one foot } \left(\frac{\text{mrem}}{\text{h}}\right) = [(WO - WC_1)\left(\frac{BSCF}{2}\right)] + WC_2 \quad (21)$$

where

BSCF = beta surface calibration factor; normally having a value of 4.

Equation (20) is only applied if the ratio of the area of the CP window to the area of the source is greater than one.

The total activity produced during rotating rack irradiations (in mCi) was estimated by equation (19).

After the long activation, the irradiated samples were moved to clean 2-dram polyvials, placed in a proper lead cask and transferred to the Ge(Li) spectrometer system for counting. Then one sample was

counted for 6 hours. The ^{75}Se peak at 264 keV has not been observed due to the compton effect and the high dead time. Since the half-live of ^{75}Se is 120 d, the irradiated samples were placed in a Pb-lined cave for three weeks. This allowed the radioisotopes ^{24}Na ($T_{1/2}$ = 15 h), ^{82}Br ($T_{1/2}$ = 35 h) and other short-lived radionuclides to decay to negligible levels to increase counting accuracy for ^{75}Se. The counting time for each sample was one day. This counting time allows the ^{75}Se peak to be identified. Table 2 summarizes the INAA parameters for short and long activation.

Table 2. INAA Parameters

1. Short Activation

Facility: Pneumatic Transfer (Rabbit)

Power level = 1MW ($\varphi = 9 \times 10^{12}$ n cm^{-2} s^{-1})

Irradiation time = 27 s

Decay time = 25 s

Counting time = 40 s

2. Long Activation

Facility: Rotating Rack

Power level = 1MW ($\varphi = 3 \times 10^{12}$ n cm^{-2} s^{-1})

Irradiation time = 13 h

Decay time = 21 d

Counting time = 1 d

6. Gamma-Ray Spectrometer System

After the unknown and standard samples are irradiated, they can be analyzed by observing the gamma-rays emitted upon decay of the radioisotopes. This analysis usually involves the evaluation of complex gamma-ray spectra. The high energy resolution of germanium spectrometers make them the detectors of choice for this type of analysis.

6.1. Counting Equipment

For the long activation analysis two gamma ray spectrometers were used, a coaxial Ge(Li) and a low-energy photon spectrometry (LEPS). A Princeton Gamma Tech (PGT) coaxial Ge(Li) semiconductor detector with 97 cm^3 active volume housed in a 10 cm thick background lead shield was used to measure the gamma ray energy spectrum of a sample after activation.

The Ge(Li) spectrometer system is composed of a high voltage power supply (ORTEC 459), a preamplifier (PGT RG-11), an amplifier (ORTEC 572), a counter/timer (Canberra 1776), and an 8192 channel multichannel analyzer (ORTEC 918A). The multichannel analyzer consists of a buffer which collects and stores all counts verses channel number data and a Leading Edge personal computer which controls the buffer and performs data analysis. The block diagram of Fig. 4 shows how the components are interconnected.

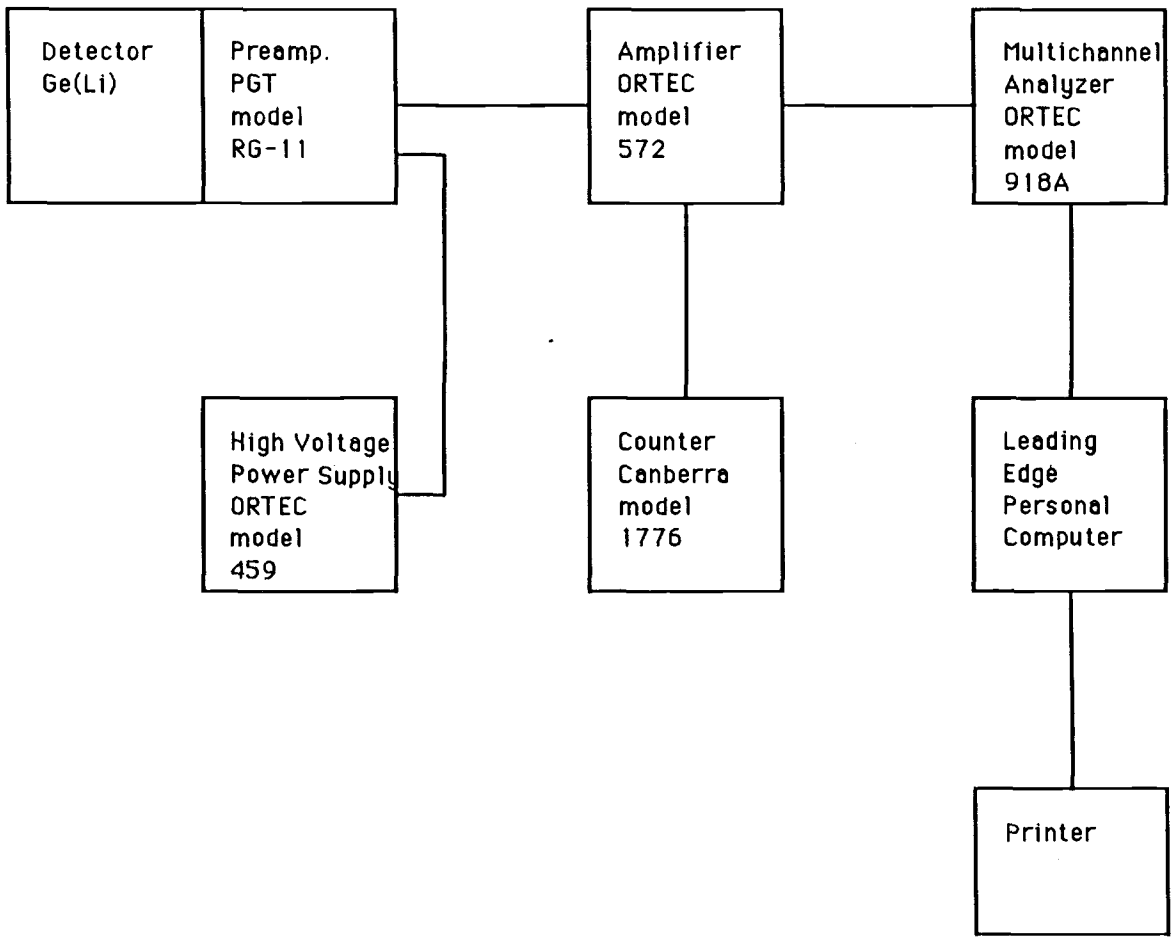

Fig. 4. A Schematic Diagram of The Electronic Setup of The Ge (Li) Detector.

The PGT Ge(Li) detector used in this work had a 13% relative efficiency (relative to a 58 cm^2 NaI(Tl) detector at 1.332 MeV, ^{60}Co) and a full width at half-maximum of the system was 2.1 keV at 1.332 MeV with a peak to Compton ratio of 47:1. A source to detector distance of 10 mm was used for all counting.

To analyze low energy gamma rays a low-energy photon spectrometry (LEPS) detector was used. The LEPS is a planer high-purity germanium photon detector designed for use in application over the approximate energy range of 3 keV to 1 MeV. The High-Purity Germanium (HPGe) LEPS's active area was 1000 mm^2 with a thickness of 3 mm. This system was composed of a high voltage power supply, a preamplifier, an amplifier, counter/timer, and a multichannel analyzer. The multichannel analyzer (MCA) included a buffer for data collection and storage was controlled by a Leading Edge personal computer. The block diagram for the LEPS system is shown in Fig. 5.

For the short activation samples, a HPGe coaxial detector was employed. The HPGe detector was accompanied by a high voltage power supply, a preamplifier, an amplifier, a counter/timer, and a 4196 channel multichannel analyzer. The HPGe detector configuration is shown in Fig. 6. This detector has a 29.1% efficiency (relative efficiency at 1.33 MeV, ^{60} Co) and a full width at half-maximum resolution of the system was 1.70 keV with a peak to Compton ratio of 66 : 1.

