# Comparison of two ultra-sensitive methods for the determination of $^{232}$Th by recovery corrected pre-concentration radiochemical neutron activation analysis

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# Comparison of two method of recovery corrected PCRNAA for the determination of thorium in various biological and environmental matrices

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The determination of isotopic thorium by alpha spectrometric methods is a routine practice for bioassay and environmental measurement programs. Alpha spectrometry has excellent detection limits (by mass) for all isotopes of thorium except $^{232}$Th due to its extremely long half-life. This paper discusses improvements in the detection limit and sensitivity over previously reported methods of pre-concentration neutron activation analysis (PCNAA) for the recovery corrected, isotopic determination of thorium in various matrices. Following irradiation, the samples were dissolved, $^{231}$Pa added as a tracer, and Pa isolated by two different methods and compared (extraction chromatography and anion exchange chromatography) followed by alpha spectrometry for recovery correction. Ion exchange chromatography was found to be superior for this application at this time, principally for reliability. The detection limit for $^{232}$Th of $3.5 \times 10^{-7}$ Bq is almost three orders of magnitude lower than for alpha spectrometry using the PCRNAA method and one order of magnitude below previously reported PCNAA methods.

***Introduction***

A number of radiometric and non-radiometric methods have been used for the determination of $^{232}$Th in biological and environmental samples. These include alpha spectrometry[1,2], gamma ray spectrometry[3], instrumental neutron activation analysis (INAA)[3], radiochemical neutron activation analysis (RNAA)[4,5,6,7,8,9], pre-concentration neutron activation analysis (PCNAA)[10], absorption spectroscopy[11], and inductively coupled plasma mass spectrometry (ICP-MS)[3,12,13,14,15]. However, only alpha spectrometry following radiochemical separation allows the determination of the thorium isotopes with the greatest dosimetric impact for biological samples, $^{228}$Th, $^{230}$Th, and $^{232}$Th. Alpha spectrometry also allows the use of a tracer (e.g. $^{229}$Th or $^{234}$Th) for chemical yield determination[1]. While alpha spectrometry offers good radiometric detection limits ($2.8 \times 10^{-4}$ Bq/sample)[2], the very long half-life of $^{232}$Th ($1.4 \times 10^{10}$ years) makes the mass detection limit fairly high (~70 ng) compared to isotopes with shorter half-lives.

Neutron activation analysis has long been used for the determination of $^{232}$Th via the (n,$\gamma$) reaction and subsequent beta decay of the short lived $^{233}$Th ($t_{1/2}$=22.3 min) product to $^{233}$Pa ($t_{1/2}$=27.0 days). $^{232}$Th has large (n,$\gamma$) cross-sections ($\sigma_\gamma$=7.37 b, I=85 b) and $^{233}$Pa is determined by measuring the 300 (6.2%), 312 (36%) or 340 (4.2%) keV gamma rays. In radiochemical neutron activation analysis (RNAA) for the determination of $^{232}$Th, $^{233}$Pa is separated from matrix elements following neutron activation to minimize interferences and reduce the gamma-ray background[4,5,6,7,8,9]. While this technique is capable of much lower detection limits for $^{232}$Th compared to alpha spectrometry, RNAA is not suitable for isotopic thorium analysis.

The authors previously reported[16] a combined method that coupled alpha spectrometry and NAA to determine isotopic thorium. In this method thorium is separated from the sample by ion-exchange, electrodeposited onto a vanadium disk, $^{228,\ 229,\ 230}$Th determined by alpha spectrometry and $^{232}$Th determined by INAA. $^{229}$Th was added to the samples to determine chemical yield of the thorium separation and electrodeposition steps. This paper discusses extending the method by subsequent recovery corrected separation of the $^{233}$Pa by two different methods (extraction chromatography and anion exchange chromatography), electrodeposition, and subsequent gamma-ray spectrometry.

## EXPERIMENTAL

### *Preparation of reagents and irradiation vials.*

A thorium standard ($^{232}$Th) for neutron activation analysis was prepared by dissolving $Th(NO_3)_4 \bullet xH_2O$ (Johnson, Matthey, & Co.) in 1 M $HNO_3$ and the isotopic concentration ($^{228}$Th, $^{230}$Th, $^{232}$Th) determined by alpha spectrometry. The $^{229}$Th tracer used for the determination of isotopic thorium was prepared from the National Institute for Standards and Technology (NIST) Standard Reference Material (SRM 4328A). $^{231}$Pa was prepared from Amersham Certified Reference Materia PNP10010l. Working solutions were prepared by volumetric dilution of a known weight of reference material to an appropriate working concentration (~0.2 Bq/mL).

