Electrorefining of Copper

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Abstract

The electrorefining of copper to reduce the levels of natural alpha and gamma emitters has been studied by tracer techniques. It is concluded that codeposition of radiogenic lead may occur, and probably has limited the performance of low-background proportional counters.

Introduction

Any implementation of proportional counters for SNO requires conductive materials for the cathode and the anode, and, of the many candidates, copper suggests itself as one that might be prepared at the necessary level of purity. The "coinage metals" in general can be prepared by electrodeposition from solution, a selective process that discriminates against many more chemically reactive materials. In particular, U, Th, and Ra are not likely to be electrolytically deposited from aqueous solution, absent special techniques to deposit them specifically.

The most stringent purity requirement for ^{3}He detectors applies to the anode material, because α particles from the wall enter the gas and create a continuous background that underlies the ^{3}He(n,p)T peak. For example, if the anode surface contains U and Th chains in equilibrium at 2 pg/g each, then 525 counts per year underlie the peak. The photodisintegration background from construction materials at comparable levels is only 50 detected events per year.

The α background has been studied by Monte Carlo methods. If the alpha emitters are uniformly distributed in the wall material, then 24.9% of alphas originating within a layer whose thickness is equal to the range enter the gas. The distribution of 5 MeV α's is shown in Fig. 1, together with the energy spectrum from ^{3}He(n,p)T. In the region of the 764-keV

neutron capture peak, the alpha intensity is 3.5×10^{-5} per keV per alpha decay. If, for example, a window of 20 % must be set around the neutron peak (in practice the peak intensity and background would be simultaneously fitted without cuts), then the alpha intensity is 5.4×10^{-3} per alpha decay. With the reference design and the SSM flux, an alpha background below 10%, or 170 y^{-1} is desired. This corresponds to an alpha activity of 3.1×10^{4} y^{-1} in a thickness of one range unit (9.2 mg/cm^2 in Cu). The U series consists of 8 α's and Th 6, so this activity is equivalent to 0.8 pg/g U or 3.4 pg/g Th. The surface alpha activity at this level is 0.17 $m^{-2}d^{-1}$.

The most dramatically successful use of electrorefined copper is the ^{76}Ge double beta decay experiment of the Pacific Northwest Laboratories - University of South Carolina group (Brodzinski et al.[1]). The machined copper cap and other copper parts of their detector assembly were replaced with electrorefined material, with the result shown in Fig. 2. All the prominent lines in the upper spectrum are absent in the lower one. Brodzinski et al. do not give a quantitative estimate of the residual level of activity in their copper, but we have made an estimate based on the intensity of the ^{212}Pb line at 238.4 keV. The copper detector cap is approximately 3 mm thick, 85 mm high and 85 mm diameter. The photopeak and solid-angle efficiency factor is estimated to be about 38%, and average self-absorption about 50%. With an upper limit of 6 events in the peak in 124 days (9 events when corrected for the renormalization of time in the second spectrum), the purity of the copper is better than 4 pg/g (referred to ^{232}Th).

The concept of applying coatings to the inner walls of proportional counters to reduce α backgrounds is far from novel. A Soviet group[2] developing a neutrino experiment submerged a cluster of ^{3}He counters in Lake Baikal and observed the α backgrounds. The counters were stainless steel cylinders coated on the inside with a 60-μ layer of "an organofluorine compound having an activity 10 times less than the steel." The rates recorded were about 100 $m^{-2}d^{-1}$. The Irvine group that developed the NC-CC neutrino experiment with D_2O that is very similar to the principle of SNO prepared Cu-coated counters by the same general

methods we propose to use. Pasierb's thesis[3] describes this in detail. With untreated stainless steel coatings, an alpha rate of 3000 $m^{-2}d^{-1}$ was recorded. An electroplated copper layer reduced the rate to 750 $m^{-2}d^{-1}$.

While the efforts in both cases to reduce the α background were successful to a degree, the improvements are surprisingly modest in light of the success achieved by the PNL-USC group. The background levels reached correspond only to the ng/g level of Th and U, and are orders of magnitude above the level required for SNO. We believe that, by application of the tracer method described below, we have made some progress toward understanding this paradox.