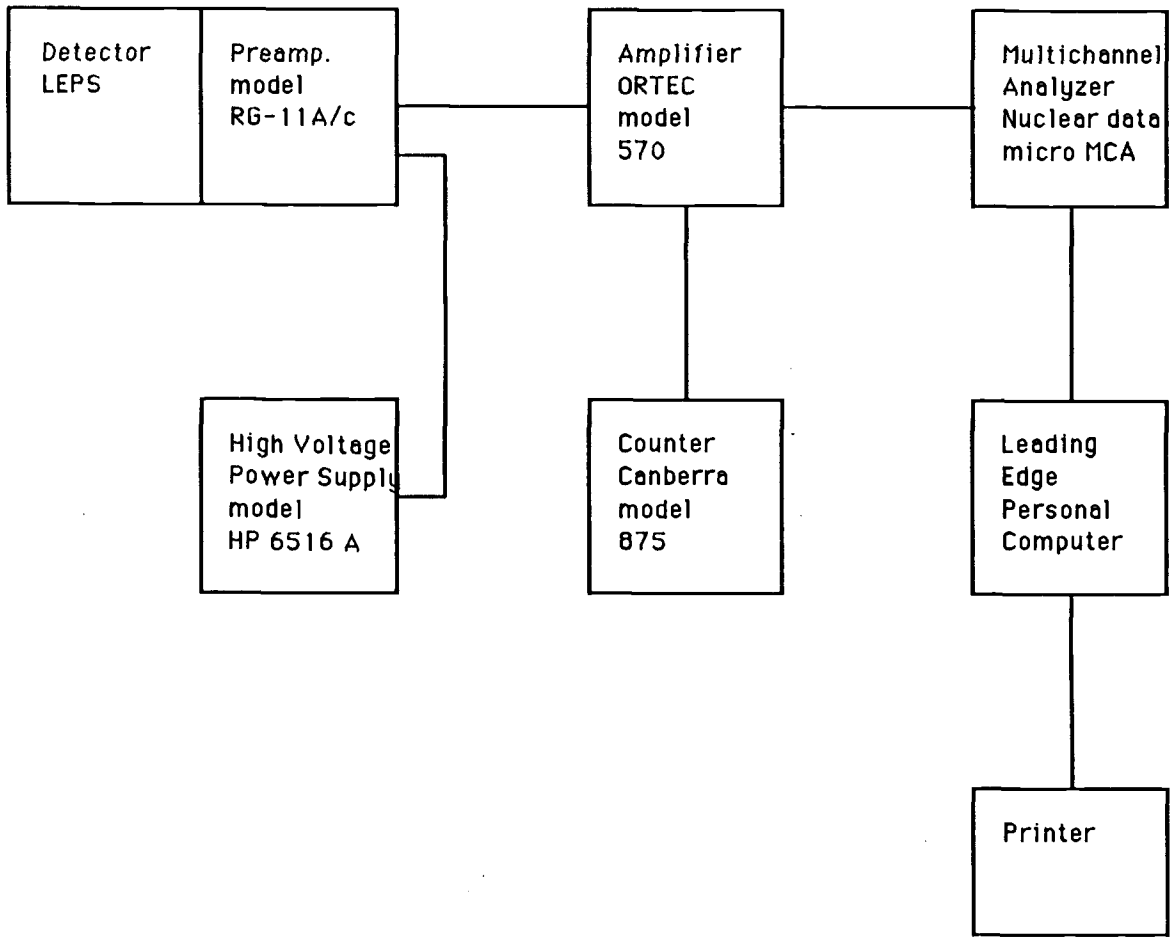

Fig. 5. A Schematic Diagram of The Electronic Setup of The LEPS Detector.

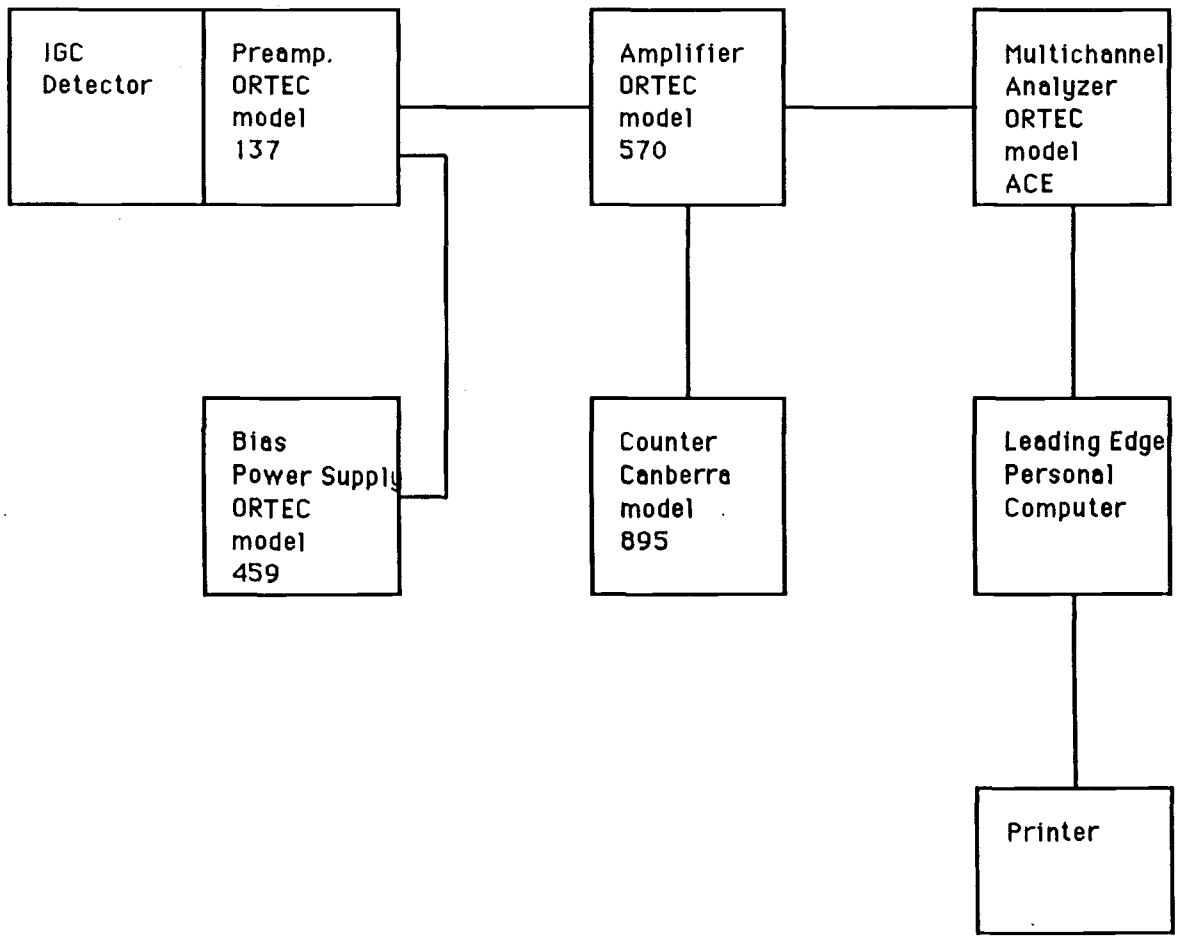

Fig. 6. A Schematic Diagram of The Electronic Setup of The IGC Detector.

6.2. Energy and Efficiency Calibration

Since the key feature of most gamma-ray spectrometers is a linear relation between the magnitude of the voltage pulse generated from the gamma-ray detector and the energy deposited in the detector crystal by a gamma-ray, the counting system must be calibrated to determine the exact form of this linear relationship for the spectrometer.

