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EVALUATION OF A PHOTO-ELECTRON REJECTING ALPHA LIQUID SCINTILLATION (PERALS) SPECTROMETER FOR THE MEASUREMENT OF ALPHA-EMITTING RADIONUCLIDES (U)

by

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Summary

Results from the evaluation of a PERALS spectrometer for
alpha particle measurements by liquid scintillation ·
counting in samples from the nuclear fuel cycle are
presented. Examples of PERALS spectra of process, waste,
and environmental samples containing Th, U, Pu and Am from
the Savannah River Site are shown. The advantages,
disadvantages, and limitations of the PERALS technique are
discussed.

1. Introduction

The accurate, sensitive measurement of actinide radionuclides
frequently requires quantitative detection and analysis by alpha
spectrometry of the alpha particle emissions associated with their
decay. The short ranges and stopping characteristics of the alpha
radiation in matter make this task inherently difficult. Actual
samples routinely encountered in the nuclear fuel cycle often
contain the alpha activities as mixtures in complex matricies at
levels from hundreds of microcuries to a few picocuries. The
conventional technique for measurement of alpha-emitting actinides
by high resolution silicon surface-barrier detectors requires the
preparation of thin uniform sources prior to counting in vacuum.
This method is very sensitive to source preparation and the
reproducibility of the source to detector geometry [1].

Self-absorption of the alpha particles in the source results in
energy loss; a nonuniform source causes the average path length of
travel of an alpha particle in the source to vary. Both effects
distort the pulse height (energy) spectrum, producing broad peaks
with low energy tails. This can result in poor precision in
obtaining net peak areas for quantitative analysis. Although peak
fitting has been used in isolated cases for the analysis of alpha
spectra [2], it requires sources prepared with considerable care,
and has not found wide spread application as in the analysis of
gamma-ray spectra from semiconductor detectors. Sources for alpha
spectrometry are usually prepared by depositing micrograms of the
element onto a flat, polished metal disk by electroplating from an
aqueous medium, or by evaporation of microliter droplets of aqueous
or organic solutions [3][4]. Drop deposition often uses spreading
agents to enhance the uniformity of the deposit, and is followed by
flaming or firing under vacuum [5] to remove the organic material
and leave an essentially weightless residue. A properly prepared
source weighs less than 50 micrograms per square centimeter,
seriously limiting the sensitivity for nuclides such as Th-232,
U-235 and U-238 which have long half-lives and low specific
activities (curies per gram). The best energy resolution obtained
by these methods for 4-6 MeV alpha particles is about 20 KeV Full

Width at Half Maximum (FWHM). 50-100 KeV FWHM resolution is more typical in routine operations.

Successful source preparation presupposes the chemical purification of the element before deposition. The presence of bulk impurities during the deposition can severely degrade the quality of the source produced and the resolution of the energy spectrum. The separations are normally performed by ion exchange chromatography and can be long and tedious. Samples are counted at source to detector distances of 2-4 cm, with absolute counting efficiencies (pulses detected per 100 alpha particles emitted) of 30-40%, depending upon the active area of the detector.

There has been extensive development of organic scintillators as detectors in nuclear technology [6], particularly in the fields of neutron measurement and liquid scintillation counting (LSC). LSC is most commonly used for the measurement of radionuclides which decay by the emission of low energy beta particles, such as H-3 and C-14 [7]. Basson and Steyn used LSC to measure polonium alpha activity as early as 1954 [8]. It has natural advantages in its ease of sample preparation, essentially 100% counting efficiency, and elimination of self-absorption effects. Sources are prepared for measurement by dissolving or dispersing in a scintillation cocktail containing one or more components dissolved in an aromatic hydrocarbon solvent. The cocktail composition is designed to homogenize the sample and scintillator, absorb the total kinetic energy of the decay particle, and convert it to visible light at a wavelength that can be detected by a photomultiplier tube. Processes that inhibit the energy transfer to the scintillator, resulting in loss of light at the detection wavelength, are collectively known as quenching.

Commercial LSC systems that are widely used for beta particle measurements have had some applications in the measurement of Pu and Am [9][10]. The National Institute of Standards and Technology has used both commercial systems and an alpha particle/gammma-ray coincidence unit based on LSC for standardization of actinides [11]. However, the poor energy resolution for alpha particles (600-1000 KeV FWHM), and high backgrounds from beta particles and photoelectrons from gamma-ray interactions limit their applications.

Recent advances in the development and application of LSC to alpha spectrometry have provided an alternative method that is simple, convenient, and accurate. Extensive development work in this technique is summarized in a monograph on alpha spectrometry using LSC [12] that provides both a clear description of the physical basis of the method and brief examples of radiochemical procedures applied to problems in nuclear technology. The technique employs a liquid scintillation detector with electronic pulse shape discrimination (PSD) for beta-gamma pulse rejection, and direct extraction of the activity of interest into a water insoluble organic phase containing the scintillator.

Alpha particles deposit energy in the scintillator at 100 KeV per micron producing triplet excited states in organic molecules and ions. Beta particles deposit 1 KeV per micron or less, exciting

mostly singlet states that quickly decay. PSD takes advantage of
the longer decay time of light produced by alpha particle
interactions to select the alpha pulses for spectrometry and reject
those from beta particles or gamma-ray events. The combination of
PSD and extractive scintillation achieves low backgrounds and low
but adequate energy resolution in the alpha particle counting. The
choice of extractant and chemical composition of the aqueous phase
allows selectivity and flexibility in the sample preparation which
in many cases compensates for the low resolution.

The original research for this technique used a prototype detector
that was not commercially available. But recently a version of the
spectrometer, the PERALS system, was produced and marketed by Oak
Ridge Detector Laboratory (ORDELA). One of the first production
units was obtained for evaluation with a variety of analytical
samples from process control, waste management, and environmental
sources at the Savannah River Site.

2. Principles of the PERALS Method

The PERALS spectrometer includes a sample holder in a hemispherical
counting chamber, photomultiplier tube, preamplifier, linear
amplifier and PSD circuitry in a small, self-contained unit that
occupies three slots in a standard Nuclear Instrument Module rack
[fig. 1]. A high voltage power supply capable of providing 500-1000
volts and a multichannel analyzer (MCA) for pulse height analysis
(PHA) are the only additional equipment needed. For the experiments
at the Savannah River Laboratory the PERALS was connected to a
Canberra Series 35 PLUS MCA [fig. 2]. Fig. 3 shows a schematic of
the PSD process and a block diagram of components in a PSD system is
shown in fig. 4.

The PSD system in the PERALS unit measures the time length of each
incoming pulse and converts the time signals to voltages whose pulse
heights are proportional to time. A single channel analyzer
examines each of the time pulse heights and generates a logic signal
(gate pulse) for each one above an adjustable, low-level
discriminator, set to reject the lower voltage pulses from
beta/gamma events. For each input pulse the PERALS system outputs
an amplified voltage pulse for energy analysis, and a pulse shape
signal whose pulse height is proportional to the time length of the
incoming pulse. Alpha pulses only are selected for PHA by requiring
time coincidence between the energy output (after an appropriate
delay) and the gate signal generated by the PSD. A total spectrum of
all events can be collected by disabling the coincidence gate;
requiring anticoincidence with the gate pulse gives a spectrum of
the rejected pulses. Time separation between beta-gamma and alpha
pulses can be examined by connecting the PERALS pulse shape output
to the MCA. A typical Time Spectrum produced by a PSD unit is shown
in fig. 5.