Method

The levels of naturally occurring radioactivity being too low for ready measurement, we have carried out electrorefining tests with a tracer of ^{232}U in equilibrium with its daughters. This 70-year isotope feeds 1.9-y ^{228}Th, after which the decay chain is identical to that of natural ^{232}Th. Copper was plated onto the outer surface of a stainless-steel beaker that fitted snugly over the cap of a low-background hyper-pure Ge detector. The vertical-axis detector, made by Princeton Gamma-Tech, had a thin Be window, and a nominal efficiency of 22%. The plating recipe used was that of Brodzinski et al.:

$CuSO_4$	188 g/l
H_2SO_4	75 g/l
HCl	30 mg/l
Thiourea	3 mg/l
$CoSO_4$	1 mg/l

Two liters of solution were prepared and heated to 50 C. The anode was a cylinder of copper stock sheet 0.5-mm in thickness, and the cathode was the stainless beaker immersed slightly more than half-way. It was found that current densities of only 5-10 mA/cm^2 were allowable if excessive dendritic growth was to be avoided, in contrast to the 40

mA/cm^2 used by Brodzinski et al. (In a private communication, Brodzinski has advised us that it is essential to recirculate and filter the electroplating solution continuously. Small particles of oxide act as nucleation sites for dendrite growth.)

The detector energy scale was calibrated with an NBS ^{152}Eu standard. Runs were taken as follows:

RUN 1. Empty Detector. 25,000 sec. (BKG1.D)

RUN 2. ^{152}Eu calibration source (5.762 x 10^4 s^{-1} on May 1, 1978). 601 sec. Source located 26 cm above detector face. Data taken July 17 1991. (CAL00717.D)

RUN 3. Stainless steel beaker (no Cu). 173,000 sec. (SSBKR.D)

RUN 4. ^{232}U source. 6278 sec. 10 nCi located approximately 4 cm above the detector. (U2320001.D)

RUN 5. 150 gm of Cu plated onto a beaker. 100,000 sec. Deposition took 70 h at 1.4 A. Counting began 115 h after the end of deposition. (CUBKR.D)

RUN 6. 53 gm of Cu plated onto a beaker from a solution containing 2.5 nCi of ^{232}U. 100,000 sec. Deposition took 24 h at 1.4 A. Counting began 18 h after the end of deposition. (HOTBKR.D)

RUN 7. Recount beaker of Run 6 100 days after the beginning of Run 6. 100,000 sec. (HOTBKR2.D)

The most interesting comparisons are between runs 4, 5, and 6, the low-energy parts of which are shown in Fig. 3a, 3b, and 3c. The only line visible in run 6 attributable to the ^{232}U tracer is the 238.4-keV line from 10.6-h ^{212}Pb (the strongest in the original tracer spectrum). Its rate in spectrum 6 is 370 times lower than it would be if all the tracer had deposited on the Cu (ignoring solid angle corrections between the ^{232}U

source geometry and the beaker geometry, which would make this number larger still).

There are also lines in spectrum 6 from ^{214}Pb and ^{214}Bi. These are ^{222}Rn decay products. The air in the detector shield is flushed out with boil-off nitrogen, and normally no radon lines are seen, but in this case counting was begun immediately after placing the sample in the detector. Also, a protective layer of Mylar was put between the "hot" beaker and the detector. It is likely that some of the activity was present on the plastic owing to electrostatic attraction of decay products.

The low level of tracer in the electrodeposited material qualitatively confirms the purifying effect of the process, but quantitative conclusions depend on models for how the observed ^{212}Pb activity is incorporated in the copper. The simplest picture is that the tracer is simply entrained with the copper by being trapped in grains, voids, etc. Since the fraction of dissolved copper deposited was 35%, the corresponding rejection factor is at least 130.

However, a model that explains all the data much better is that Pb is appreciably electrodeposited along with Cu. If this is the dominant mode by which ^{212}Pb appears in the spectrum, the Pb is supported by ^{228}Th in equilibrium in solution, but drops out as it is electrodeposited, yielding only half as much final Pb as would be the case for a long-lived isotope. It then decays before and during counting, and a further decay correction of 0.32 is required. In this case the rejection factor becomes 20.

That ^{212}Pb was deposited specifically is demonstrated by the absence of the 238-keV line in Run 7, taken many half-lives later (see Fig. 3d). This demonstrates conclusively that the Pb is not supported by 1.9-y ^{228}Th, which would be the case if the tracer had simply been entrained during the copper electrodeposition. The possibility that ^{224}Ra, ^{220}Rn, or ^{216}Po might have been deposited can be rejected on the basis of chemical properties, and, in the case of ^{216}Po, a very short half-life. There is, however, one possible objection to this argument, namely that the ^{212}Pb

could result from radon. While that cannot be ruled out, the short half-life (56 s) of the ^{220}Rn parent makes it somewhat unlikely.