The calibration source of known gamma energies was used to fit gamma ray energy data versus the channel number. Also, the source was used to fit the absolute efficiency versus channel number.

For the long activation, a calibration standard (SRM 4275-B-53) mixed isotopes source was used to calibrate the Ge(Li) and LEPS systems for data reduction. Table 3 summarizes the nuclear properties of the calibration standard. The source was placed 10 mm away from the Ge(Li) detector and counted for 1000 s. Then, the EG & G ORTEC software program GELIGAM, version 2.05 was employed to fit gamma ray energy data versus the channel number from 86 to 1596 keV by using a single quadratic equation. The following equation was obtained for Ge(Li) detector using the SRM source.

$$\text{ENERGY} = 0.123 + 0.249\ \text{CHAN} + 9.74 \times 10^{-9}\ \text{CHAN}^2 \qquad (22)$$

Table 3. Nuclear Properties of Calibration Standard SRM 4275-B-53

Calibration Date: 1-May-83

Nuclide	Half Life (days)	γ-Energy (keV)	Percent Abundance	Yield (γ/Sec)	Activity (μCi)
^{155}Eu	1741	86.543	30.8	7865	0.7162
^{155}Eu	1741	105.308	20.5	5432	0.7162
^{154}Eu	3127	123.14	40.50	18790	1.223
^{125}Sb	996.45	176.334	0.18	53.77	0.8073
^{154}Eu	3127	248.04	6.59	3184	1.223
^{125}Sb	996.45	380.435	1.52	448.5	0.8073
^{125}Sb	996.45	427.889	29.44	8794	0.8073
^{125}Sb	996.45	463.383	10.45	3092	0.8073
^{154}Eu	3127	591.74	4.84	2279	1.223
^{125}Sb	996.45	600.557	17.78	5224	0.8073
^{125}Sb	996.45	635.895	11.32	3338	0.8073
^{154}Eu	3127	723.3	19.70	9249	1.223
^{154}Eu	3127	873.19	11.50	5613	1.223
^{154}Eu	3127	996.32	10.30	4805	1.223
^{154}Eu	3127	1004.76	17.89	8331	1.223
^{154}Eu	3127	1274.45	35.50	16060	1.223
^{154}Eu	3127	1596.48	1.67	816.2	1.223

Since the coefficient of $CHAN^2$ in equation (22) is negligible compared to the other terms, this relation could be considered linear.

The gamma energy (keV) versus channel number calibration measured with the mixed SRM source, is shown in Fig. 7.

The GELIGAM program also uses the following equations to fit the efficiency curve, one on each side of a point of inflection (176.00 keV). The form of the equation is

$$\ln (Eff) = a + b \ln E + c \ln E^2$$

For an inflection point at 176 keV, the efficiency fit is

$$Ln(EFF) = -21.539 + 7.941\ Ln(keV) - 0.823\ Ln(keV)^2 \qquad (23)$$

for $E < 176$ keV and

$$Ln(EFF) = 7.1307 - 2.497\ Ln(keV) + 0.1235\ Ln(keV)^2 \qquad (24)$$

for $E > 176$ keV.

The efficiency calibration curve obtained with the SRM source is shown in Fig. 8. The efficiency curve spans an energy range of 80-1760 keV, which covers the radioisotopes measured.

All unknown and standard samples were counted at a distance of 10 mm away from the detector.

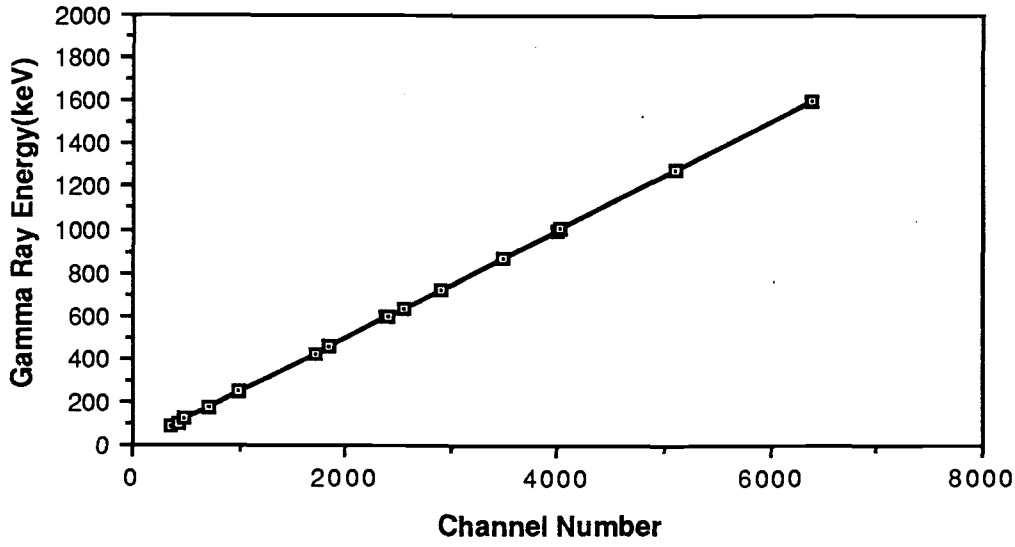

Fig.7. Channel Number-Gamma Energy Calibration Taken by Ge(Li) Detector with Mixed SRM Source.

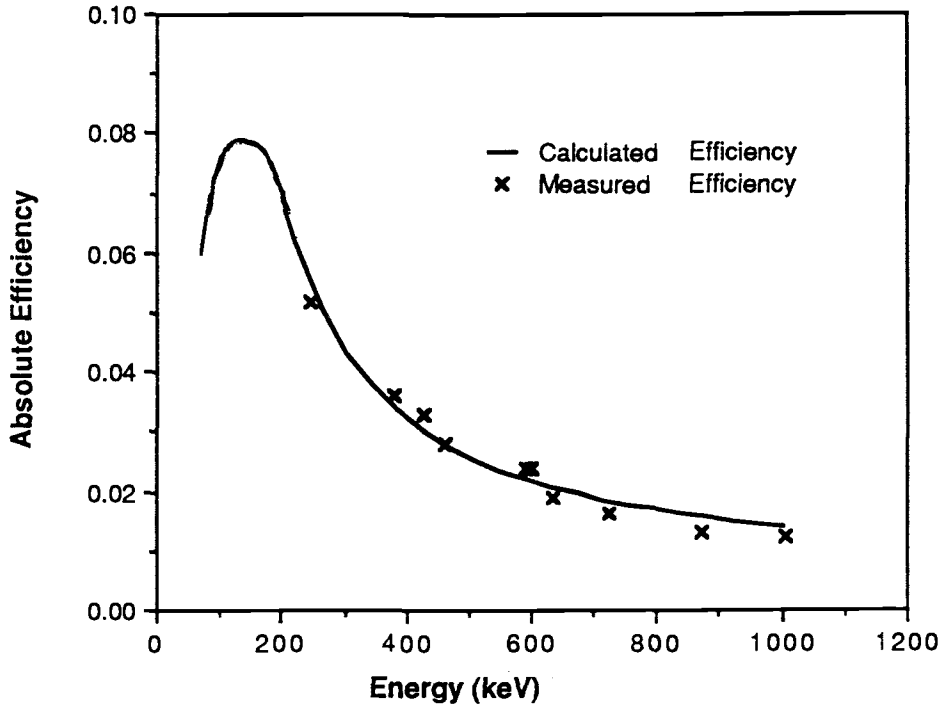

Fig.8. Gamma Ray Efficiency Curve for the Ge(Li) Detector Taken with the Mixed SRM Source.