Samples were processed by liquid-liquid extraction of the
radionuclides from the aqueous solution into the organic phase, as
illustrated in fig. 6. Several milliliters each of dilute nitric
acid, containing the alpha activity, and the extractive scintillator

were sealed in small glass vials and were homogenized for several
minutes by a vibratory mixer. The phases were allowed to separate
and a 1.0 milliliter portion of the organic phase was transfered to
a glass culture tube. The presence of oxygen in the scintillator
degrades resolution and PSD. It is purged from the scintillator by
sparging with argon for several minutes. The argon was passed
through a gas drying tube (dessicant and molecular sieve) to remove
any moisture, and resaturated with xylene immediately before
introduction into the sample.

The tube is sealed and placed in the counting chamber of the PERALS
system, with the entire preparation step requiring about 5 minutes.
The air space in the counting chamber between the glass tube and the
reflector/phototube surfaces is filled with an inert silicone oil to
improve light transmission and maintain energy resolution. The cap
for the chamber is safety interlocked to disable the high voltage
supply when the cap is removed, preventing damage to the phototube.

Bis(2-ethylhexyl) phosphoric acid (HDEHP) was chosen as the
extractant for the study since the extraction behavior of Pu and
other actinides with this agent from dilute nitric acid solutions is
well documented [13], and it has acceptable levels of quenching
[14]. The chemical selectivity is controled by changing the acid
concentration and/or oxidation states of the actinides in the
aqueous phase. 2-(4'-biphenylyl-6-phenylbenzoxazole) (PBBO) was
used as the scintillator, and naphthalene was added to improve
energy and pulse shape resolution [15]. The extractive scintillator
was prepared from reagent grade chemicals without additional
purification or special handling, and contained 4.0 grams PBBO, 60
grams HDEHP and 200 grams of naphthalene in 1 liter of scintillation
grade p-xylene.

3. PERALS Measurements

A variety of samples from process and environmental sources was
chosen for evaluating the utility of the PERALS technique, with
particular attention given to those that presented difficulties for
analysis by conventional alpha spectrometry. Samples of low
specific activity radionuclides like Th-232 or U-238, trace actinide
impurities in actinide products, and actinides in complicated
matricies from waste or environmental samples were selected for
analysis with the PERALS.

Initial tests of the PERALS spectrometer were performed with a Th
standard solution containing a certified elemental concentration in
dilute nitric acid. Th-232 and Th-228 were extracted from 0.1% by
volume nitric acid. Under these conditions actinides in +3, +4, and
+6 oxidation states are quantitatively extracted into the
scintillator. The extraction can be used to assay the total
actinide content in a sample. The discriminator on the PSD was set
by placing a 1-5 microcurie gamma-ray source of Co-60 or Cs-137
against the outside of the PERALS sample chamber to generate
photoelectrons in the detector, and then adjusting the discriminator
to reject the pulses. The 4.00 and 5.40 MeV alpha peaks of Th-232
and Th-228 provide a convenient energy calibration and resolution

check. Repeated extractions were made, producing total elemental concentrations of 1 microgram to 50 milligrams of Th per milliliter of scintillator. The overall efficiency for the extractions and counting was 95 +/- 5% (one relative standard deviation) based upon integration of the Th-232 alpha peak at 4.00 MeV.

Fig. 7 is a PERALS spectrum of a 40-milligram Th sample. Energy resolution was 250-350 KeV FWHM for peaks in the range from 4-6 MeV and was not significantly changed by the amount of sample in the scintillator or by the presence of a few microcuries of beta-gamma emitters. Daughter activities in the decay chain begin to grow into the Th spectrum above 5.40 MeV immediately after extraction. The assymetric shape of the 8.78 MeV peak from Po-212 appeared to be due to an upper level cut off peculiar to the PERALS amplifier and pulse height circuits. They are designed to produce pulses of 0.3 to 1.0 volt per alpha MeV and a nominal output of 0 to 8 volts.

Extracted samples were stable for at least several days. After a week or more the intensity of the Th-232 alpha peak began to decrease in repeated counts of an extracted sample. The drop in count rate first appeared in the spectra taken with PSD and was not seen in those taken in singles mode (coincidence gate off), indicating that the time resolution was affected first. Similiar behavior was noted within a day or two in samples extracted from higher acid concentrations, or where oxidizing agents were present in the aqueous phase. Samples containing significant amounts of organic material were pretreated by wet ashing by repeated heating to near dryness with 60% nitric acid before extraction from 0.1% acid.

A 56-hour measurement of low level Th activity extracted from a water sample is shown in the top of fig. 8. The lower half of the figure is a spectrum from a background sample of high purity deionized water treated and counted in an identical fashion. Process samples spiked with known amounts of Pu-239, Am-241, and depleted uranium were extracted and measured with the PERALS (fig. 9). The small tail on the upper side of the Pu-239 peak in the top spectrum was due to the presence of small amounts of Pu-238 and Am-241. Likewise the low side tail on the Am-241 peak was probably due to traces of Pu-239.

One of the more difficult actinide measurements involves their determination in highly radioactive waste streams from chemical reprocessing. Relatively small amounts of alpha activity are contained in a caustic sludge of inert chemicals from the dissolution and subsequent neutralization of irradiated fuel and target elements. Large quantities of beta-gamma emitting fission products, mostly Sr-90 and Cs-137, are also present in the sludge samples. Processing of the waste into a form suitable for storage in a repository requires the accurate measurement of the major alpha emitting radionuclides. A sludge sample that had been dissolved in acid was diluted and the alpha activity from the equivalent of 20 micrograms of the sludge was extracted and assayed in the PERALS.

The center and bottom spectra in fig. 10 were taken with and without PSD. The total alpha activity in the sample is essentially all due

to Pu-238 and Am-241 whose alpha energies cannot be resolved by alpha spectrometry. Their contributions were resolved by repeating the extraction after increasing the acid concentration of the aqueous phase to 1% nitric acid and oxidation of the plutonium with potassium bromate. With this treatment the plutonium is selectively extracted while the americium remains in the aqueous phase. The extracted solutions were stable for only a few hours and were counted immediately after preparation. The Pu-238/Am-241 activity ratio in the sample was about nine to one.

The initial extraction quantitatively separated the actinides from 0.2 microcuries of Sr-90/Cs-137. However Y-90, the daughter of Sr-90, is also present in equilibrium in the sample and extracts with the actinides. The top spectrum in fig. 10 shows the rejected pulses from the 2.3 MeV beta particles of Y-90. The identity of their source was confirmed by their decrease with a 65-hour half-life characteristic of Y-90.

Analytical measurement of trace alpha emitting impurities are made in a number of actinide product streams. They include, for example, trace Pu-239 in depleted uranium, Pu-236 in Pu-238 produced for thermoelectric heat sources, and U-232 in recycled enriched uranium. The analyses usually require long (12-24 hour) counts of electroplated sources with pulse pile-up rejection to maintain resolution at high count rates. Contamination of the detectors by recoil nuclei ejected from the samples often limits the use of the detectors for other samples. The high sample loading of actinides in the PERALS system extractants makes it very useful in the detection of Pu-239 in depleted uranium, and U-232 and its daughters in enriched uranium. The dominant alpha activity in recycled, enriched uranium is U-234 with an alpha energy of 4.76 MeV, shown in the top spectrum of fig. 11. An enlargement of the spectrum in the bottom half of the figure shows the region above 5.3 MeV (above channel number 80) that can be used to determine the activity of U-232 and its daughters.