All reagents ($HNO_3$, HCl) were trace metal grade (Fisher Scientific). De-ionized water was used for the preparation of all solutions and was prepared to 18 MΩ using distilled water in a Nanopure™ system.

Flip-top polyethylene vials (Fisher scientific) were soaked for 24 hr in 40% $HNO_3$ (v/v), rinsed with de-ionized water 2-3 times, and then soaked for 24 hr in de-ionized water. The vials were drained, soaked in acetone for 24 hr, and then dried in a laminar flow hood.

Electrodeposition disks were prepared from 0.25 mm thick sheets of 99.7% pure vanadium (Aldrich) machine punched to 5/8" diameter planchets. Disks were rinsed with acetone prior to use.

***Sample preparation***

Samples were prepared by adding $^{232}Th$ from various concentration standards (diluted from the $Th(NO_3)_4$ stock solution) to acid cleaned glass beakers. A reagent blank was also prepared and analyzed with each set of samples. The radiochemical recovery was determined by adding approximately 0.08 Bq (5 dpm) of $^{229}Th$ tracer to each sample aliquot. Two mL of 0.36 M $NaHSO_4$ was added to each sample following separation to prevent radiochemical losses during subsequent electrodeposition steps. The sample was then taken to dryness and wet ashed with concentrated $HNO_3$. Samples were electroplated according to the method of Glover et al[10]. Samples were dissolved in 5 mL of 0.75 M $H_2SO_4$, several drops of thymol blue indicator added, and then transferred into electrodeposition cells followed by two subsequent 3 mL rinses of 0.75 M $H_2SO_4$. The pH of the sample solution was adjusted to 1.5-2 using concentrated $NH_3$. One important difference was the use of 99.7% pure vanadium planchets rather than stainless steel planchets typically used for electrodeposition.

***Determination of thorium by alpha spectrometry.***

After electrodeposition the $^{228}$Th, $^{230}$Th, $^{232}$Th, and the $^{229}$Th tracer in each sample were determined by alpha spectrometry in a Canberra Alpha Analyst system equipped with 450 mm$^2$ detectors calibrated over the range of 3.5 to 7 MeV in 1024 channels. Samples were counted on the second shelf (approximately 0.5 mm source-to-detector distance) which yielded approximately a 20% efficiency (counts/$\alpha$ emission). Detectors were energy calibrated using secondary sources of approximately 1 Bq each of $^{234}$U, $^{238}$U, $^{239}$Pu, and $^{241}$Am. The detectors were efficiency calibrated using secondary sources containing approximately 15 Bq of $^{242}$Pu. These secondary sources were calibrated using NIST SRM 4906L, a $^{238}$Pu point source, at the greatest source-to-detector geometry (~4 cm) to minimize geometry differences between the point source and the 5/8" planchet used for sample preparation. Background counts for each detector were of 300,000 seconds duration and samples were counted for 100,000 to 300,000 seconds. The chemical yield of the separation and electrodeposition steps was obtained by the ratio of the net counts of $^{229}$Th versus the expected count rate of the decay corrected tracer.

***Determination of $^{232}$Th by PCRNAA (ion exchange method)***

Samples were irradiated at the 1 MW TRIGA III fueled research reactor located at Washington State University for 6 hours with a thermal neutron flux of $6.5 \times 10^{12}$ cm$^{-2}$s$^{-1}$. The samples were allowed to decay for approximately 12 hours in the pool to allow the short lived activation products to decay.

The vanadium planchets were dissolved using10 mL of 8 M $HNO_3$/0.025 M HF spiked with approximately 0.2 Bq of $^{231}$Pa in an covered polyethylene beaker (Azlon™)

suitable for heating to 130 °C. The addition of HF is required to keep the Pa in solution as it will rapidly hydrolyze. Also, this ensures the Pa was in chemical equilibrium with the $^{231}$Pa tracer which was also in 8 M $HNO_3$/0.025 M HF. Following completion of this exothermic reaction, the beaker was heated at 90 °C for 15 minutes to insure completion of the reaction. 90 mL of 9 M HCl were then added to the sample and allowed to cool to room temperature.

