THE INVESTIGATION OF SPICES BY USE OF INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

A Thesis

by

JATARA ROB WISE

Submitted to the Office of Graduate Studies of Texas A&M University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2008

Major Subject: Health Physics

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ABSTRACT

The Investigation of Spices by Use of Instrumental Neutron Activation Analysis. (August 2008) Jatara Rob Wise, B.S., Lamar University Chair of Advisory Committee: Dr. John W. Poston, Sr.

The spices consumed in the U.S. diet contain many elements other than the pure spice that many assume they eat. In particular, most of these spices contain radionuclides that are absorbed from the ground soil and water that contains trace contaminants. For this research, instrumental neutron-activation analysis (INAA) was used to determine the activities of U-235 fission products in common spices. Using this information, the concentrations of natural uranium in these spices and the doses to individuals consuming the spices were calculated.

 Nine spices and two standard reference materials were selected for analysis. The spices chosen were cinnamon, cumin, turmeric, oregano, thyme, cayenne, ginger, chili powder, and paprika. For comparison, NIST-certified "orchard leaves" and "spinach leaves" were used. The spices and standards were placed in polyethylene vials and heatsealed. The samples were divided into irradiation groups of 30 seconds, 12 hours, and long irradiations of 10 to 12.8 hours. After irradiation, all samples were counted on an HPGe detector for time periods ranging between 10 minutes to 65 hours. After counting, the results were analyzed using Genie 2000 software. The Genie 2000 analysis revealed no detectable fission products for samples irradiated for 30 seconds or counted for short

times. However, long counts revealed the high-yield U-235 fission products molybdenum-99 and what appeared to be cerium-144. However, after comparing the experimental values with the calculated values, it was determined that the experimental values of Ce-144 were not credible and the focus shifted solely toward Mo-99. From Mo-99 activities, uranium content could be calculated.

Using this information, the committed dose equivalent (CDE) and the committed effective dose equivalent (CEDE) for ingestion of uranium was calculated. The CEDE values were based on an assumed ingestion of 6.5 grams of each spice per year. The doses from ingesting these spices ranged from CDE and CEDE doses of 4.31E-05 mSv and 3.08E-06 mSv, respectively. Based on these measurements consumption of these spices, even when combined, would not result in annual CDE or CEDE doses approaching the limits for the public of 50 mSv and 1 mSv, respectively, for a year of chronic ingestion.

DEDICATION

I would like to dedicate this work to everyone who has helped me get to where I am today. This includes my family, inspirational non-family members, and countless individuals who had the patience to spend time with me and teach me the difference between right and wrong. I would like to give loving thanks to my wife Kellum B. Wise, who has given me unwavering support and love. I would also like to thank my mother Viola Wise, my sister Monica Wise, my two nieces Zaniya and Jala, and my nephew Jeremiah. Most of all I would like to give thanks to GOD, who lends an ear to listen and understands problems that no man can.

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I would like to acknowledge everyone who helped make this research possible. I would like to thank my committee, Dr. Warren Reece (member), Dr. Bill Batchelor (member), and Dr. John Poston, Sr. (chairman) for giving me the prized opportunity to study health physics at Texas A&M University. I would also like to thank Dr. Latha Vasudevan and Albert Tejerina for spending valuable time instructing and training me for various tasks.

I would also like to thank all of my professors in the Department of Nuclear Engineering at Texas A&M University for providing first-class teaching, instruction, and competence in everything associated with health physics.

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CHAPTER I INTRODUCTION

The use of spices and condiments in various foods and as medicinal remedies has been the practice since early humans gathered around rock-to-rock stricken fires for meals and healing ceremonies. It continues today as families gather around modern-day fireplaces for dinner or the application of herbal remedies for minor ailments. While most cultures use spices and condiments to season or preserve food, many people have little or no idea what is in their spice of choice. Normally, one would think everything that is in the spice is labeled on the container's list of ingredients. More in-depth thinking would reason that the spice probably contains fine particles of native soil or there may be some level of cross contamination with other spices during manufacturing, processing, and packaging. Albeit all of these are possibilities of what is in the spices we consume, there is relatively little thought given to the amount of radioactivity or the radionuclides contained in them.

 The most efficient way to determine the radiological composition present in spices and condiments is by use of Instrumental Neutron-Activation Analysis (INAA). This technique has been used by some investigators to identify the radionuclides present and to quantify the radionuclide activity levels in the spices. Another method of note is the Track-Etch Method (TEM); a technique by which damage by fission products are made visible for counting through electrochemical etching.

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This thesis follows the style of Health Physics*.*

There have been various studies in foreign countries concerning the radiological content in spices consumed in the daily dietary intake (DDI). In India, the use of spices in preparation of daily meals is prevalent. Some of the most commonly used spices are turmeric, cumin, and curry (a mixture of different seasonings to create a specific flavor or consistency). Sharma and his colleagues investigated eighteen spices and condiments common to the Indian diet. Their results revealed uranium concentrations from less than 0.3 picograms per gram (pg g^{-1}) to nearly 80 pg g^{-1} (Sharma et al. 1981).

Spice and condiments are also used for medical purposes. Some of the world's largest mineral deposits can be found in South Africa. These mineral deposits contain uranium and, therefore, the surface soil used to farm and grow food contains trace quantities of uranium. Thirty herbal remedies were collected from traditional healers and analyzed. The results showed concentrations of uranium above 40,000 parts per billion (ppb) in eight remedies and a mean uranium concentration of 15,000 ppb in the remaining herbs (Steenkamp et al. 2005). The unusually large uranium concentrations found by Steenkamp and colleagues made particularly interesting to study uranium concentration in spices found in the U.S. market.