4. Conclusions

The PERALS spectrometer has now been used for over a year at the Savannah River Site. In numerous examples, PERALS has shown itself to be a truly practical instrument for alpha spectrometry, and at the very least an equal alternative to semiconductor detectors for the analysis of many actinide samples. It combines the two desirable features of PSD and selective solvent extraction into a single, serviceable system.

The final source preparation and counting is fast, simple, and quantitative. The small bias below 100% efficiency was accounted for by slight losses in transfer of the organic aliquot, and rejection of a small fraction of the alpha pulses by the PSD. The low resolution of the energy spectrum is the PERALS biggest disadvantage but is more than compensated for by the chemical selectivity, consistently reproducible peak shapes, and wide dynamic range for sample loading in the scintillator. For low specific activity actinides PERALS samples held 200-500 times the weight of

sample normally mounted for surface-barrier detectors.

PERALS source preparation did not require significant prior chemical separations for most analyses and eliminated the need for equipment for aliquot mounting, evaporation, and plate flaming or electrodeposition. A vacuum pump, trap, and manifold was also not needed for counting in vacuum.

Simple peak integration algorithms built into most MCAs are all that is required in the way of data analysis for many cases. For analyses where multiplets are encountered, the constant, near-Gaussian peak shape should be quite amenable to peak fitting techniques.

In low-level counting applications a detection sensitivity of 0.01 picocurie per milliliter of sample was reached. Increasing the sensitivity further would require preconcentration of the sample and/or longer counting times (up to a week). PERALS samples prepared by the simple technique used in this work were not always stable for that length of time. Containment of the alpha activity inside the sample vial allowed measurement of samples with activity levels varying over six orders of magnitude, without cross-contamination or increasing detector background rates.

5. Acknowledgment

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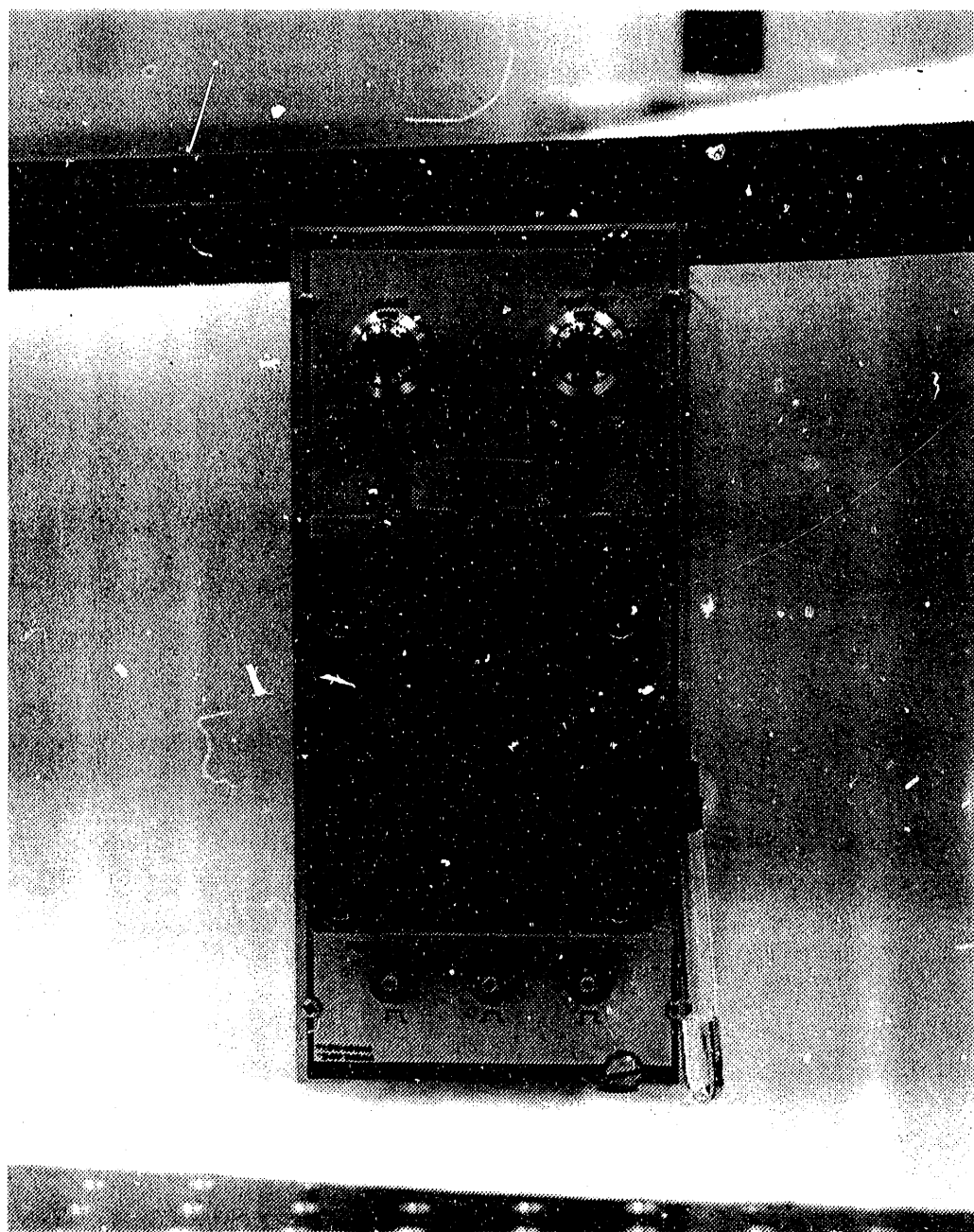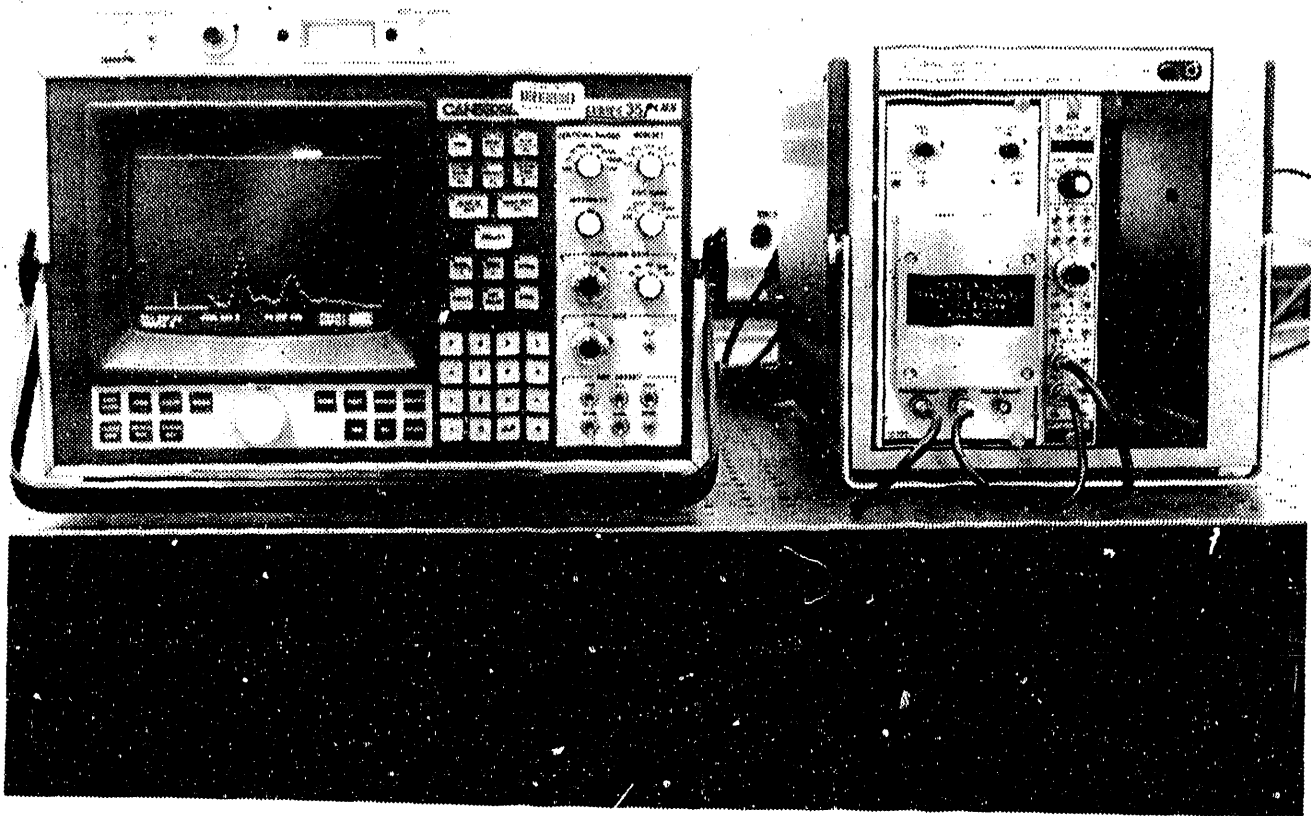
FIGURE No. 1. Photograph of PERALS module and sample.