The following energy calibration equation was obtained for the LEPS detector within the SRM source.

$$ENERGY = 0.3587 + 0.05\ CHAN + 1.29 \times 10^{-8}\ CHAN^2 \qquad (25)$$

The gamma energy (keV) versus channel number calibration measured on the LEPS with a mixed SRM source is shown in Fig. 9. The efficiency calibration curve obtained with the SRM source is shown in Fig. 10.

For short activations, a standard ^{152}Eu disk source was used to calibrate the counting system. Table 4 summarizes the nuclear properties of this calibration standard. The source was placed 70 cm away from the detector and counted for 1000 s. The following equation was obtained with the ^{152}Eu source.

$$ENERGY = 3.457 + 0.498\ CHAN + 3.024 \times 10^{-7}\ CHAN^2 \qquad (26)$$

The channel number versus gamma energy (keV) calibration measured on the Intrinsic Ge(Li) with ^{152}Eu source is shown in Fig. 11.

The GELIGAM program also uses the following equations to fit an efficiency curve, one on each side of a point of inflection (160 keV).

For an inflection point at 160 keV, the efficiency fit is:

$$Ln(EFF) = -6.191 + 0.2929\ Ln(keV) \qquad (27)$$

for $E < 160$ keV and

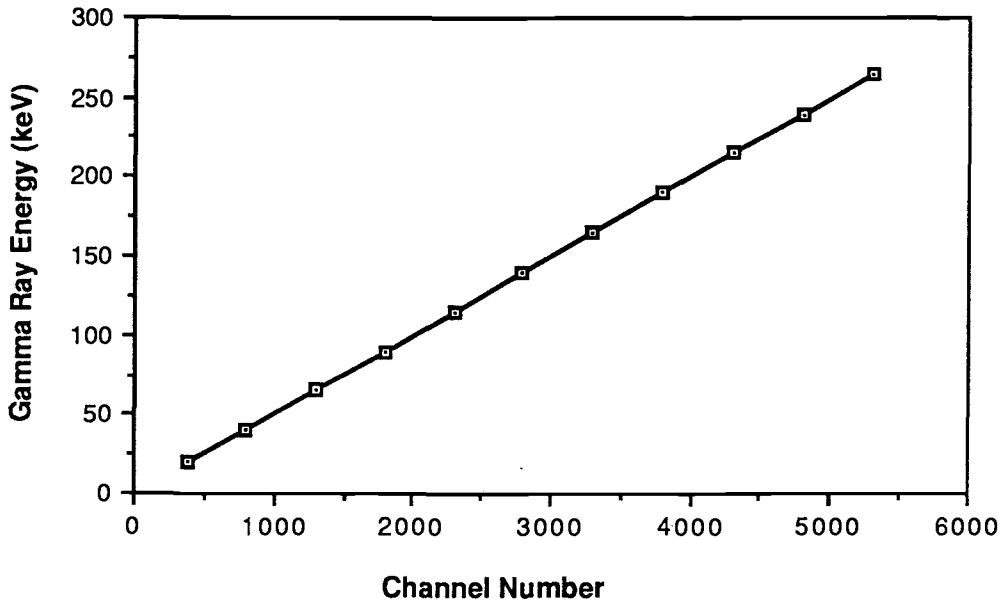

Fig.9. Channel Number-Gamma Energy Calibration Taken by the LEPS Detector with the SRM Source.

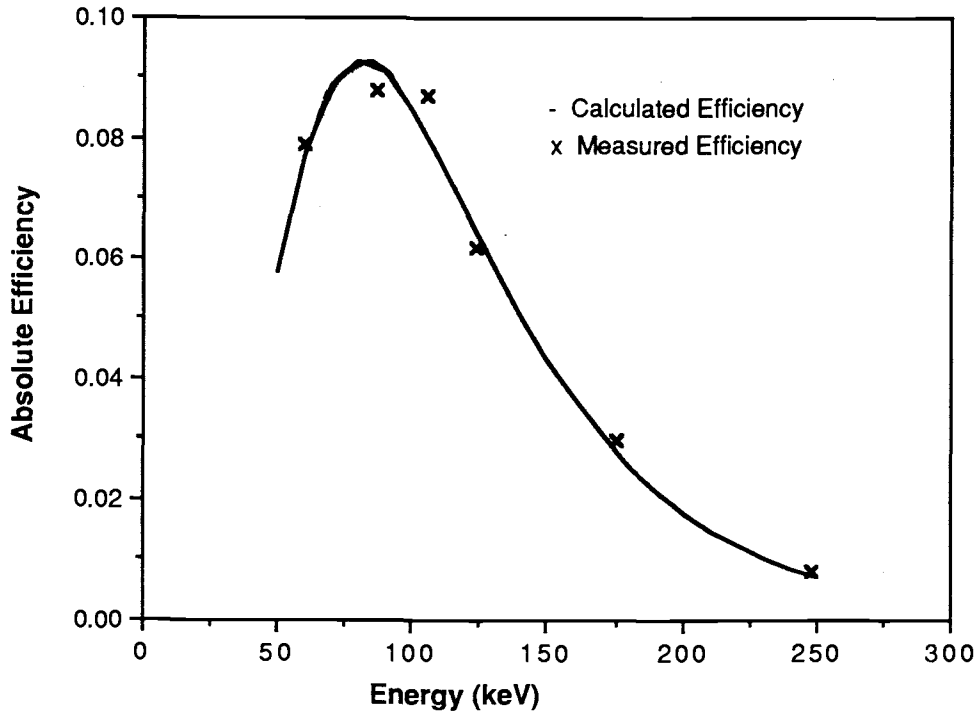

Fig.10. Gamma Ray Efficiency Curve for the LEPS Detector Taken with the SRM Source.

Table 4. Nuclear Properties of Calibration Standard ^{152}Eu

Calibration Date: 1-Feb-85

Nuclide	Half Life (days)	γ-Energy (keV)	Percent Abundance	Yield (γ/Sec)	Activity (μCi)
^{152}Eu	4964	121.779	28.32	11872	1.133
^{152}Eu	4964	244.693	7.51	3148	1.133
^{152}Eu	4964	344.281	26.67	11180	1.133
^{152}Eu	4964	411.115	2.28	956	1.133
^{152}Eu	4964	433.98	3.12	1308	1.133
^{152}Eu	4964	778.91	12.96	5433	1.133
^{152}Eu	4964	867.32	4.16	1744	1.133
^{152}Eu	4964	964.131	14.62	6129	1.133
^{152}Eu	4964	1112.02	13.56	5684	1.133
^{152}Eu	4964	1299.04	1.61	675	1.133
^{152}Eu	4964	1407.954	20.85	8741	1.133