It is well known that the earth's crust contains many naturally-occurring radionuclides and thus contributes to the natural background radiation. A small amount of this background radiation comes from man-made sources such as radioactive waste disposal, emissions from the burning of fossil fuels, nuclear power, medical uses of radiation and radioactivity, etc. Other sources of radiation that contribute to the background are cosmic rays, solar radiation, radioactivity inside the body from the food,

water, and the air we breathe, and radon gas. With all these possible sources, the question arises as to what levels of radioactivity are we consuming from the food we eat? This research is intended to focus on the levels of radionuclides present in the food we consume. More precisely, what are the levels of radionuclides in the spices and condiments commonly found in the U.S. diet? In this research, Instrumental Neutron-Activation Analysis (INAA) was be used to analyze a representative group of spices commonly found in the U.S. diet. After selecting and obtaining the spices, samples were prepared for irradiation in the nuclear reactor at Texas A&M University's Nuclear Science Center (NSC). The remaining samples were irradiated, for a specified time, using the pneumatic "rabbit" system at the NSC. All of the samples were then irradiated using standard irradiation procedures. After irradiation, the samples were removed from the reactor and the gamma emission spectra analyzed using a high-purity germanium detector (HPGe) available at the NSC. After analyzing these samples, specific attention will be given to:

- The presence of high-yield fission products of the U-235 isotope, and
- The calculation of radiation doses due to ingestion of the spices.

CHAPTER II

BACKGROUND

II.1 Instrumental Neutron-Activation Analysis

 Instrumental Neutron-Activation Analysis (INAA) is a sensitive analytical technique to precisely and accurately determine unknown elemental concentrations in various materials (James 2008). The concept behind INAA consists of preparing and irradiating small samples (usually milligram quantities) with thermal neutrons in a nuclear reactor to produce or activate specific radionuclides. Once irradiated, these nuclides produce characteristic gamma-rays which can be counted using a high-purity germanium (HPGe) detector. The energy of the gamma rays and their occurrence rates can be measured, leading to the identification and determination of the radionuclide activity in the sample. The measuring of the gamma-ray energy spectra is known as gamma spectroscopy and computer software is commonly used to determine the concentrations of the various elements in the sample usually in the upper range of parts per million (ppm) down to an lower limit of parts per billion (ppb) or less.

 When a material is bombarded with neutrons in a nuclear reactor, a number of events can occur depending on the spectrum of neutron energies present. The most common reaction is the (n, γ) reaction for activation products, however for this research the primary interest is in the (n, f) reaction for uranium.

II.2 The Fission Process

The fission process was discovered in 1938 by Otto Hahn, Lise Meitner, and Fritz Strassmann. U-235 is one of the most studied fissile radionuclides to date. Fission into two equal fragments is by no means the most probable mode in thermal-neutron fission; quite asymmetric divisions are much more favored, the maximum fission product yields occurring at A (mass number) = 95 to A=138 (Friedlander et al. 1964). Half lives of these fission products range from seconds (e.g., Kr-94, 1.4 seconds) or less to very long half lives (e.g., Nd-1244, 1.3 x 10^{11} years) to stable nuclides (e.g., Ba-138). The fission yield of a nuclide is the fraction or the percentage of the total number of fissions which leads directly or indirectly to that nuclide.

The focus of this work will be on high-yield fission products produced in the fission of U-235 rather than activation of a particular target material. Figure 1 shows the fission product yields as a function of mass number for the thermal-neutron fission of U-235. Note that the maximum fission yield for any radionuclide is less than 10%. In addition, although all data points are not shown in this figure, there are about 300 different nuclides (most radioactive) produced in the thermal-neutron fission of U-235.

Figure 1. Yield of fission-product chains as a function of mass number.

The primary interest here was in two high-yield fission products of U-

235. These two fission products were molybdenum-99 and cerium-144. The Genie 2000 software (see Chapter II.5) analyzed the information from the HPGe detector and calculated the activity or specific activity of the radionuclides in the sample generated by the software. The activity was checked by the following formula:

$$
A = N\lambda_{fiss}
$$

where,

A is the fission product activity,

N is the number atom of the fission product, and

 λ_{fiss} is the decay constant of the fission product.

The number of atoms of the fission product, N, is given by:

$$
N = (C)(m_s) \left(\frac{1}{m_{238}}\right) (Y_{235}) (N_A) (\sigma_{235}) (\phi) (t_{irr}) (Y_{fiss})
$$

where,

C is the concentration of uranium in the sample or standard,

 m_s is the mass of the sample grams,

 $m₂₃₈$ is the atomic weight of elemental uranium,

 Y_{235} is the naturally occurring fraction of the U-235 isotope,

 N_A is Avogadro's number, in units of mole⁻¹

 σ_{235} is the fission cross section of U-235 in barns,

 ϕ is the reactor fluence rate, in units of neutrons cm⁻²s⁻¹, and

 t_{irr} is the irradiation time in seconds, and

 Y_{fiss} is the yield of the primary fission product.

The decay constant λ_{fiss} for a single radionuclide is defined as:

$$
\lambda_{fiss} = \frac{\ln(2)}{T_{1/2}}
$$

w here,

 $T_{1/2}$ is the half-life of the radionuclide.

With this formula induced activity from the fission of U-235 is directly related to the mass of natural uranium in the sample. Using NIST-certified standards the whole analysis process from activation to output generated by the Genie 2000 software can be checked.