FIGURE No. 2. Photograph of PERALS in Portable Nuclear Instrument
Bin with MCA and High Voltage Supply in lab as used for this study.

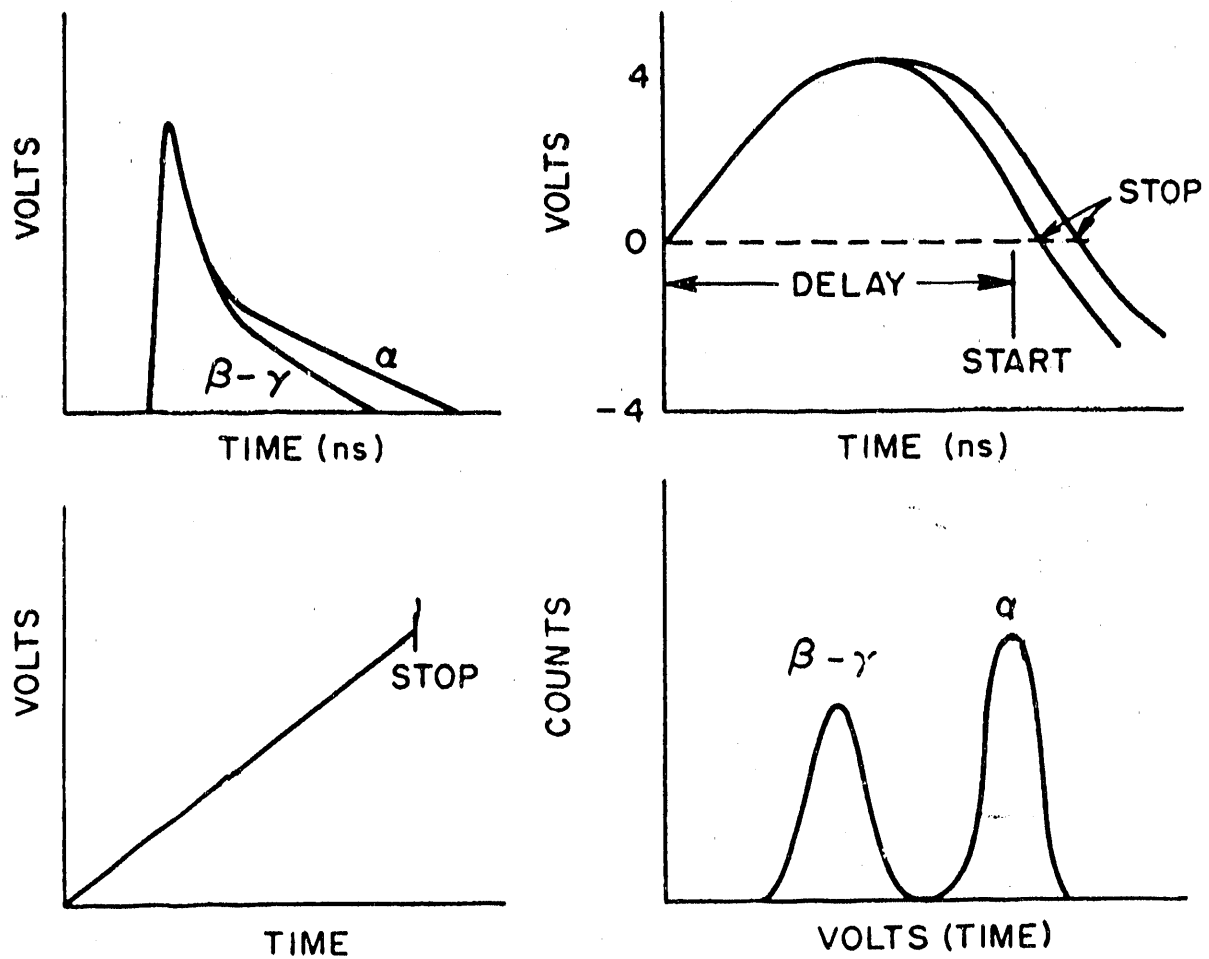## PULSE-SHAPE DISCRIMINATION

FIGURE No. 3. Schematic of PSD process. Alpha pulses last 30 nanoseconds longer than beta/gamma events (upper left) and analysis of integrated pulses is delayed to this time region (upper right). A voltage ramp rises until the pulse crosses zero (lower left) and a time spectrum of the pulses is generated (lower right). (fig. from ref. 11, reproduced with permission of the author).
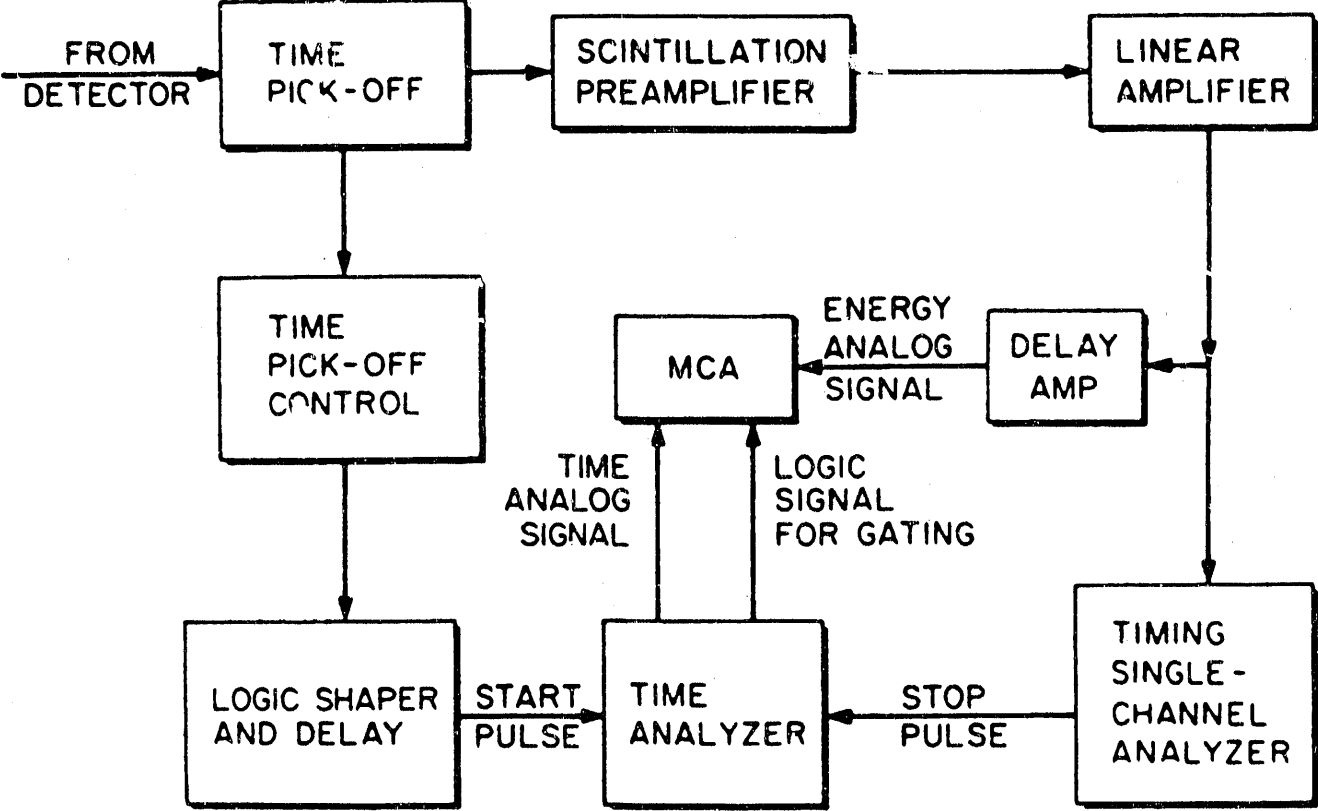
FIGURE No. 4. Block diagram of electronic components in a PSD system. (fig. from ref 11, reproduced with permission of the author).
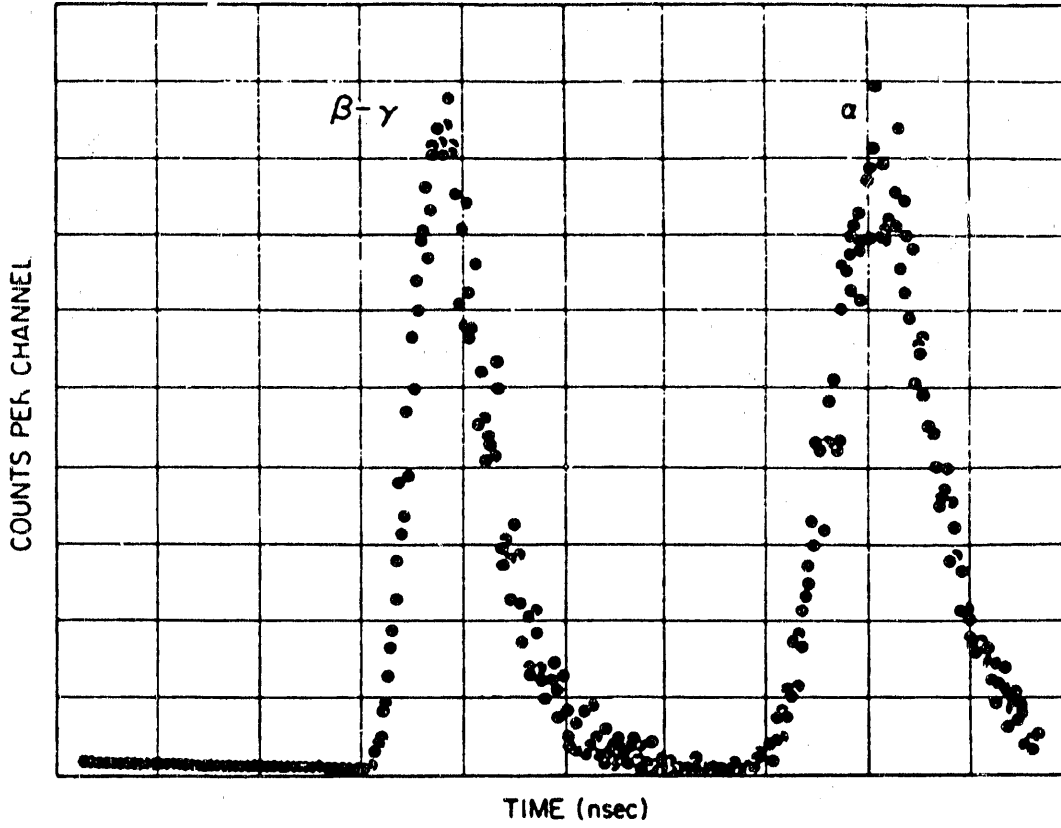
FIGURE No. 5. Time spectrum of pulses from alpha and beta/gamma interactions from a PSD system. (fig. from ref 11, reproduced with permission of the author).