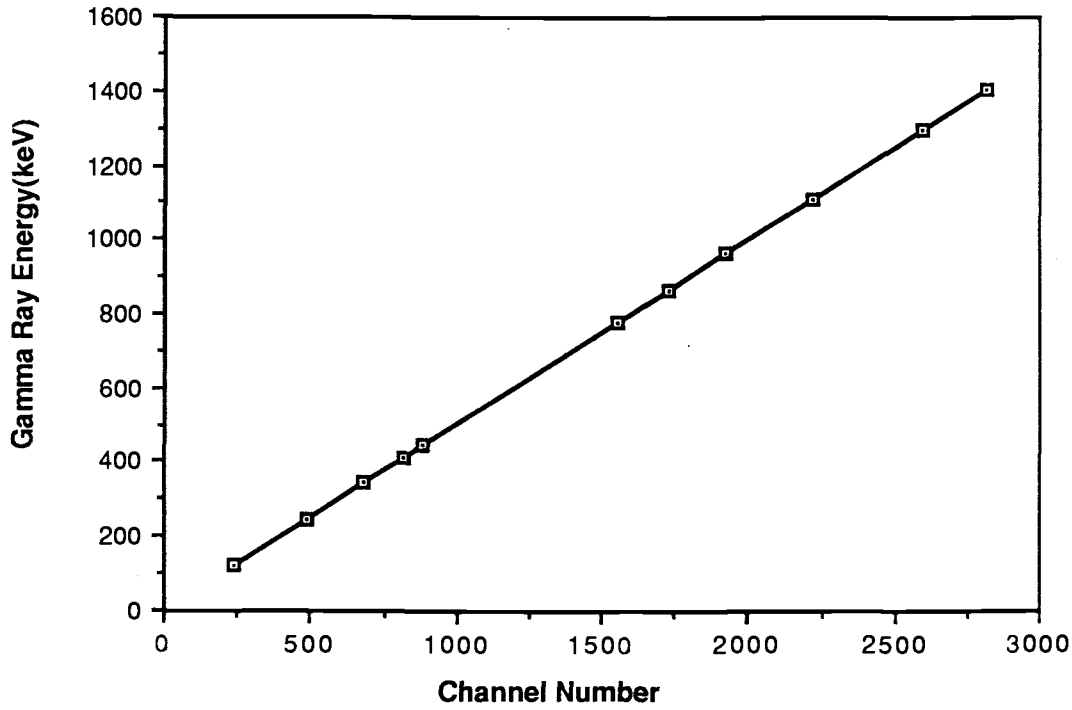

Fig.11. Channel Number-Gamma Energy Calibration Taken by the Intrinsic Ge(Li) Detector with the ^{152}Eu Source.

$$\text{Ln(EFF)} = 0.235 - 1.1325\ \text{Ln(keV)} + 0.0314\ \text{Ln(keV)}^2 \qquad (38)$$

for E > 160 keV.

The efficiency calibration curve obtained with ^{152}Eu source is shown in Fig. 12.

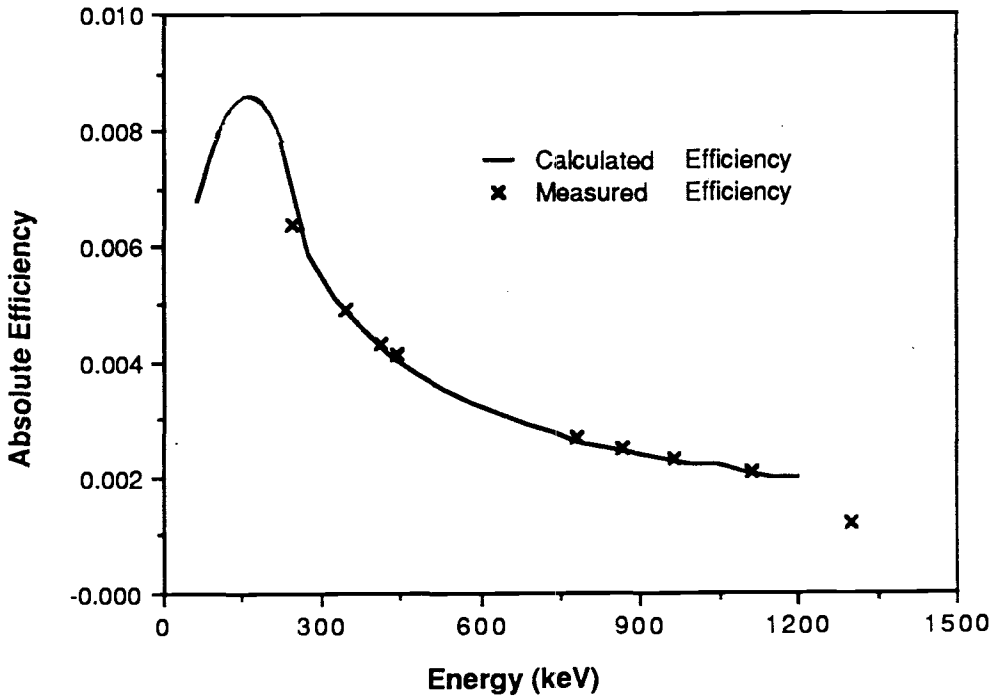

Fig.12. Gamma Ray Efficiency Curve for Intrinsic Ge Detector Taken with the ^{152}Eu Source.

6.3. Data Reduction

The interpretation of gamma-ray spectra obtained from a Ge(Li) detector typically involves: (1) identifying photopeaks of interest in the spectra; (2) determining photopeak energies; (3) calculating net counts under the photopeak areas; (4) and determining the concentrations of the elements from which the gamma-ray emitters were generated [6].

Since the system was energy calibrated (see section 5.2), the photopeaks of interest and their energies had been located and identified.

The shape of the gamma-ray pulse height distribution, i.e., the number of counts as a function of pulse height (gamma ray energy) is shown in Fig. 13.

To calculate the net counts (N) under a photopeak and its associated uncertainty (σ) the following formula was used [9]:

$$N = T - C \qquad (29)$$

where

N = net counts under photopeak,

T = total counts in the n channels of the photopeak,

and

C = total counts in the n Compton background channels = $\frac{n}{2}\left(\frac{t_1}{n_1} + \frac{t_2}{n_2}\right)$

The associated uncertainty is given by:

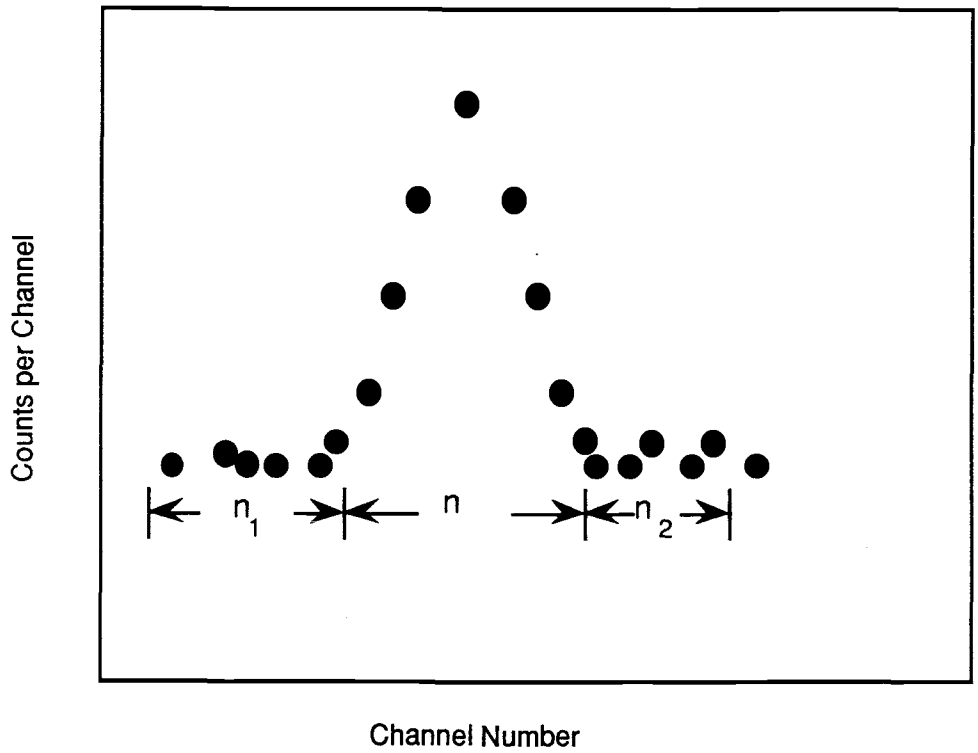

Fig.13. Definition of Photopeak Parameters for Peak Area Calculation.

$$\sigma = [\frac{n^2}{4} (\frac{t_1}{n_1^2} + \frac{t_2}{n_2^2})]^{1/2} \quad (30)$$

where

t_1= total counts in n_1 channels to the left of photopeak.

t_2= total counts in n_2 channels to the right of photopeak.