II.3 The Pneumatics System and Standard Irradiation

The pneumatics system at the NSC is an elaborate system of stainless steel and polyethylene tubes that stretch from the laboratory areas to the reactor core. A sample is placed in a secure chamber and transported via a blast of carbon dioxide $(CO₂)$ gas through the tubes into the reactor core and returned to the laboratory area after being irradiated for a pre-set time. The pneumatics system is mainly used for INAA.

 When carrying out an experiment using the pneumatics system, the experimenter has access to the system through the laboratory controller by receiving a "permit" or "green light" from the control room in the reactor area. The laboratory controller allows the investigator to determine the sample irradiation time by means of a two-way intercom system between the laboratory and the control room. When the irradiation is complete, the controller provides a "return" option to return the sample to the laboratory at any time regardless of the irradiation time remaining.

 Contained in the south station are two surge volumes to minimize any pressure transients when the system is in operation. Also contained in the south station are various solenoid isolation and regulating valves that supply approximately 80 pounds per square inch (psi) of $CO₂$ pressure to the receivers. The NSC also has a north $CO₂$ supply station that is similar to the south station. Both the north and south stations have "pressure adequate" system indication which will sound an alarm in the control room if the system pressure is too low for proper operation.

Before the pneumatics system can be used, the pressurized $CO₂$ gas supply has to be lined up for the specific laboratory that will be used in the process. A typical setup of a pneumatics system at a nuclear reactor site is shown in Figure 2.

Figure 2. Typical pneumatics system setup (Baranyai 2008).

The pneumatics system is a great tool for experiments that require short irradiation times. It is commonly used as a teaching tool in graduate and undergraduate courses. For this research, the pneumatics system was used identify quickly any possible unexpected radionuclides in the samples before the standard "long tube" irradiations were done.

 Standard irradiation or the "long tubes" is the most common irradiation technique at the NSC. Standard irradiation is a fairly straightforward process. First, the samples were weighted and packaged into polyethylene vials, placed in aluminum cans and

sealed. Then, the cans are placed in long tubes and lowered down near the reactor core in a specific geometric position and irradiated for periods ranging from 10 minutes to over 100 hours.

II.4 High-Purity Germanium (HPGe) Detector

For this research, INAA was used. The crux of the INAA process is measurement of the characteristic gamma rays after neutron activation. The HPGe detector at the NSC was used for the gamma-spectroscopy analysis and because the detector is so important, it is necessary to discuss HPGe characteristics.

 When performing gamma-ray spectroscopy it is important to have a depletion layer or active volume that is as thick as possible since the gamma rays are extremely penetrating radiation. The thickness of the depletion region, d, is given by the following expression:

$$
d = \sqrt{\frac{2\epsilon V}{eN}}
$$

where,

ε is the dielectric constant,

V is the reverse bias voltage,

e is the electronic charge, and

N is the net impurity concentration in the bulk semiconductor material.

Using silicon or germanium of normal semiconductor purity, depletion depths beyond 2 or 3 mm are difficult to achieve despite applying high bias voltages that are near the

breakdown level (Knoll 2000). The small band gap of germanium requires that an HPGe detector be operated at liquid-nitrogen temperature to reduce thermally-induced leakage currents, otherwise known as noise. Therefore, for more accurate gamma-ray spectroscopy, a more purified class of germanium is required. This more purified or ultrapure germanium is commonly known as "intrinsic" or "high-purity" germanium and detectors manufactured from this ultrapure germanium are usually called intrinsic or high-purity germanium (HPGe) detectors (Knoll 2000). While HPGe systems are operated at liquid-nitrogen temperatures to reduce noise, they can be kept at room temperature when not in use (Turner 1995). This setup makes it unnecessary to move or relocate the detector to a temperature controlled setting.

 HPGe detectors have specific principal configurations required for their use. For example, large single crystals of germanium can be grown slowly from commercial volume germanium that has gone through many processes to reduce impurities to as low as 10^9 atoms per cm³. This is the most highly-purified germanium that currently can be produced commercially. If the remaining low-level impurities are acceptors (such as aluminum), the electrical properties of the semiconductor crystal grown from this material is mildly p-type and π -type is the designation used to represent this type of ptype material (Knoll 2000). The depletion region is normally formed at $(p^+ v)$ or an $(n^+$ π) junction, not as an n-p junction. The two principal configurations are the planar configuration and the coaxial configuration. The planar configuration has an active volume of 10 to 30 cm^3 and the coaxial configuration has an active volume of less than

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or equal to 400 cm^3 . A schematic of the planar configuration of an HPGe detector is shown in Figure 3.

Figure 3. Configuration of a planar HPGe detector. The germanium semiconductor may be v type (p⁺ contact is rectifying), π type (n⁺ contact is rectifying), or lithium drifted (Knoll 2000).

As mentioned, the total active volume available in planar detectors does not exceed 10 to 30 cm³. To produce a detector with a large active volume needed for gamma-ray spectroscopy, a different approach is used. The large-volume detector is constructed in cylindrical or coaxial geometry as shown in Figures 4 and 5 (Knoll 2000).

Figure 4. Coaxial detector geometry. Shown are three common shapes of large-volume coaxial detectors. Each represents a cross-sectional view through the axis of a cylindrical crystal. The outer electrode is extended over the flat front (left) surface in both closed-ended cases (Knoll 2000).

Figure 5. Coaxial detector cross-sections. The HPGe material may be either high-purity p or n-type. The corresponding electrode configurations are shown for each type (Knoll 2000).