The ion exchange columns were prepared using a 10 mL Fast Rad™ polyethylene column (Environmental Express LTD) with 200 mL plastic reservoir containing 10 mL of Biorad AG 1x8 resin, 100-200 mesh. The columns were washed with 5 column volumes of 0.5 M HCl to remove all actinides and pre-conditioned with 5 column volumes of 9 M HCl prior to addition of the samples. Glass components were not used for any step in these procedures due to the presense of HF in the samples.

Immediately prior to addition to the column, 2 mL of 0.5 M $Al(NO_3)_3$ was added to the sample, the sample stirred thoroughly, and then added to the column. The beaker was rinsed three times with 9 M HCl and these rinses were also added to the column. Each step was allowed to pass completely through the column prior to addition of the next wash step. The column was washed with 5 column volumes of 9 M HCl, then rinsed twice with 2.5 column volumes of 8 H $HNO_3$. The Pa was then eluted with 10 column volumes of 9 M HCl/0.025 M HF into a polyethylene beaker. The samples were electroplated using the same method for both the ion exchange method and the extraction chromatography method (described below).

***Determination of $^{232}$Th by PCRNAA (extraction chromatography method)***

Protactinium may be isolated using extraction chromatographic techniques not based on the presumed extractant (CMPO in the case of the TRU column), but rather the solvent TBP in which the CMPO is contained on the column. TBP has been one of the compounds used historically for the liquid-liquid extraction of protactinium. The vanadium planchets were dissolved in the same fashion as described for ion exchange (10 mL of 8 M $HNO_3$/0.025 M HF spiked with approximately 0.2 Bq of $^{231}$Pa in a plastic beaker suitable for heating to 130 °C (Fisher brand), heating covered for 15 minutes at 90 °C). 17 mL of deionized water was then added to the beaker which effectively dilutes the concentration of the $HNO_3$ to 3 M. 500 mg of ascorbic acid was then added (convert any iron present from $Fe^{3+}$ to $Fe^{2+}$) and the sample heated on a hot plate until it turned green after which the solution was allowed to cool to room temperature. 1 mL of 1 M $Al(NO_3)_3$/3 M $HNO_3$ was added to the sample immediately prior to addition to the column and the solution stirred.

This solution was then added to a TEVA™/TRU™ tandem column (TEVA on top of TRU) which had been pre-conditioned with 3 M $HNO_3$. The sample was allowed to pass completely though the tandem column setup, and then the tandem columns were washed with 12 mL of 3 M $HNO_3$. At this point the TEVA column was discarded, 10 mL of 4 M HCl used to wash the TRU column, and then the sample was eluted into a polyethylene beaker with 15 mL of 4 M HCl/0.5 M HF. The sample is then electroplated as described below.

### *Electrodeposition of Pa*

It was quickly determined that a modification of the electrodeposition method would be required for completion of this work due to the HF used in the elution of Pa. This method and its evaluation will be discussed in detail elsewhere. A brief description of the method involves adding 1 mL of 9 M $H_2SO_4$ to the eluent (in a plastic beaker capable of heating to130 °C) and evaporating to a constant volume at 90 °C ($H_2SO_4$ does not evaporate at this temperature) and then following the previously described method with a pH of 2, an electrodeposition time of 1.5 hours, at a constant current of 0.75 amps. Samples were then counted by alpha spectrometry for 100,000 seconds in the previously described system.

## RESULTS AND DISCUSSION

### *PCRNAA by ion exchange chromatography*

Ion exchange chromatography was found to provide a very credible reduction in background interferences and consistently high recoveries (95 ± 5 %). Figure 1 shows an example of a sample counted after irradiation but prior to radiochemical separation of Pa for 80,000 seconds on a 48% HPGe detector in a low background shield containing 2 μBq of $^{232}$Th with a higher than typical $^{192}$Ir content (notice the 308 and 316 keV peaks) which surround the 312 keV peak used to determine the $^{233}$Pa. Figure 2 shows the results of this same sample following RNAA by ion exchange chromatography as previously described counted for the same time and duration. The $^{192}$Ir content was reduced by factor of 30 for this example, and is typically much higher, in many cases with only trace levels of $^{192}$Ir remaining. Background for the 312 keV region was reduced by a factor of

10-15 for the samples, resulting in a significant improvement in both the detection limit and the ability to determine $^{232}$Th in the blank. The effective detection limit for the method using the conditions as stated is 3.5 x$10^{-7}$ Bq for $^{232}$Th and it is capable of 3-5% precision at levels above the limit of quantification.