EQUILIBRATE

PIPETTE SCINTILLATOR

SPARGE

PLACE IN DETECTOR
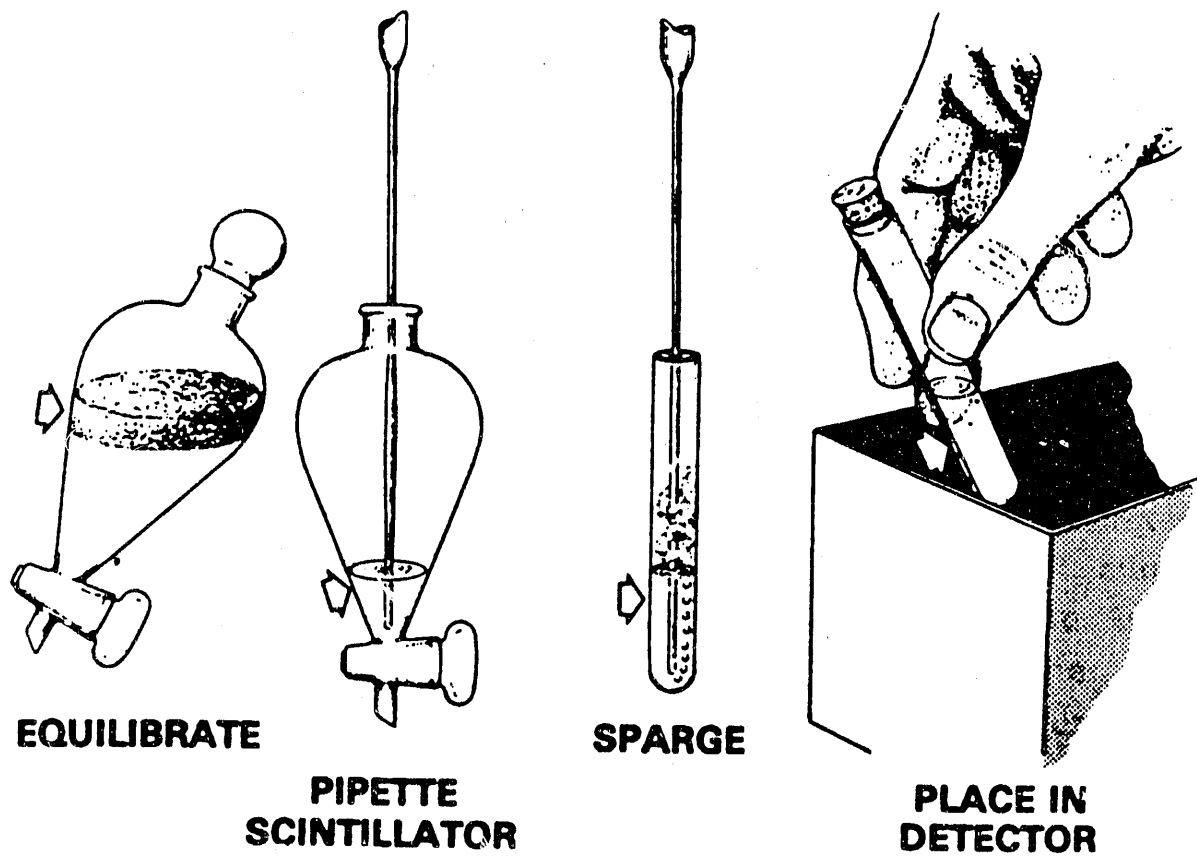
FIGURE No. 6. Sample preparation for PERALS analysis. (fig. from ref. 11, reproduced with permission of the author).