When completely assembled, the complete HPGe detector system consists of two basic components; the detector itself and the dewar, which contains the liquid nitrogen. HPGe detectors are the ideal detectors when gamma-ray spectroscopy is required. Besides offering superior energy resolution, HPGe detectors offer reasonable precision and

accuracy along with consistency. These are the reasons the detector system was chosen for this research. Figure 6 shows a schematic cross-section of the detector and the dewar. Figure 7 shows the cryostat-detector above the liquid nitrogen dewar.

Figure 6. Diagram showing the location of an HPGe detector (Knoll 2000).

Figure 7. Common horizontal configuration (Knoll 2000).

II.5 Genie 2000 Software

 The technique of neutron-activation analysis involves two basic steps, which are the actual neutron activation itself and then gamma-ray spectroscopy with the HPGe detector. Both of these are useless unless there is a way to analyze the results of the spectrum obtained using the HPGe detector. In this research, the software used for that task was Genie 2000. To identify a radionuclide, the Genie code uses matrix formalism. This formalism takes into account all peaks of a nuclide entered into the analysis library with their proper branching ratios (Genie 2000 Customization Tools Manual, 2004). At first the program builds a matrix of possible identifications by comparing each radionuclide in the analysis library against observed peaks (Genie 2000 Customization Tools Manual, 2004). Only radionuclides that meet certain criteria are accepted into the matrix (Genie 2000 Customization Tools Manual, 2004). The radionuclide will be

identified once it successfully meets the required criteria with a confidence index more than the threshold selected by the user.

 For this research, once the nuclide was identified, the parameter of most interest was the activity. The Genie 2000 software reports the activity per unit mass, given in units of microcuries per gram $(\mu Ci\ g^1)$. To calculate the activity, the Genie 2000 software first identifies the radionuclide by comparing the gamma-ray energies detected against known energies in its library. The software determines the activity of the gamma ray(s) emitted by the radionuclide by matching this energy with the corresponding efficiency () from the efficiency vs. energy curve of the HPGe detector. The efficiency is related to the activity by the following relation:

$$
\epsilon = \frac{the\ measured\ count\ rate\ of\ a\ standard}{actual\ decay\ rate\ of\ a\ standard}
$$

From this formula, the equation can be rearranged to find the activity. The efficiency vs. energy curve was generated via an efficiency calibration performed by the NSC staff. Figure 8 shows efficiency vs. energy curve for NSC HPGe detector.

Figure 8. Efficiency vs.energy curve.

CHAPTER III

MATERIALS AND METHODS

III.1 Pneumatics System Samples

For the first analysis, cinnamon, cumin, and turmeric (all powdered) were acquired from a local supermarket. The identification labels given to the spices were K (cinnamon), C (cumin), and T (turmeric). The standard reference material used in this stage of the experiment was NIST-certified orchard leaves. These NIST-certified (see Appendix C) leaves provided a means of comparison and were identified with the label X (orchard leaves). The spices and the standard were weighed and placed into plastic vials. First, the plastic vials were weighed alone and masses recorded as M_1 . Next, the spices and standards were placed in individual plastic vials, each weighed and recorded as M_2 . By difference, the mass of the spice was recorded as mass M_3 . The experiment plan at this phase called for the spice vials to contain approximately 200 milligrams of sample and for the vials containing the standard to contain approximately 100 milligrams. After the samples were weighed and packaged, two random cinnamon, turmeric, and cumin samples were selected. In all, thirty-six vials were prepared, eight samples of each spice and twelve standards.

Individual samples were placed in tubes in the pneumatic "rabbit" system and irradiated for 30 seconds to provide a quick check to identify for surprising radionuclides. After the 30-second irradiation, the samples were counted within. The samples were counted for 10 minutes on the HPGe detector. After being counted, the results were analyzed using the Genie 2000 software to identify the radionuclides present in the sample. The results can be found in Chapter IV.

III.2 Standard Irradiation Samples (12.8-hours)

The second stage involved a longer irradiation of the samples. After consultation with the NSC staff and knowing that a 30-second irradiation was insufficient to observe any detectable radionuclides, an irradiation time of approximately 12.8 hours was selected (this corresponded to a two shift irradiation). This group of samples was weighed and packaged in plastic vials using the exact same method as the first group of samples. These samples were also placed in three aluminum cans, put in the standard "long tubes," and irradiated for approximately 12.8 hours. The reason for this longer irradiation time was to make any radionuclides that may be present in the spices considerably more active and, hence, make it easier to identify the radionuclides. After consultation with the NSC staff, a period of seven days was chosen to allow short-lived radionuclides to decay. The majority of the samples were counted for 10 minutes to identify any notable activation products. As expected there were no detectable fission products with this short counting time. After further discussions with the NSC staff that samples K_6 , C_4 , and T_3 were counted for 65 hours to reveal fission products that were not detected with a shorter 10-minute count. After analyzing the samples using the Genie 2000 software, the results were interpreted and can be found in Chapter IV.

III.3 Standard Irradiation Samples (12-hours, 10-hours)

The third stage of this research involved the selection of more spices for an even broader investigation of the spices consumed in the United States. As was done in the first stage, these spices were obtained from a local grocery store. The spices chosen were thyme, ginger, paprika, chili powder, cayenne, and oregano, all in powdered form. The standard reference material chosen for this stage was NIST-certified "trace elements in spinach leaves," the certificate information can be found in Appendix D. The identification labels given to the spices were B (thyme), G (ginger), P (paprika), N (chili powder), E (cayenne), O (oregano), and R for the standard. These samples were weighed and packaged in vials in the same manner as for previous irradiations. In all, 48 samples were prepared, which consisted of 5 samples of each spice and 18 samples of the standard with an approximate mass of 200 milligrams for the spices and 100 milligrams for the standard. In addition to these samples, one larger sample of each spice was also prepared for irradiation. The only difference being roughly a factor of 4 increase in mass. The larger mass samples were irradiated for 10 hours and counted for 2 hours. Each spice group was placed in a separate aluminum can along with three standards and irradiated for approximately 12 hours using the long tubes. After a period of seven days had passed (to allow short-lived radionculides to decay), one sample from each spice group was counted. The results can be found in Chapter IV. A table of the involved masses can be found the Appendix E.