***PCRNAA by extraction chromatography***

Extraction chromatography also showed itself to be capable of the task, significantly reducing the background from the irradiated vanadium planchet (Figure 3). This figure is misleading if directly compared to the first two figures because it was measured using a 20% HPGe detector with only a lead brick cave. The natural background radiation is readily observable as compared to the measurements of the samples for the anion exchange chromatography. Recoveries of up to 95% were achieved with this method, however slow columns and even column stoppage marred the reliability of the method. Eichrom has recently admitted correcting a quality control problem with fine particles in the resins which if corrected may provide method with improved reliability. If this improved reliability is achieved then significant waste reduction (~50 mL by extraction chromatography versus 200 mL for ion exchange methods) may be achieved. If Eichrom columns improve to their listed 0.7 mL per minute flow rate, then the Eichrom method will require approximately 90 minutes compared to about 300 minutes for the ion exchange method. Additionally, the reduced elution volume will allow for much quicker drying than the ion exchange method as well as reduced acid damage to the hood system during dry down.

The extraction chromatography method does not completely remove the scandium contents of the sample but does significantly reduce them. Detection limits for the

method will be similar to those reported by ion exchange chromatography provided that the protactinium recovery remains consistently high.

One other factor that may be important is that ion exchange columns seem to be more tolerant of inattention (they can sit dry for several hours with no adverse affects on the recovery) and will give the busy chemist more time to work the separation into their time schedule than afforded by extraction chromatography.

## CONCLUSIONS

Two methods of radiochemical neutron activation analysis were evaluated and compared. Both methods were found to achieve the desired results, reduction in interferences and background, but the ion exchange method was found to be more reliable. However, with improvements in flow rate and reliability of the extraction chromatography columns, significant reduction in waste and time may be achieved.

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## LIST OF FIGURES

Figure 1: 80,000 second gamma-ray spectrum of 2 μBq of $^{232}$Th by PCNAA on a 48% HPGe detector

Figure 2: 80,000 second gamma-ray spectrum of 2 μBq of $^{232}$Th by PCRNAA following ion exchange chromatography on a 48% HPGe detector

Figure 3: 80,000 second gamma-ray spectrum of 2 μBq of $^{232}$Th by PCRNAA following extraction chromatography on a 20% HPGe detector