Conclusions

The evidence that Pb may codeposit with copper allows one to make sense of otherwise puzzling phenomena:

1. The excellent performance of electrorefined copper in gamma spectrometry. The only long-lived radiogenic Pb is 22-y ^{210}Pb, which, with its daughters, emits only one gamma, 46.5 keV. Close inspection of the lower part of Fig. 2 reveals that there is indeed a low-energy line within a few keV of this energy. Bremsstrahlung from the pure β decay of ^{210}Bi also seems to be visible in Fig. 1 of Brodzinski et al.

2. ^{210}Pb is, on the other hand, a very serious contaminant for proportional counters because of the 100% α emission from ^{210}Po. Hence the disappointing performance of electrodeposited copper in such applications is understandable.

Further research will be carried out on the purification of copper. Various strategies to discourage the deposition of Pb are being considered. Isotope dilution (the same approach used by Brodzinski et al. to reduce the deposition of Co) is a promising method. The use of chemical complexing agents, preprocessing the plating bath to precipitate lead, avoiding use of copper anodes, and careful control of electrolytic overvoltage may also prevent the Pb from coming through.

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References

1. R. L. Brodzinski, H. S. Miley, J. H. Reeves, and F. T. Avignone III, Nucl. Instr. Methods in Phys. Research A292, 337 (1990).

2. I. I. Gurevitch et al., I. V. Kurchatov Institute Preprint IAE-4986/2, 1989.

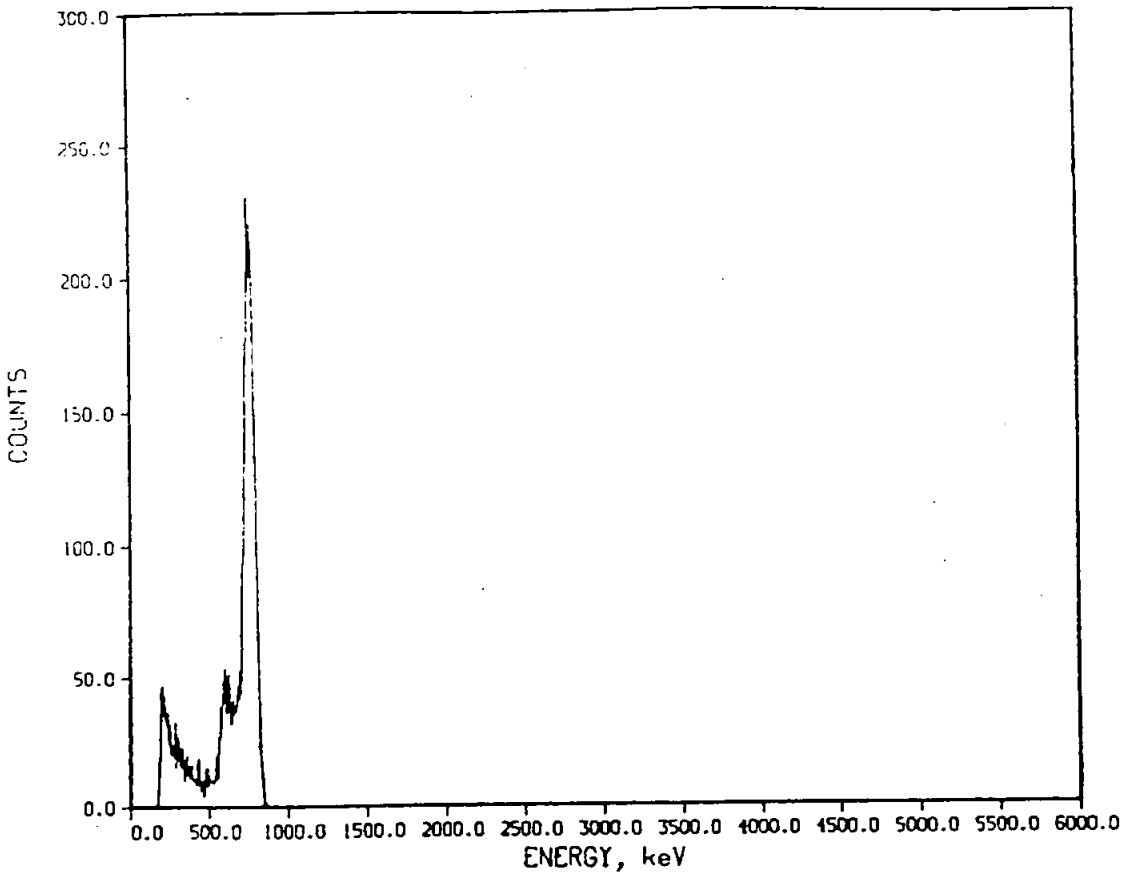
3. E. L. Pasierb, PhD Thesis, UC Irvine 1979.