CHAPTER IV

RESULTS AND CONCLUSIONS

IV. 1 Pneumatics System Results

After the samples had been packaged, irradiated, counted on the HPGe detector, and analyzed, the Genie 2000 software provides an analysis report that must be interpreted by the investigator. For this research, the primary interest was in the reported activity calculated by methods shown in part II.4 of Chapter II. When U-235 fissions, there are over 300 fission products are produced with half-lives ranging from fractions of a second to thousands of years. In addition, some of the fission products are stable (e.g. Mo-100, Nd-148, and Sm-154). For this research, the search for fission products was reduced to radionuclides that could be detected at least seven days after the EOI and radionuclides with high yields. Since all samples irradiated by standard methods were counted at least seven days after irradiation, many of the fission products had decayed away. Many other fission products were present but, the primary interest was in the fission products with high yields.

 The data revealed that there were no detectable U-235 fission products for 30 second irradiations. The only radionuclides found were some (n, γ) activation products such as K-42 and some common radionuclides associated with background radiation such as K-40. An example of the Genie 2000 report for a 30-second irradiation of sample K_3 can be found in Appendix A.

IV.2 Fluence Rate Calculations

 Table 1 lists samples that were irradiated for 12.8 hours and counted for 10 minutes. Here also there were no detectable fission products due to the short count time. The most common radionuclides were Fe-59 and Zn-65. In an attempt to gain confidence in the values that the Genie 2000 software provided, the reactor fluence rate was calculated (using Genie 2000 activity values) by the following formula:

$$
A = (m_{std})(C_{std})(N_A)(w_{rad})^{-1}(Y_{Rad})(\sigma_{Rad})\phi(\lambda_{Rad})
$$

wh ere,

 m_{std} is the mass of the standard,

 C_{std} is the radionuclide concentration of the standard found on the NIST certificate,

 N_A is Avagadro's constant,

 w_{Rad} is the atomic weight of the radionuclide in units of grams per mole,

 Y_{Rad} is the yield of the the radionuclide,

 ϕ is the fluence rate at the irradiation position,

 σ_{Rad} is the thermal-neutron cross section for the production of the radionuclide, and

 λ_{Rad} is the decay constant of the radionuclide.

All quantities were known except the reactor fluence rate and the equation can be solved to find the reactor fluence rate, ϕ . Table 1 shows the fluence rate calculations for orchard leaves samples that were irradiated for 12.8 hours and counted for 10 minutes.

Sample	Mass(g)	Radionuclide	Activity (μ Ci g^{-1})	φ (neutrons cm ⁻² s ⁻¹)
X_3	0.1082	$Fe-59$	$1.5E-02$	$5.3E+12$
		$Zn-65$	$3.2E-02$	$8.5E+12$
X_5	0.1026	$Fe-59$	1.9E-02	$6.9E+12$
		$Zn-65$	2.8E-02	$7.6E+12$
X_6	0.104	$Fe-59$	1.7E-02	$6.4E+12$
		$Zn-65$	2.4E-02	$6.5E+12$

Table 1. Fluence rate calculations using orchard leaves samples.

The average neutron fluence rate based on Fe-59 activities was found to be 6.2E+12 neutrons $\text{cm}^{-2}\text{s}^{-1}$ and the average neutron fluence rate based on Zn-65 activities was found to be $7.5E+12$ neutrons $cm⁻²s⁻¹$. These values agree well with the actual fluence rate value of 7.1E+12 neutrons $cm⁻²s⁻¹$ used at the NSC for this irradiation position.

IV.3 Uranium Concentration Calculations

For samples irradiated and counted for considerably longer times, the presence of U-235 fission product(s) was expected. While it is important to know the activity of the sample, the quantity sought is content of uranium in the spice, which is usually given in parts per billion. The content can be calculated from the activities using a simple ratio formula. The known content and measured activity of the standard was related to an unknown content and experimentally calculated activity of a spice sample. The unknown content of the spice sample was calculated using the following formula:

$$
m_{ratio}\left(\frac{A_{St}}{C_{St}}\right) = \left(\frac{A_{Sp}}{C_{Sp}}\right)
$$

where,

 m_{ratio} is the mass ratio of the standard to the sample,

 C_{St} is the uranium content of the standard,

 A_{St} is the activity of the standard,

 C_{Sp} is the uranium content of the spice, and

 A_{Sp} is the activity of the spice.

As mentioned in the Background section, the Genie 2000 software was used to determine the activity of a sample from the counts obtained using the HPGe detector. The calculated value for the activity of uranium in the NIST-certified orchard leaves is shown in Table 2. Also, the number of counts needed for the Genie 2000 software to identify the activity of the fission product is given by:

minimum counts = $(A)(t_C)(\epsilon)$

where,

A is the activity of the fission product, in units of becquerel's (Bq),

 t_c is the length of time the sample is counted, and

is the detector efficiency.

The expected activity of the NIST-certified orchard leaves and the minimum number of counts to see that activity for Ce-144 can be readily estimated using known information.