**Figure 1**

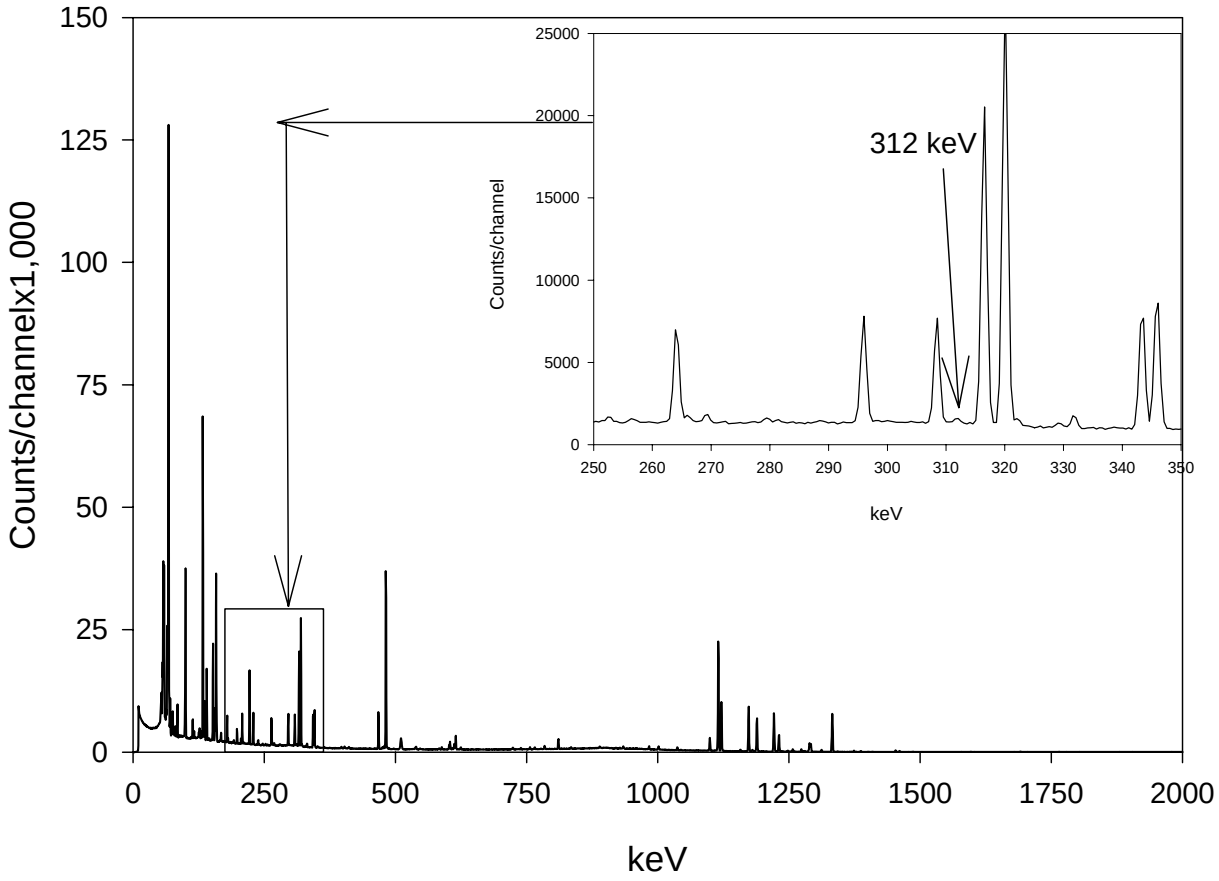
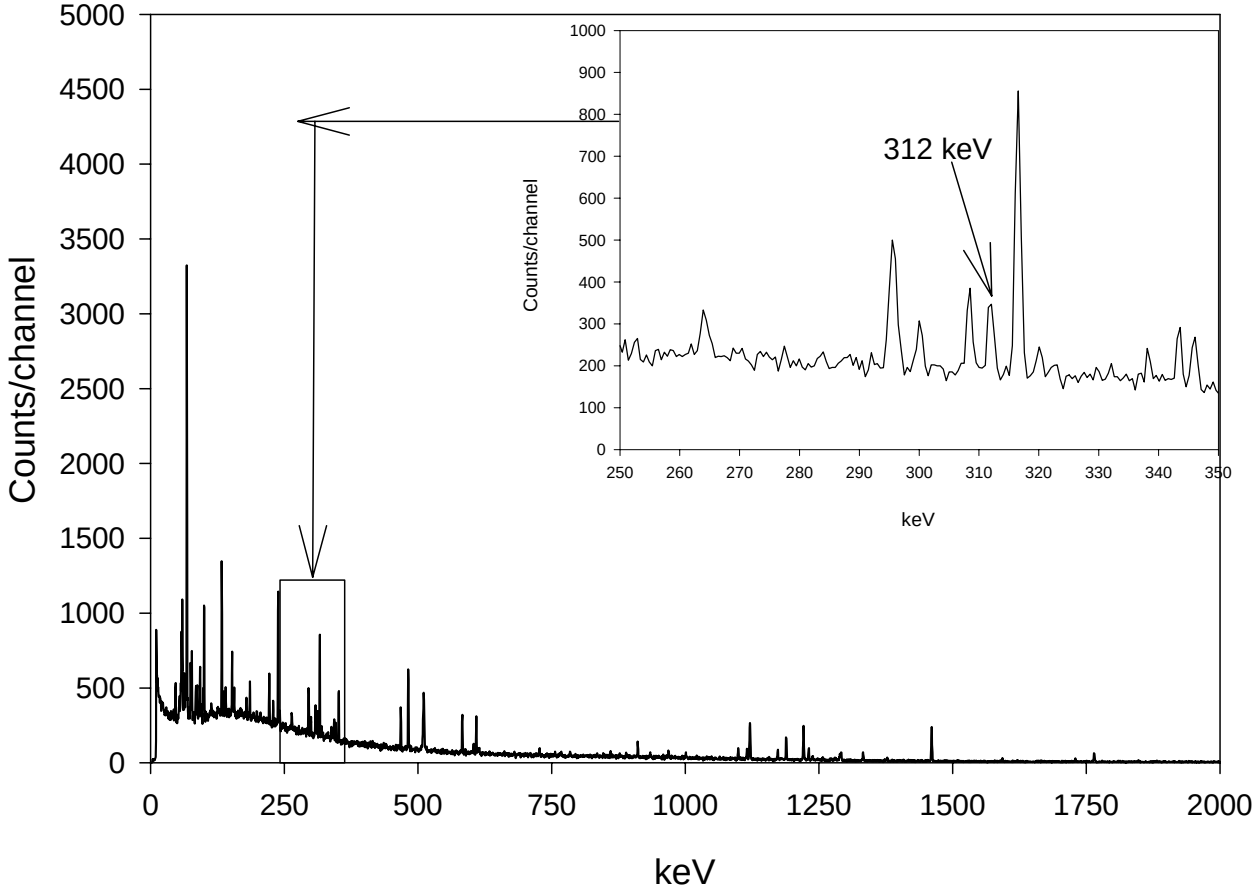