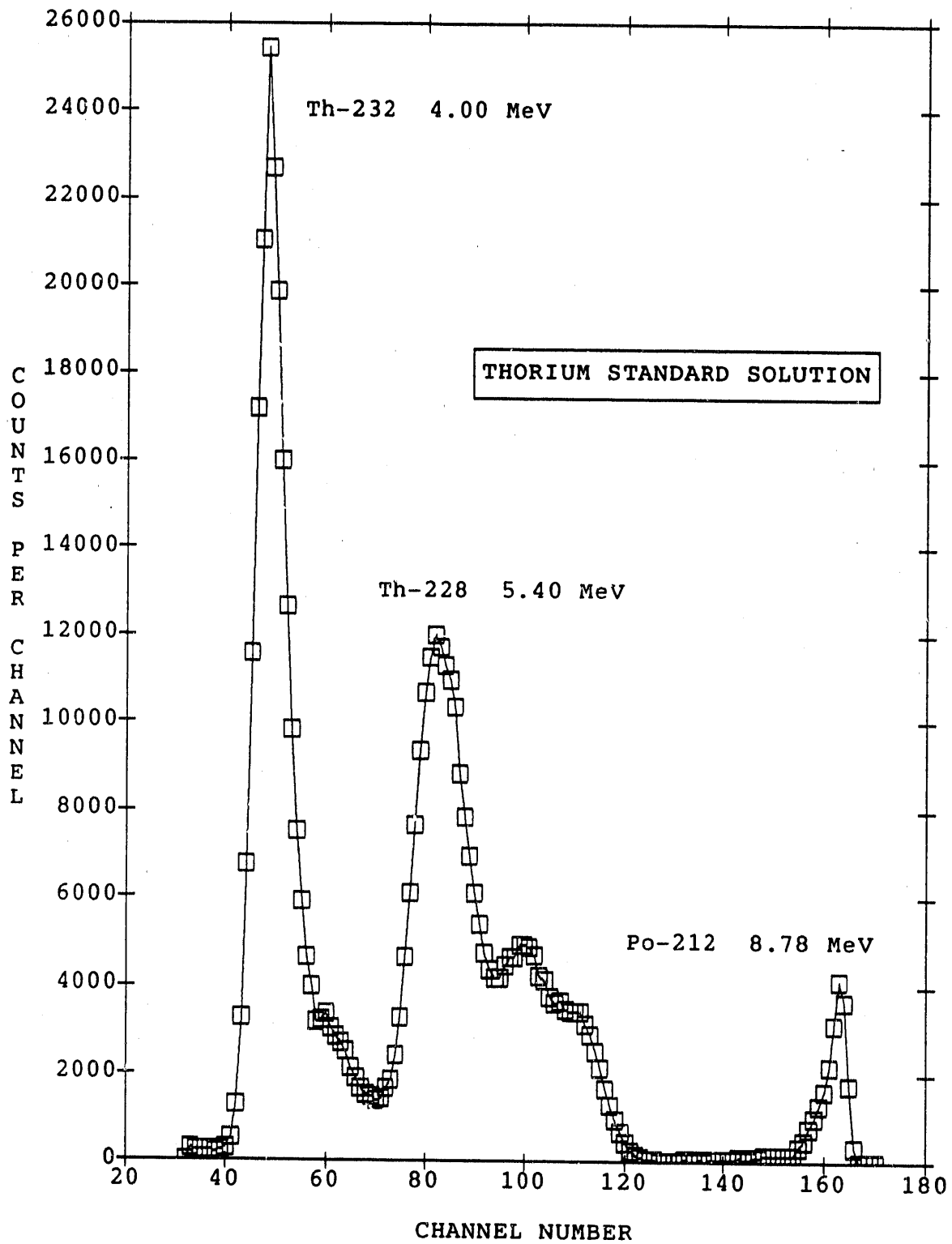
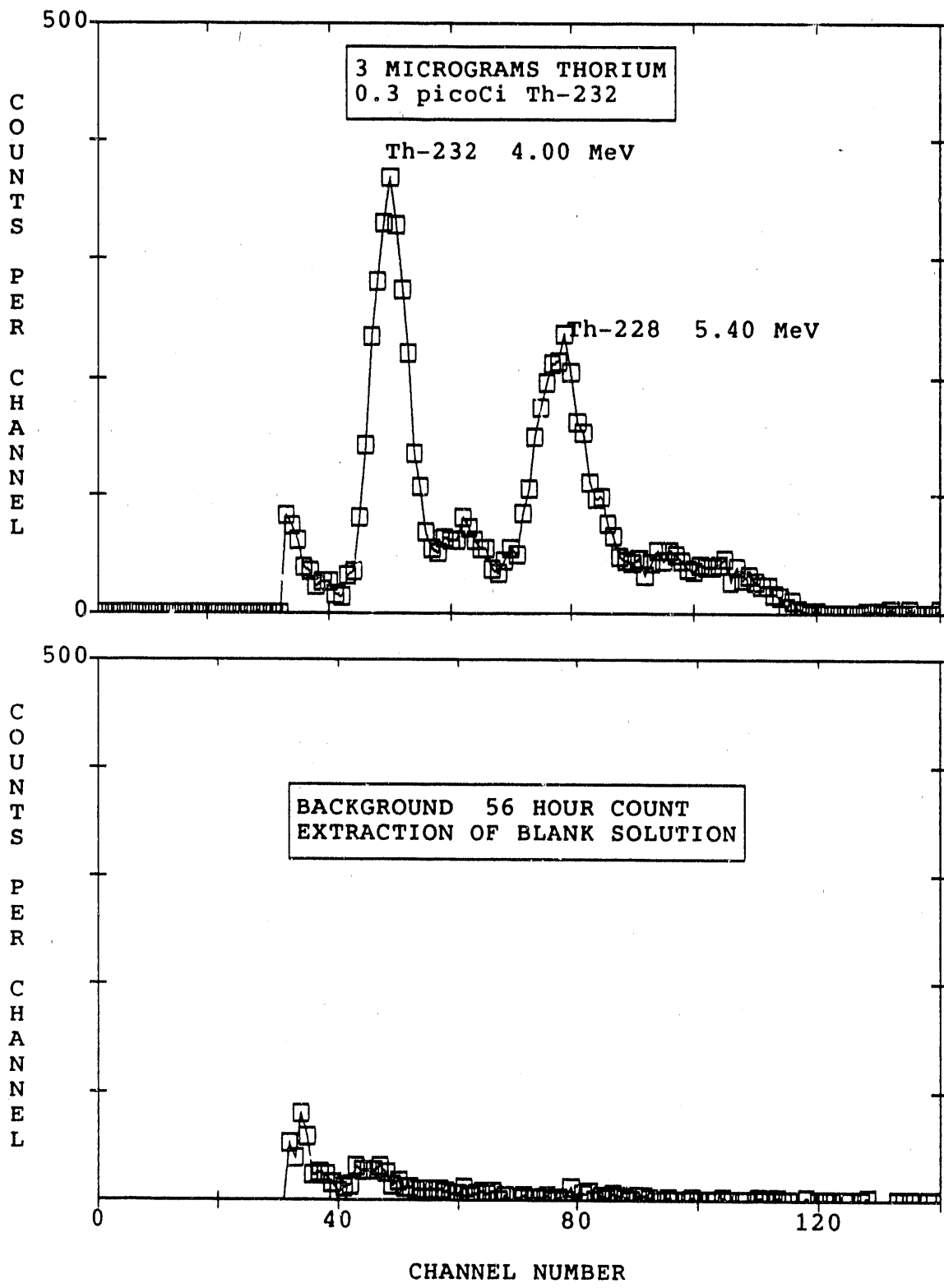FIGURE No. 7. PERALS spectrum of 40-milligrams of Th extracted from 0.1% nitric acid into HDEHP/PBBO/xylene. FWHM resolution of 280 keV for the 4.00 MeV alpha peak.