Table 2. Expected uranium activity and minimum counts calculation.

The above calculation is for activity from the U-235 fission product Ce-144 in orchard leaves, also listed is the expected counts and the expected activity, if counted for 12 hours. However, all samples analyzed with the Genie 2000 software consistently reported Ce-144 activities on the level of 1E-03 μ Ci g⁻¹. The latter value was extremely puzzling and a number of investigations were conducted to clarify this discrepancy. These investigations included;

- numerous and extensive recalculations
- counting the empty irradiated polyethylene vials (blanks) for uranium activity
- interference radionuclides with similar energies and half-lives as Ce-144

• high-background radiation levels in the detector room at the NSC.

After numerous recalculations, no calculation errors were found and the blanks and background contributed negligibly. The samples were also placed in new polyethylene vials and recounted. The recount confirmed earlier results, which eliminated the possibility of contamination in the vial. The background levels at the NSC were tested via an "empty count," for which the HPGe detect remained empty (free of samples), for 12 hours to determine the background levels. The "empty count" revealed no Ce-l44 or uranium background. After performing these investigations and ruling out the three aforementioned possibilities, it was concluded that the Genie 2000 software was identifying an interfering radionuclide with similar energy or there was a systematic problem with the Genie 2000 software.

 A similar calculation was performed for activity of Mo-99 in spinach leaves and was found to be 2.6 μ Ci g⁻¹for the spinach leaves. For Mo-99, there was better agreement between the predicted activity value and the Genie 2000 software activity value for two of the spices. Table 3 shows the uranium concentration calculated from Mo-99 activity. In Table 3, the uranium content was calculated for two samples with Mo-99 present is reasonable compared to the NIST-certified spinach leaves.

Table 3. Uranium content for samples with Mo-99 activity.

Sample	Label	M ratio	\sim s _t (ng g ⁻¹)	$A_{St}(\mu Ci\ g^{-1}$	$A_{\text{Sn}}(\mu Ci~g^{-1})$	$\bf{C_{Sn}}(ng~g^{-1}$
Oregano		1.96	:55	.41E-03	4.36E-03	245
Paprika			.55	.41E-03	.94E-03	

These agreements lead to the decision to analyze larger mass samples to investigate Mo-99 rather than Ce-144 which was plagued with small activities. Ce-144 has a half-life of 285.9 days and Mo-99 has a half-life of 2.75 days. There was a small window of opportunity to detect Mo-99 due to its short half-life and after time passed to allow short lived activations to decay. However, the half-life of Ce-144 is less active and its half-life is 104 times longer. Normally, there would have been no problem detecting Ce-144 but due to its small activity more time would have been needed to allow short lived isotopes to decay and a considerably longer count would have been needed. Mo-99 was more active than Ce-144 which made it possible to be detected in samples counted within 7 to 8 days after Genie 2000 software activity corrects for radioactive decay, correcting to the EOI but if the nuclide has decayed to negligible levels before being counted, obviously nothing can be done.

Samples with larger masses were analyzed (see Appendix F) to further confirm the above results for uranium concentration due to Mo-99 activity. Table 4 shows the results (note that the subscript L denotes the larger masses that were used).

Sample	Label	M ratio	$C_{St}(ng g^{-1})$	$A_{St}(\mu Ci~g^{-1})$	$A_{Sp}(\mu Ci~g^{-1})$	$C_{Sp}(ng g^{-1})$
Ginger	G_{L}	706692	155	5.07E-03	$.34E-03$	
Paprika		707455	155	5.07E-03	1.61E-03	29
Cinnamon	K_{L}	2.00157	155	5.07E-03	2.48E-03	38

Table 4. Additional larger mass calculations.

The Genie 2000 software initially reported the activity of the spinach leaves standard three times larger than the calculated value of $2E-3 \mu Ci$ g⁻¹ after a 2 hour count. The activity was reduced to only 2.5 times larger after a longer count of 12 hours. The Genie 2000 software reports these larger values because the peaks are so small that it systematically overestimates the activities. Figure 9 shows the plot of the spinach leaves spectrum with an arrow identifying the 140.5 keV peak of Mo-99 (note the scale is counts vs. energy).

Figure 9. Counts vs. energy.

Errors of this magnitude are acceptable due to:

- if they are systematic the ratios will cancel
- the answers are so low bounding values are acceptable

• the window of opportunity is limited by the half-lives if activation products and Mo-99.

There was not much that could have been done to make the concentration levels more accurate with this method (see Future Work).

IV. 4 Dose Calculations

 With the uranium content established, committed dose equivalent (CDE) and committed effective dose equivalent (CEDE) received from the consumption of the spices can be calculated. The following dose estimates were based on the consumer ingesting 6.5 grams of spice per year, inhalation of the spice was not considered. With the assumptions established, the formula used to estimate the CDE was:

$$
CDE = \frac{I_{Sp}}{ALI_N} \times 50 \, rem
$$

where,

C DE is the committed dose equivalent for ingestion,

 I_{Sp} is the intake of the spice, and

 ALI_N is the non-stochastic annual limit on intake for uranium (5E+05 Bq) based on 50 rems to the bone surfaces (ICRP 1979).

The CEDE values were calculated using the following formula:

$$
CEDE = \frac{I_{Sp}}{ALI_S} \times 5 \, rem
$$

where,

C EDE is an estimate of the committed effective dose equivalent for ingestion,

 I_{Sp} is the intake of the spice, and

ALI_S is the stochastic annual limit on intake for uranium (7E+05 Bq) based on 5 rems

(ICRP 1979).