**Figure 2**



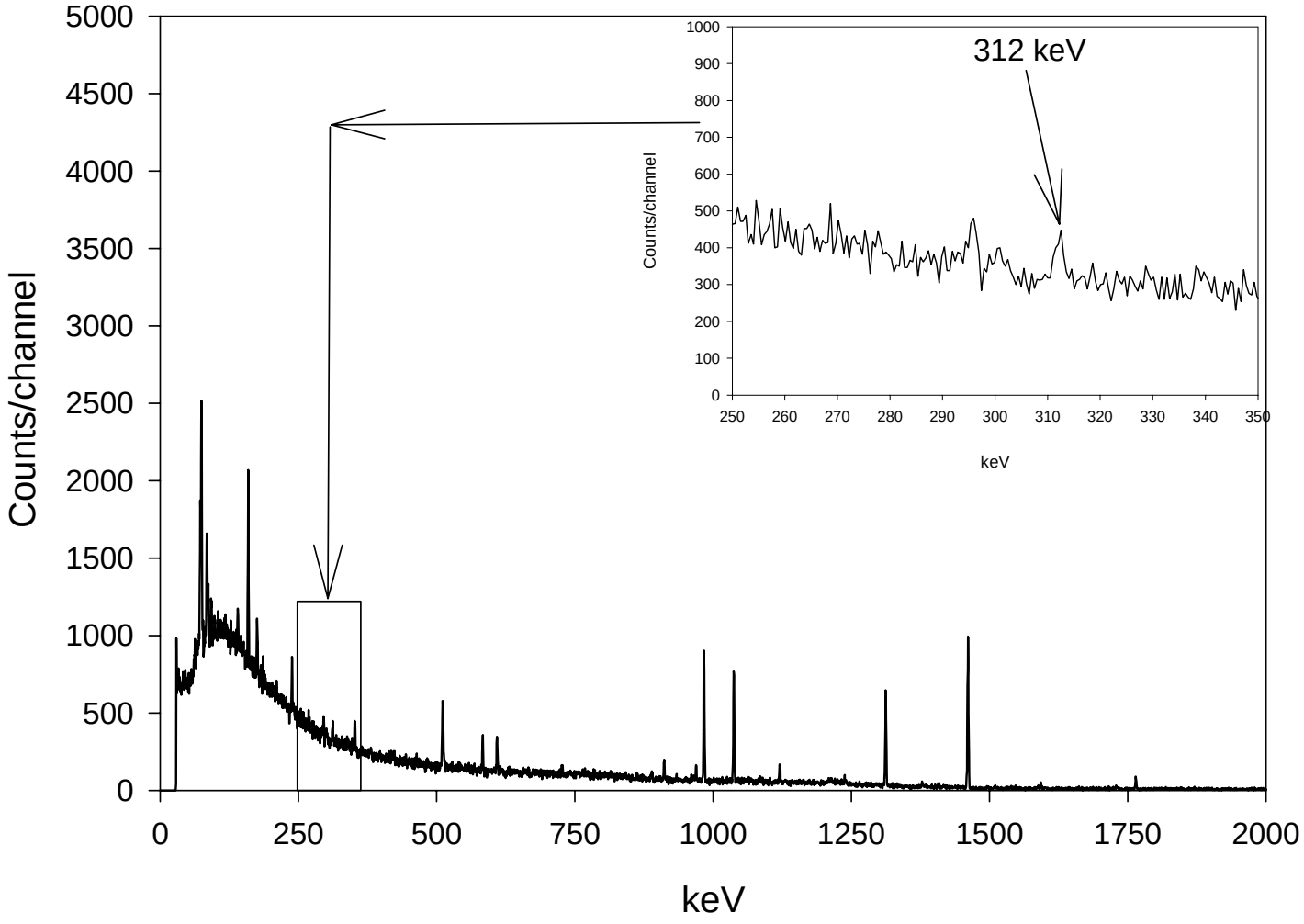



**Figure 3**