Note that N will be between N-σ and N+σat at 67% of the time. Therefore, the net counts under a photopeak with associated uncertainty is given by:

$$N \pm \sigma = T - C \pm [\frac{n^2}{4} (\frac{t_1}{n_1^2} + \frac{t_2}{n_2^2})]^{1/2} \quad (31)$$

When $n_1 = n_2$, Eq. (31) simplifies to:

$$N \pm \sigma = T - C \pm [T + C (\frac{n}{2n_1})]^{1/2} \quad (32)$$

Equation (16) has been employed to determine the concentrations of the elements from which the gamma-ray emissions were generated.

For the data obtained from the short activation counts for 40 seconds, a spreadsheet program was used to calculate the concentrations in parts per million (ppm). This program, developed at OSU, uses equations (17) and (18) in section 3. The decay of the radionuclide during counting and the dead time of the detector were accounted for in the program.

6.4. Background Counting

When making radioactivity measurements, the background radiation must be counted and subtracted from the gross counting rate of the sample to determine the net sample activity.

In this study, for long irradiations, the background was counted for one day. It was found that the ^{75}Se photopeak was not detectable above the background due to the radionuclides listed in Table 5. For short activation, the background was counted for 40 s and no ^{77m}Se peak was observed.

Table 5. Radionuclides and Their Energies That Have Been Found from The Radiation Background

Radionuclide	Half life (year)	Energy (keV)	Abundance %
^{226}Ra	1600	168	3.28
		295.2	19.2
		351.2	37.1
		609.3	46.1
		1120	15.0
		1764	15.9
^{228}Ra	5.75	238.6	64.9
		510.8	11.5
		583.1	46.0
		794.8	4.8
		911.1	29.0
		968.9	17.0
^{40}K	1.28×10^9	1460.8	10.7

7. Results And Discussion

In order to verify the technique for measurement of selenium which is used in this work, a set of samples with a known concentration of selenium from the same stock solution were analyzed as blind samples and other replicate samples of a National Bureau of Standards, bovine liver were analyzed.

The results of the replicated standard test are presented in Table 6. The mean selenium content in the standard solution samples is 1.72±0.03 ppm. The total error of the measurement was estimated as the square root of the sum of squares of the individual errors divided by the total sample numbers. These data show that a high degree of precision is present in the measurement.

Table 7 shows the mean value of the measured selenium concentration in the bovine liver NBS-standard is 0.70±0.02 ppm. The certified value is 0.71±0.07 ppm. To verify that these values agree the following hypothesis is tested:

It was assumed that a normal sampling distribution of mean selenium concentration was appropriate. Since the sample size is small (n = 5), the hypothesis can then be tested by a *t* test with level of significance 0.05. The steps in the analysis are as follows [16].

Table 6. Se Concentration in Replicate Standard Samples

Replicate Sample No.	ppm±error
1	1.73±0.07
2	1.72±0.07
3	1.73±0.07
4	1.73±0.07
5	1.71±0.08
mean	1.72±0.03

Table 7. Se Concentration in Bovine Liver Obtained by Short Activation

Replicate Sample No.	Se Concentration ppm±error
1	0.69±0.07
2	0.69±0.04
3	0.70±0.05
4	0.69±0.04
5	0.72±0.05
mean	0.70±0.02
Certified value	0.71±0.07

H_o = null hypothesis (μ) = 0.71±0.07 ppm (The certified mean Se content per one gram sample).

H_a = alternative hypothesis ≠ 0.71±0.07 ppm.

$$\text{Test statistic } (t) = \frac{\bar{x} - \mu}{s/\sqrt{n}} \qquad (33)$$

where

$\bar{x}$ = the mean Se content per one gram sample = 0.70 ppm,

s = population standard deviation and

n = number of samples.

Therefore

$$t = \frac{0.70 - 0.71}{0.01/\sqrt{5}} = -2.2$$

Since the 95% (confidence interval) for the t-statistic with four degrees of freedom (df = 5 - 1 = 4) is from -2.78 to 2.78 (see appendix B), it follows that H_o would be rejected if t is greater than 2.78 or less than -2.78. In our case, the t value falls within the confidence interval and the null hypothes is not rejected. Hence, we can not conclude that the means are different at the 0.05 alpha level.

The percent error using the certified value as the " true value " can be calculated from the following formula:

$$\text{Error percent} = \frac{\text{true value - measured value}}{\text{true value}} \times 100 \qquad (34)$$

For this analysis technique an error of 1.4% was observed.

This means that the value of the Se content for the standard samples is 98.6% accurate and that the technique has a very high accuracy.

Table 8 shows the mean value of the measured Se concentration in the bovine liver NBS-standard is 0.73±0.04 ppm. The certified value is 0.71±0.07 ppm. To verify that these values agree the following hypotheses:

H_o = null hypothesis (μ) = 0.71±0.07 ppm

H_a = alternative hypothesis $\neq$ 0.71±0.07 ppm.

Therefore

$$t = \frac{0.73 - 0.71}{0.01/\sqrt{5}} = 4.5$$

Since the 95% (confidence interval) for the *t*-statistic with four degrees of freedom (df = 5 - 1 = 4) is from -2.78 to 2.78, it follows that H_o would be rejected if *t* is greater than 2.78 or less than -2.78. In our case, the *t* value falls outside the confidence interval and the null hypothes is rejected. However, Since the 99% (confidence interval) for the *t*-statistic with four degrees of freedom (df = 5 - 1 = 4) is from -4.6 to 4.6, the null hypothes is not rejected.

Table 8. Se Concentration in Bovine Liver Obtained by Long Activation

Replicate Sample No.	Se Concentration ppm±error
1	0.73±0.08
2	0.71±0.11
3	0.74±0.07
4	0.72±0.13
5	0.75±0.07
mean	0.73±0.04
Certified value	0.71±0.07

For this analysis technique an error of 3% was observed. This means that the value of Se content for the standard samples is 97% accurate and this means that long activation analysis for Se has high accuracy.

In general, the data in Tables 7 and 8 show good measurement precision and agreement with the certified value and most values of the individual samples fall within the certified value of 0.71±0.07 ppm. This means that a small error had been introduced in the weighing, pipetting, and activation process(flux gradient), and in counting the unknown and standard samples. In addition, this means that the major error is contributed from the integration of a full-energy peak.

The Se content and associated measurement error for each of the samples of natural water collected from the well in south Philomath in Benton County (see Fig.1), are presented in Table 9. The mean value of the Se in the well water is 0.02±0.001 parts per billion.

It should be mentioned that Se extraction efficiency was not calculated for samples 1 and 2, because the OSU Radiation Use Authorization could not be obtained within the time scope of this project. However, comparison between these samples' results with other samples' results which were not chemically separated provides good evidence that chemical separation works fairly well.

The data presented in Table 9, shows that Se content of water samples was found to be insignificant and definitely not dangerous.

Table 9. Se Concentration in Oregon Well Water Sample Measured by Ge(Li) Detector

Sample Number	Se Concentration ppb±error
1*	0.03±0.001
2*	0.02±0.001
3	0.03±0.002
4	0.02±0.001
5	0.01±0.001
mean	0.02±0.001

* Selenium chemical extraction employed

The mean value is substantially less than the drinking water standard set by the U. S. Environmental Protection Agency, i.e., 10 ppb Se [3].

It is believed that the Se concentration data of the present study are the first for this particular well water. However, the amounts of Se found by Hadjimarks and Bonhorst (1961) in well water located in three counties (Jackson, Josephine, and Klamath) of Oregon were between 2 ppb and less than 1 ppb .