Table 5 shows the CDE and CEDE values for uranium dose from spice ingestion.

Table 5. Uranium dose.

As mentioned, additional analysis was performed on samples with larger masses. Table 6 shows the results of analysis (note that the subscript L denotes larger masses used).

Table 6. Uranium dose (larger masses).

Sample	Label	CDE (mSv)	CEDE (mSv)
Ginger	G_{L}	1.94E-06	1.39E-07
Paprika	P_{L}	2.34E-06	1.67E-07
Cinnamon	$\rm K_{L}$	3.07E-06	2.19E-07
	Sum	7.35E-06	5.25E-07

The ALI values of 5E+05 Bq (non-stochastic) and 7E+05 Bq (stochastic) are taken from ICRP Publication 30. Although ICRP-30 was released in 1979, the data presented in it are still used in the U.S. Federal Regulations. In Tables 5 and 6, the summed values can be interpreted as a sum of all the combined intakes of each of the spices per year. It is obvious that the CDE and CEDE values even when combined, are well below the public annual limits 50 mSv (deterministic) and 1 mSv (stochastic). Hence, there is no apparent danger from the ingestion of these spices at the presumed mass.

IV. 5 Future Work

There are numerous ways in which this work may be advanced. For in-depth advancement, it comes down to the creativity of the investigator. For instance, the Compton suppression could be studied to maximize the signal-to-noise ratio to enable the software program to better analyze the Mo-99 spectrum information. Also very long count times could be done for more accurate identification of Ce-144.

REFERENCES

- Baranyai, Rózsa. Reactor-Neutron Activation Analysis. Budapest Neutron Center. 21 January 2008. Budapest Neutron Center. 9 May 2008 <http://www.bnc.hu/modules.php?name=News&file=article&sid=8>.
- Friedlander, Gerhart, and Joseph W. Kennedy, Julian M. Miller. Nuclear and Radiochemistry. 2nd. New York: Wiley & Sons, 1964.
- Genie 2000 Customization Tools Manual. Meridian, CT: Canberra Industries, Inc, 2004.
- International Committee on Radiological Protection (ICRP), Limits for Intakes of Radionuclides by Workers. ICRP Publication 30 Part 1(1979): 83-95.
- James, William. Neutron Activation Analysis. Elemental Analysis Laboratoty. 01 February 2008 . Texas A&M University Department of Chemistry. 9 May 2008 <http://www.chem.tamu.edu/services/naa/naa.htm>.
- Knoll, Glenn. Radiation Protection and Measurement. $3rd$. New York: Wiley & Sons, 2000.
- Sharma, Lal, Manesh, Nagpaul, S.K. Chakarvarti. Trace Content of Uranium in Spices and Condiments. Health Physics 41(4) (1981): 680-682.
- Steenkamp, Stewart, Chimuka, Ewa Cukrowska. Uranium Concentrations in South African Herbal Remedies. Health Physics 89(6) (2005): 678-683.
- Turner, James. Atoms, Radiation, and Radiation Protection. 2^{nd} . New York: Wiley & Sons, 1995.

APPENDIX A

GENIE 2000 REPORT FOR 30-SECOND (10-MINUTE COUNT) IRRDIATION

*** ***** G A M M A S P E C T R U M A N A L Y S I S ***** ***

Filename: I:\CAMFILES\Jatara Wise Spice Samples\20FEB08\JW_K3_20FEB08_S

** P E A K A N A L Y S I S R E P O R T ** Detector Name: SH Sample Title: JW_K3_20FEB08_SH Peak Analysis Performed on: 5/8/2008 11:00:53 AM Peak Analysis From Channel: 1 Peak Analysis To Channel: 8192 Peak ROI ROI Peak Energy FWHM Net Peak Net Area Continuum No. start end centroid (keV) (keV) Area Uncert. Counts 1 854- 867 860.70 312.69 1.30 8.58E+001 27.62 2.42E+002 2 965- 971 968.84 352.17 0.93 2.25E+001 14.82 1.05E+002 3 1394- 1411 1403.03 510.66 1.62 1.94E+002 31.27 2.41E+002 4 1515- 1530 1522.63 554.32 1.39 6.70E+002 34.32 1.69E+002 5 1691- 1708 1699.76 618.98 1.43 3.78E+002 31.71 1.93E+002 6 1908- 1925 1917.08 698.31 1.63 2.64E+002 25.13 1.13E+002 7 1961- 1968 1964.29 715.55 0.65 3.75E+000 9.95 4.73E+001 8 2121- 2139 2130.95 776.38 1.63 5.83E+002 30.73 1.07E+002 9 2265- 2280 2271.59 827.72 1.93 1.64E+002 19.73 7.42E+001 10 2317- 2332 2323.54 846.69 1.47 1.78E+003 45.16 8.73E+001 11 2853- 2868 2863.87 1043.93 1.29 1.53E+002 20.41 8.74E+001 12 3604- 3621 3613.17 1317.46 1.85 1.22E+002 20.04 8.57E+001 13 3744- 3763 3752.82 1368.44 2.08 8.53E+002 32.39 5.72E+001 14 4001- 4011 4005.81 1460.79 1.49 2.66E+001 8.97 2.24E+001 11 1001 1011 10001 10101 1111...
15 4036- 4053 4043.70 1474.62 1.88 7.60E+001 13.53 3.30E+001
16 4169- 4191 4180.35 1524.50 1.97 2.13E+003 47.10 2.32E+001 16 4169- 4191 4180.35 1524.50 1.97 2.13E+003 47.10 2.32E+001 17 4740- 4754 4746.74 1731.26 2.08 4.68E+001 8.91 1.12E+001 18 4954- 4971 4963.68 1810.45 2.27 1.98E+002 16.23 19 5782- 5801 5791.76 2112.74 1.80 1.06E+002 12.20 1.24E+001 20 7535- 7557 7546.72 2753.38 2.50 4.44E+002 22.13 1.16E+001