FIGURE No. 8. PERALS spectrum from long count (56 hours) of low level Th sample (top) and background (bottom) from reagent blank.
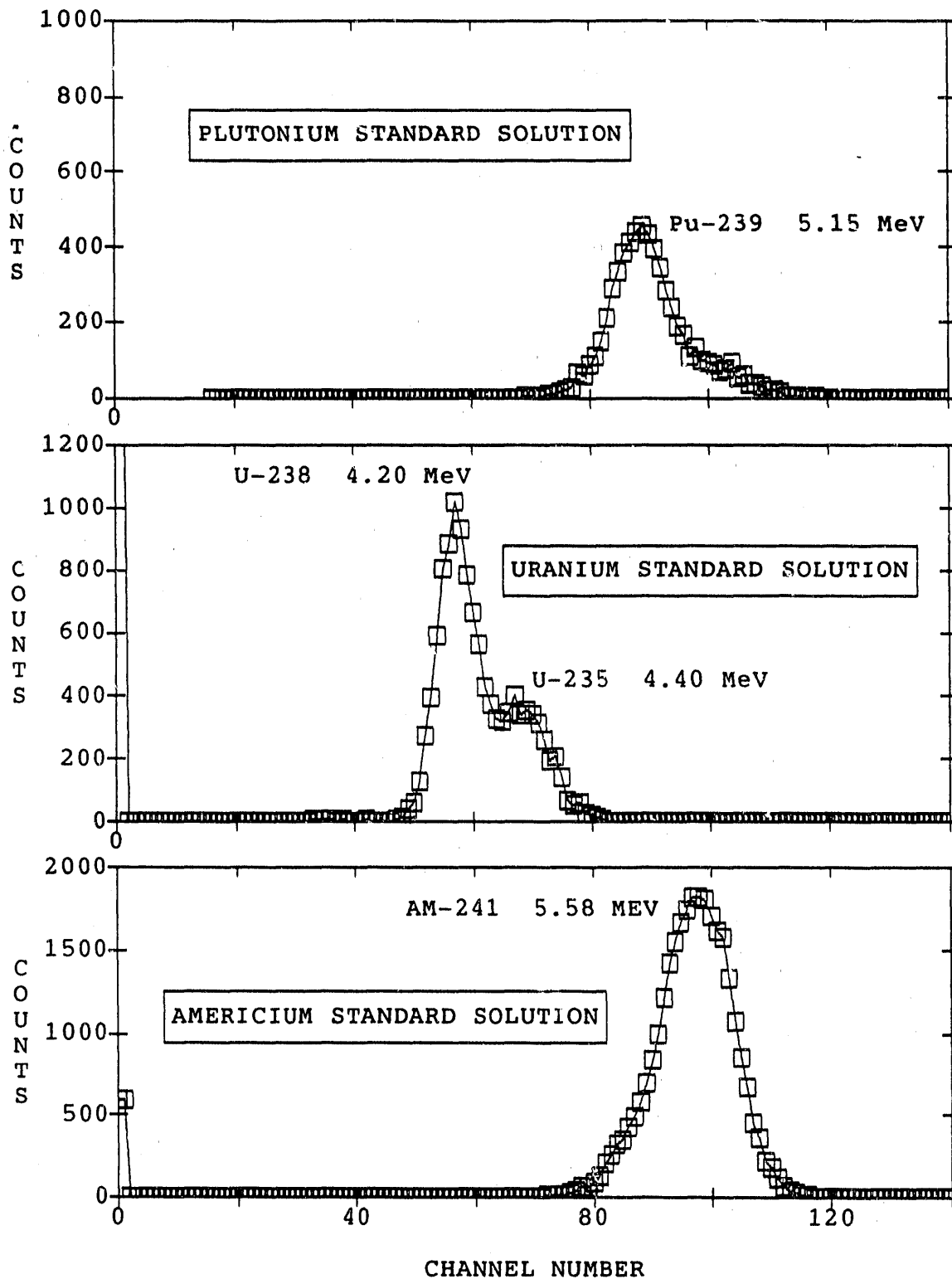
FIGURE No. 9. PERALS spectra from process samples spiked with known amounts of Pu-239 (top), depleted uranium (center) and Am-241 (bottom) and extracted.
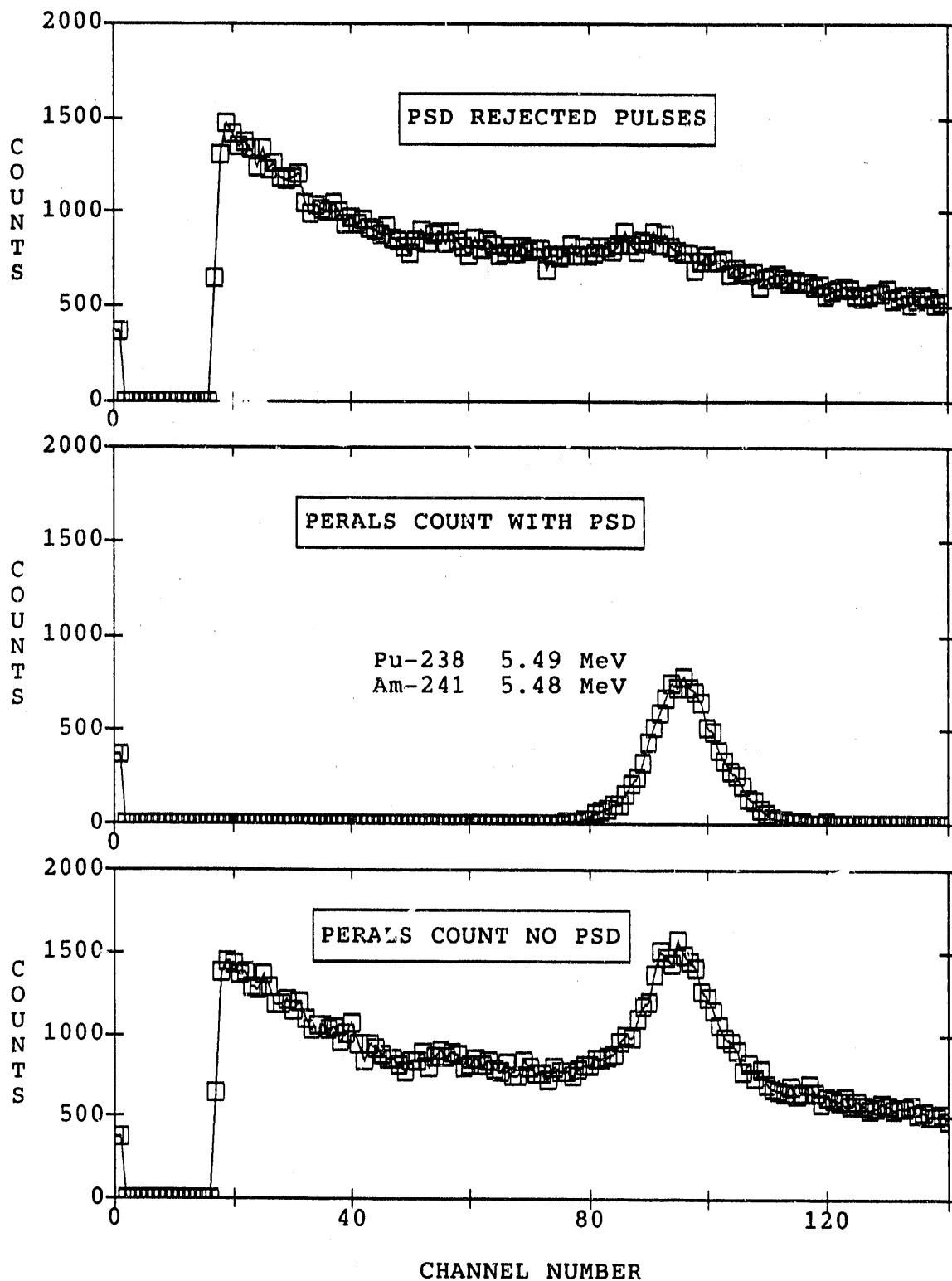