In spite of the low concentration of Se found in water, the grass around the well was investigated to see if it had accumulated Se. Table 10 shows the Se content in these Oregon grass samples. Table 10 shows that the highest mean Se content is (0.15±0.003 ppm) within a 20 m radius from the well and the lowest (0.05±0.003 ppm) is within 60 m. Also, it shows that the mean Se content within 40 m is 0.08±0.004 ppm. These samples also have been analyzed by the fluorimetric method. The results obtained from this method are 0.14, 0.04, and 0.02 ppm for distance 20, 40, and 60 m from the well, respectively. Both neutron activation analysis and fluorimetric techniques show that the Se concentration in the grass samples is a function of the distance from the well (i.e., the closet to the well, the highest Se concentration). A comparison between the two methods is presented in Table 17.

Table 10. Se Concentration (in ppm) in Oregon Grass Samples Measured by Ge(Li) Detector

Replicate Sample No.	Radius from the well		
	20 m	40 m	60 m
1	0.12±0.007	0.07±0.013	0.06±0.009
2	0.16±0.007	0.07±0.007	0.06±0.008
3	0.18±0.007	0.09±0.007	0.04±0.006
4	0.13±0.006	0.08±0.007	0.05±0.008
5	0.15±0.007	0.08±0.007	0.05±0.007
mean	0.15±0.003	0.08±0.004	0.05±0.003

In this work, the animal feedstuffs (silage, prepared feed, and grass hay) samples were activated in a flux of approximately $3x10^{12}$ n cm^{-2} s^{-1} for 13 h, held for a 21 d decay period then counted for 24 h. The silage and prepared feed samples were counted using the Ge(Li) detector. Under these conditions, the mean value of Se was found to be 0.42±0.01 ppm in the silage and 0.22±0.004 ppm in the prepared feed. The Se content for each sample of the silage and prepared feed are given in Tables 11 and 12 respectively. These samples were also analyzed by Dr. F. Adams by using the automated fluorimetric method. He found the Se concentration in silage to be 0.65 ppm and 0.23 ppm in prepared feed. A comparison between the two methods shows a high degree of consistency. This comparison is presented in Table 17. The observed concentrations are considered high in the silage samples and medium in the prepared feed samples.

The Se content in the grass hay samples is low (0.03 ppm) as determined by the fluorimetric method (Dr. Adams). It was thought that the grass hay samples could be analyzed by the Ge(Li) detector. Unfortunately, this is not true. This is due to the high count rate of the background (i.e., there is no peak observed at 264.6 keV). Therefore, it was decided to carry out the analysis using the low-energy photon spectrometry (LEPS) detector. The Se content for each grass hay sample and the mean for all samples are shown in Table 13. The data presented in Table 13, show that the mean value of the Se content is 0.03±0.004 ppm. This value shows excellent agreement with the results

Table 11. Se Concentration in Washington Silage Samples Measured by Ge(Li) Detector

Sample Number	Se Concentration ppm±error
1	0.38±0.01
2	0.42±0.01
3	0.39±0.01
4	0.46±0.01
5	0.46±0.02
mean	0.42±0.01

Table 12. Se Concentration in Nevada Prepared Feed Samples Measured by Ge(Li) Detector

Sample Number	Se Concentration ppm±error
1	0.24±0.01
2	0.20±0.01
3	0.23±0.01
4	0.25±0.01
5	0.20±0.01
mean	0.22±0.004

Table 13. Se Concentration in Montana Grass Hay Samples Measured by LEPS Detector

Sample Number	Se Concentration ppm±error
1	0.03±0.006
2	0.04±0.006
3	0.03±0.009
4	0.04±0.009
5	0.03±0.01
mean	0.03±0.004

obtained by Dr. Adams, while also verifying that the neutron activation analysis technique can yield a similar sensitivity to that obtained by the automated fluorimetric method.

It should be mentioned that the excellent sensitivity (0.03 ppm) has been achieved with the LEPS for ^{75}Se at the 136 keV photopeak, because the LEPS's efficiency at 136 keV is approximately four times higher than ^{75}Se at 264.6 keV. For further confirmation, the net counting ratio (4:1) was checked for all samples that were counted with LEPS detector and it was found almost consistent for all of them. This does not apply for ^{75}Se at the 121.1 keV photopeak because it suffers from interference with the ^{152}Eu gamma-ray at 121 keV.

The lower limit of detection of Se by short activation analysis was measured by using samples with known concentrations of Se. Thirty samples of sheep blood plasma were analyzed by the automated fluorimetric method. These samples were provided by Dr. P. D. Whanger, who in a previous study [14] categorized the samples according to their mean Se concentrations as low (0.02 ppm), medium (0.20 ppm), and high (0.50 ppm).

In this study, the sheep blood plasma were activated in a flux of approximately $9x10^{12}$ n cm^{-2} s^{-1} for 27 s and NAA was performed based on the isotope ^{77m}Se. Under these conditions, the average Se concentration for each low, medium, and high categorized samples is 0.03±0.001 ppm, 0.27±0.01 ppm, and 0.52±0.02 ppm respectively. Tables 14, 15, and 16 show the number of samples which had been activated for each category and the concentration of each individual sample.

Table 14. Low Se Concentration in Sheep Blood Plasma Measured by HPGe Detector

Sample Number	Se Concentration ppm±error
1	0.04±0.003
2	0.02±0.002
3	0.02±0.003
4	0.02±0.002
5	0.05±0.003
6	0.04±0.002
7	0.02±0.003
8	0.01±0.002
9	0-trace
10	0-trace
mean	0.03±0.001

Table 15. Medium Se Concentration in Sheep Blood Plasma Measured by HPGe Detector

Sample Number	Se Concentration ppm±error
1	0.22±0.02
2	0.23±0.02
3	0.31±0.03
4	0.22±0.03
5	0.28±0.02
6	0.29±0.02
7	0.22±0.03
8	0.26±0.02
9	0.29±0.02
10	0.33±0.02
mean	0.27±0.01

Table 16. High Se Concentration in Sheep Blood Plasma Measured by HPGe Detector

Sample Number	Se Concentration ppm±error
1	0.66±0.07
2	0.48±0.05
3	0.47±0.04
4	0.54±0.05
5	0.54±0.05
6	0.53±0.04
7	0.46±0.04
8	0.48±0.04
9	0.52±0.04
10	0.53±0.05
mean	0.52±0.02

These data show not only excellent agreement with the reported results by the above investigator, but also show that neutron activation analysis has a similar detection limit to that of the automated fluorimetric method. A comparison between the two methods is presented in Table 17.

It should be mentioned that the ^{77m}Se gamma-ray peak at 162 keV was observed with a peak height to background ratio of approximately 8:1 and did not suffer from any interferences.

Table 17. Mean Selenium Concentration Comparison Between the Automated Fluorimetric Method and Neutron Activation Analysis.

	Se Concentration (ppm)	
Biological Sample	**Fluorimetric Method***	**NAA**
Oregon Grass		
20 m from well	0.14	0.15
40 m from well	0.04	0.08
60 m from well	0.02	0.05
Silage	0.65	0.42
Prepared Feed	0.23	0.22
Grass Hay	0.03	0.03
Low Plasma	0.02	0.03
Medium Plasma	0.20	0.27
High Plasma	0.50	0.52

* Average Automated Fluorimetric results obtained by Dr. P. D. Whanger and Dr. F. Adams

8. Conclusion

Both neutron activation analysis and automated fluorimetric method have been found to be useful techniques to measure Se in silage, prepared feed, grass hay, and blood plasma. The accuracy and the sensitivity of the neutron activation analysis technique have been found to be similar to that of automated fluorimetric method. Therefore, the choice of method can only be made on grounds of urgency, convenience and availability. Neutron activation analysis has the following advantages compared to the automated fluorimetric method.