M = First peak in a multiplet region m = Other peak in a multiplet region F = Fitted singlet

Errors quoted at 1.000 sigma

= Energy line found in the spectrum. @ = Energy line not used for Weighted Mean Activity Energy Tolerance : 1.000 keV Nuclide confidence index threshold = 0.30 Errors quoted at 1.000 sigma

35

*** ***** INTERFERENCE CORRECTED REPORT ***** ***

 ? = nuclide is part of an undetermined solution X = nuclide rejected by the interference analysis @ = nuclide contains energy lines not used in Weighted Mean Activity

Errors quoted at 1.000 sigma

 $F =$ Fitted singlet

Errors quoted at 1.000 sigma

APPENDIX B

GENIE 2000 REPORT FOR A 12-HOUR (12-HOUR COUNT) IRRADIATION

*** ***** G A M M A S P E C T R U M A N A L Y S I S ***** ***

Filename: I:\CAMFILES\Jatara Wise Spice Samples\RFS08-109\JW_15APR08_SH Report Generated On : 5/8/2008 11:17:03 AM Sample Title $\qquad \qquad : \quad \text{JW_15APR08_SH}$ Sample Description : 01 Oregano Sample Identification : O1 Sample Type $\qquad \qquad :$ Sample Geometry : S1PS Peak Locate Threshold : 3.00 Peak Locate Range (in channels) : 1 - 65535 Peak Area Range (in channels) : 1 - 65535 Identification Energy Tolerance : 1.000 keV Sample Size : 2.127E-001 g Sample Taken On : 4/7/2008 9:06:00 PM
Acquisition Started : 4/15/2008 4:57:01 PM Acquisition Started Live Time $\qquad \qquad : \qquad 43200.0$ seconds Real Time $\qquad \qquad : \qquad 44020.8$ seconds Dead Time : 1.86 % Energy Calibration Used Done On : 4/15/2008

**

***** P E A K A N A L Y S I S R E P O R T ***** **

 Detector Name: SH Sample Title: JW_15APR08_SH Peak Analysis Performed on: 5/8/2008 11:17:03 AM Peak Analysis From Channel: 1 Peak Analysis To Channel: 8192

M = First peak in a multiplet region m = Other peak in a multiplet region F = Fitted singlet

Errors quoted at 1.000 sigma

Interference Corrected Activity Report 5/8/2008 11:17:05 AM Page 6

*** ***** NUCLIDE IDENTIFICATION REPORT ***** ***

 Sample Title: JW_15APR08_SH Nuclide Library Used: C:\GENIE2K\CAMFILES\STDLIB.NLB

Nuclide confidence index threshold = 0.30

Errors quoted at 1.000 sigma

46

*** ***** INTERFERENCE CORRECTED REPORT ***** ***

? = nuclide is part of an undetermined solution

X = nuclide rejected by the interference analysis

@ = nuclide contains energy lines not used in Weighted Mean Activity

Errors quoted at 1.000 sigma

 M = First peak in a multiplet region m = Other peak in a multiplet region

F = Fitted singlet

Errors quoted at 1.000 sigma

APPENDIX C

NIST-CERTIFIED "ORCHARD LEAVES" CERTIFICATE INFORMATION

Table 1. Certified Values of Constituent Elements[®]

The uncertainties shown above include both the imprecision, expressed as the standard deviation of a single measurement, and an allowance for unknown sources of systematic error.

Trace Constituents⁴

The uncertainties shown above are the imprecisions expressed as either two standard deviations of a single determination (commonly, but perhaps incorrectly, called the "95 percent confidence limit"), or the entire range of observed results - whichever of the two is larger. No additional allowance for the uncertainty from unknown sources of systematic error has been included, since these are considered to be small relative to the imprecision as expressed.

APPENDIX D

NIST-CERTIFIED "SPINACH LEAVES" CERTIFICATE INFORMATION

Table 2. Reference Concentration Values of Constituent Elements^{a,b,c}

a NIST has replaced the previously used term "non-certified" with "reference value" or "information value," as appropriate.

 $_{\rm b}$ Each reference concentration value, expressed as a mass fraction on a dry-mass basis, is an equally weighted mean of results provided by NIST and/or collaborating laboratories. The uncertainty in the reference concentration values is calculated as $U = k u_c$. The quantity u_c is the combined standard uncertainty calculated according to the ISO Guide [1], which accounts for the combined effect of the within-laboratory variance for all participating laboratories at one standard deviation and bias between methods. The coverage factor, k , is determined from the Student's t -distribution corresponding to the appropriate associated degrees of freedom and 95 % confidence for each analyte.

 $\mathbf c$ These reference values are reported on a dry-mass basis. In order for these reference values to be valid, the material must be dried according to the instructions provided above.

 $\mathrm{d}% \left\{ \mathcal{N}\right\} =\mathrm{d}\left\{ \mathcal{N}\right\}$ Data from three methods for the determination of nitrogen have been treated separately. Total nitrogen was determined by prompt gamma activation analysis; "organic" nitrogen was determined by the Dumas method; and "protein" nitrogen was determined by the Kjeldahl method.

APPENDIX E

MASS VALUES USED IN CALCULATIONS

APPENDIX F

ADDITIONAL LARGER MASS VALUES

VITA