FIGURE No. 10. PERALS spectra of actinides extracted from high level waste sample with PSD on (center), off (bottom) and rejected beta/gamma pulses (top).
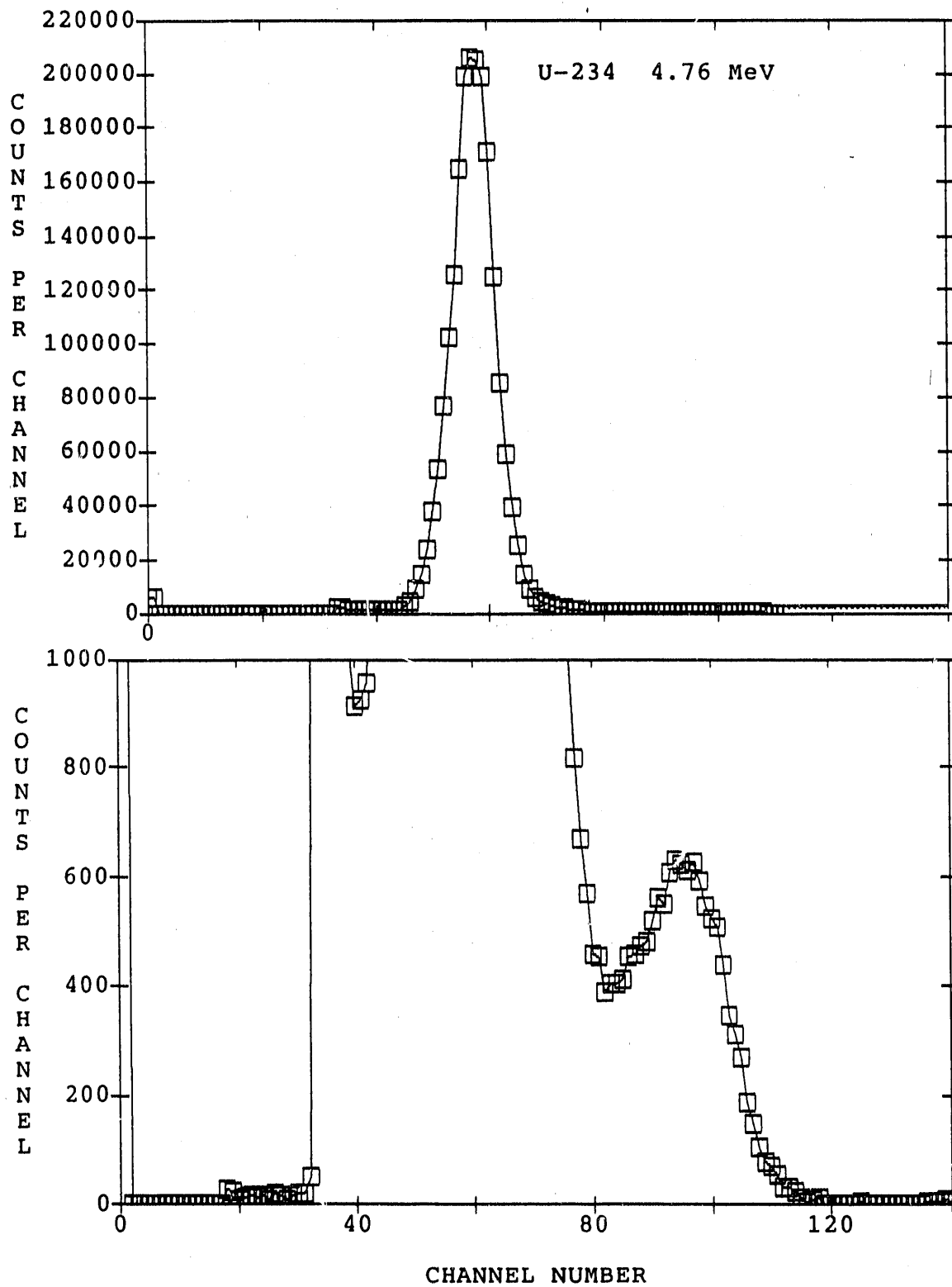
FIGURE No. 11. PERALS spectrum of recycled, enriched uranium showing the alpha activity from U-234 (top) and an enlargement of the scale in the region for U-232 and its daughters (bottom).

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