1. One of the most important advantages of neutron activation analysis is that Se can be determined accurately and quickly by using ^{77m}Se. This isotope can be irradiated, decayed, and counted at the rate of one sample per 2 min. This means that a significant number of samples can be easily analyzed in a relatively short period of time.

2. Instrumental neutron activation analysis (INAA) is a nondestructive testing technique which allows further use of the samples. This is particularly advantageous when samples are in short supply. On the other hand, ashing and wet digestion by using concentrated perchloric acid are required in the automated fluorimetric method.

3. One of the major advantages of neutron activation analysis is that Se contamination is not a problem once activation has been completed because the contaminants, not being radioactive, are not

counted in the detector. This means that many samples can be handled at one time. However, the automated fluorimetric method needs to performed with great care to avoid contamination. Therefore more time is needed for the analysis to be completed.

4. INAA of Se can be employed with small samples sizes and relative ease of sample preparation.

Neutron activation analysis, like most other available testing methods for Se content determination, can not be employed without some associated problems (disadvantages).

These disadvantages compared to automated fluorimetric method are:

1. Employing neutron activation analysis requires access to a research reactor or other neutron source and a spectrometer system. By contrast, automated fluorimetric apparatus can be found in most laboratories in universities, hospitals, etc.

2. For long activations, the major disadvantages are the delay caused by the long irradiation, and long periods of post-irradiation (two weeks at least) holding and counting. On the other hand, the automated fluorimetric method has the advantage because there is no delay needed before the analysis takes place.

3. Since radioactive materials are produced by neutron activation, special working conditions, techniques, and precautions are required for handling radioactive samples to minimize radiation exposure and control undesirable contamination. However, the samples analyzed by automated fluorimetric method can be handled without difficulty.

From the above comparison, it can not be claimed that neutron activation analysis is always the best method for quantitying Se in the materials considered in this study. However, neutron activation analysis offers a good option for determining Se in biological materials because of its simplicity and reliability. The short activation analysis method is a faster technique than that of the automated fluorimetric method for the determination of Se in biological materials. It yields good accuracy and sensitivity (0.03 ppm) which is sufficient for many investigations on Se toxicities.

A significant side benefit of this work has been the experience gained by the investigator not only in the area of neutron activation analysis, but also in many areas related to health physics, particularly in sample preparation, handling activated samples and evaluation of gamma-ray spectra using three different types of semiconductor radiation spectrometer systems. Since developing employee experience and knowledge in radiation protection and nuclear applications is part of the Kuwaiti governments goal and plan to meet current manpower and technological shortages, the experience and knowledge gained by the investigator will aid in the easing of these shortages.

The radiation protection practices of the OSU Radiation Center for activation analysis were implemented in this project not only to comply with federal, state and local regulations, but also to ensure that any exposure was kept as low as reasonably achievable. The radiation protection techniques and the recommended precautions did not cause much delay or interference with the experimental procedures.

9. Future Work

Since the time and the budget were limited for this project, the following suggestions are made for experiments to improve the accuracy and the sensitivity of the neutron activation analysis technique for determination of Se in natural water and biological materials.

Se extraction has been employed only on natural water in this project. However, the extraction efficiency has not been fully tested. An extraction efficiency test can be accomplished by using ^{75}Se as a radiotracer. The use of radiotracers has been employed to test the efficiency of separation procedures in analytical chemistry. The following procedures are advised to measure Se extraction efficiency method which are discussed in section 4. 3.

1- Ten mg of Se can be activated for 7 h to obtain the tracer ^{75}Se.

2- Dissolve and mix the tracer into 2-l of distilled water.

3- Pipette 1/2 ml amounts of the mixed water and place it into 1/2-dram polyvial.

4- To avoid the spread of contamination, the 1/2-dram polyvial should be placed into a 2-dram polyvial.

5- Count the sample for 1 or 2 h to obtain its activity (A_1). Then from the following equation, calculate the total activity(A) of the 2-l.

$$A = A_1 x \frac{V}{v}$$

Where

V = The original volume of water

v = The counted sample volume

6- Follow the procedures in section 4.2 for Se concentration and extraction.

7- After the extraction has taken place, pipette the upper organic phase which contains the DAN selenite and place it into a 1/2-dram polyvial.

8- Repeat step 4.

9- Count the sample to obtain its activity (A_2).

10- Compare between the two net photopeak areas (cpm) for the 264.6 keV γ-ray of ^{75}Se. The separation efficiency percent can be calculated from the following formula:

$$\text{Efficiency} = \frac{A_2}{A} \times 100$$

This investigation proved the concept of measuring Se concentration in water by analyzing the sample from the well in Benton County. A study of many different wells for the same county will provide more data and information on the Se content of subsurface water which will lead to better understanding of the hydrogeochemistry of Se in Oregon.

To improve the accuracy and the sensitivity for determination of Se in grass samples, it is suggested that grass samples be activated for 100 h, followed by a decay period of 60 d, and counting on the Ge(Li)

spectrometer for 12 h. These activation parameters will increase the sensitivity approximately 7 times and reduce the associated errors. This experiment can be performed at the OSU TRIGA reactor.

It should be mentioned that the encapsulation method which was employed for grass samples and discussed in section 4.3 is approved by the Reactor Operations Committee only for 13 MWh, or less, irradiation time. For more than 13 MWh, the primary containment must be a flame-sealed quartz or welded aluminum container and 2 dram polyethylene vial or vented 4-dram polyethlene vial or aluminum container for the secondary containment.

The investigator would like to recommend that determination of Se content in grass, silage, prepared feed and natural water be done by using the pneumatic transfer facility (Rabbit System) for short activation analysis for measuring either $^{77m}Se(T_{1/2}$ = 17.5 s) gamma-ray or ^{81m}Se ($T_{1/2}$ = 18 min) pure beta emitter.

Finally, since the Se content of human and animal feedstuffs varies widely due to the methods of preparation, the climatic conditions during the growing season etc., many investigators have started to use and compare different techniques for the determination of Se contents in foods and feeds. I suggest that neutron activation analysis should be used to determine the Se content in various biological and non-biological materials and it should be compared with other techniques currently employed. More specifically, the method should be compared with the automated fluorimetric method since it is still widely used and

with the X-ray fluorescence spectrometry since that is a nondestructive technique.

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APPENDICES

Appendices

Appendix A

Table 18. Certified Values of Constituent Elements of Bovine Liver

Element	Content ($\mu g\ g^{-1}$)	Element	Content ($\mu g\ g^{-1}$)
Arsenic	0.047±0.006	Mercury	0.004±0.002
Cadmium	0.44±0.06	Molybdenum	3.5±0.5
Calcium	120 ±7	Rubidium	12.5±0.1
Cobalt	0.21±0.05	Selenium	0.71±0.07
Copper	158 ±7	Silver	0.04±0.01
Iron	194 ±20	Strontium	0.138±0.003
Lead	0.135±0.015	Uranium	0.00071±0.00003
Magnesium	600 ±15	Vanadium	0.099±0.008
Manganese	9.9±0.8	Zinc	123±8

Appendix B

Table 19. *t* - CRITICAL VALUES [16]

Confidence Level	90%	95%	99%	99.9%
Degrees of Freedom				
1	6.31	12.7	63.66	636.62
2	2.92	4.30	9.93	31.60
3	2.35	3.18	5.84	12.92
4	2.13	2.78	4.60	8.61
5	2.02	2.57	4.03	6.86
6	1.94	2.45	3.71	5.96
7	1.90	2.37	3.50	5.41
8	1.86	2.31	3.36	5.04
9	1.83	2.26	3.25	4.78
10	1.81	2.23	3.17	4.59
z critical values	1.645	1.96	2.58	3.29
level of significance for a two- tailed test	0.10	0.05	0.01	0.001
level of significance	0.05	0.025	0.005	0.0005