Figure Captions

Fig. 1. Monte Carlo simulations of (top) $^{3}He(n,p)T$ spectrum in pure He with 10% FWHM detector resolution. The "wall effect" wherein the proton or triton strikes the wall before stopping in the gas, can be seen. (Bottom) Spectrum of 10^5 α's originating within one range unit of the wall and entering the gas.

Fig. 2 Ge-detector spectra from Ref. 1. (Top) Original machined copper cap. (Bottom) Electrodeposited copper cap. Note the possible evidence for the 46.5-keV gamma from ^{210}Pb near the bottom end of the lower spectrum.

Fig. 3. a) Spectrum of ^{232}U and daughters. b) Spectrum of copper deposit from inactive solution. c) Spectrum of copper deposit from solution containing ^{232}U. Only the ^{212}Pb line at 238.4 keV can be attributed to the activity added to the solution. d) Copper plated from solution with ^{232}U tracer, 100 days after deposition.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250.0
200.0
150.0
100.0
50.0
0.0
COUNTS
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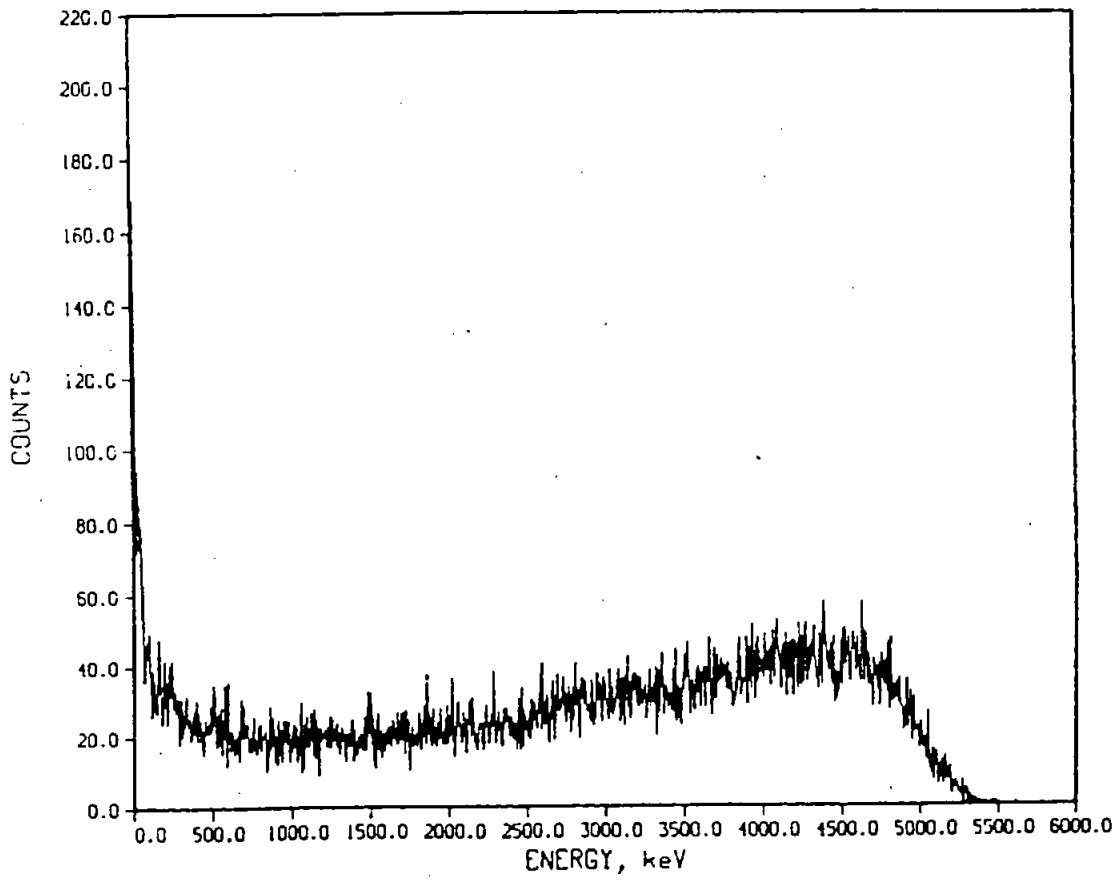
ENERGY, keV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200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
COUNTS
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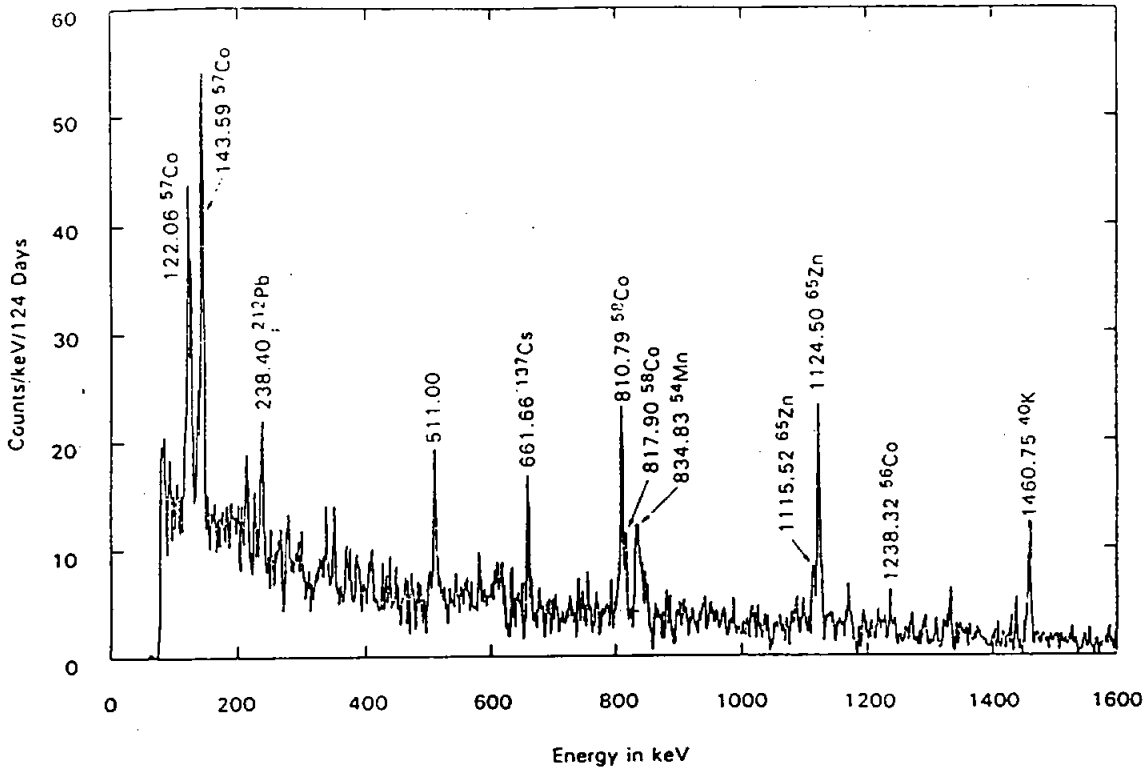
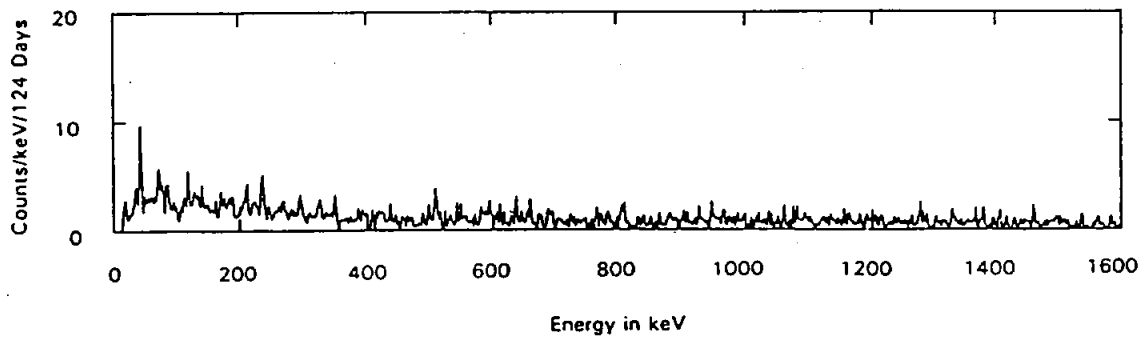
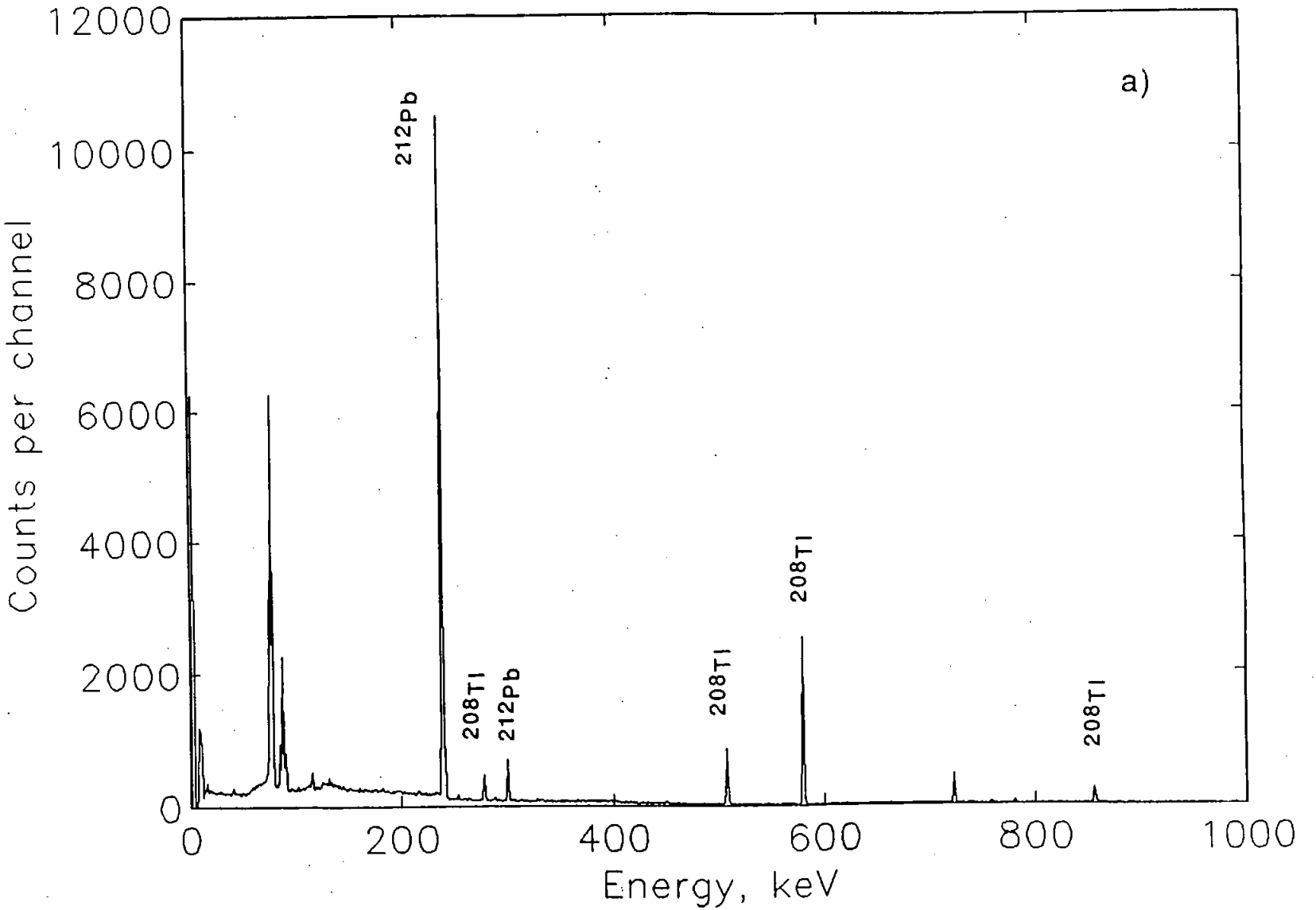
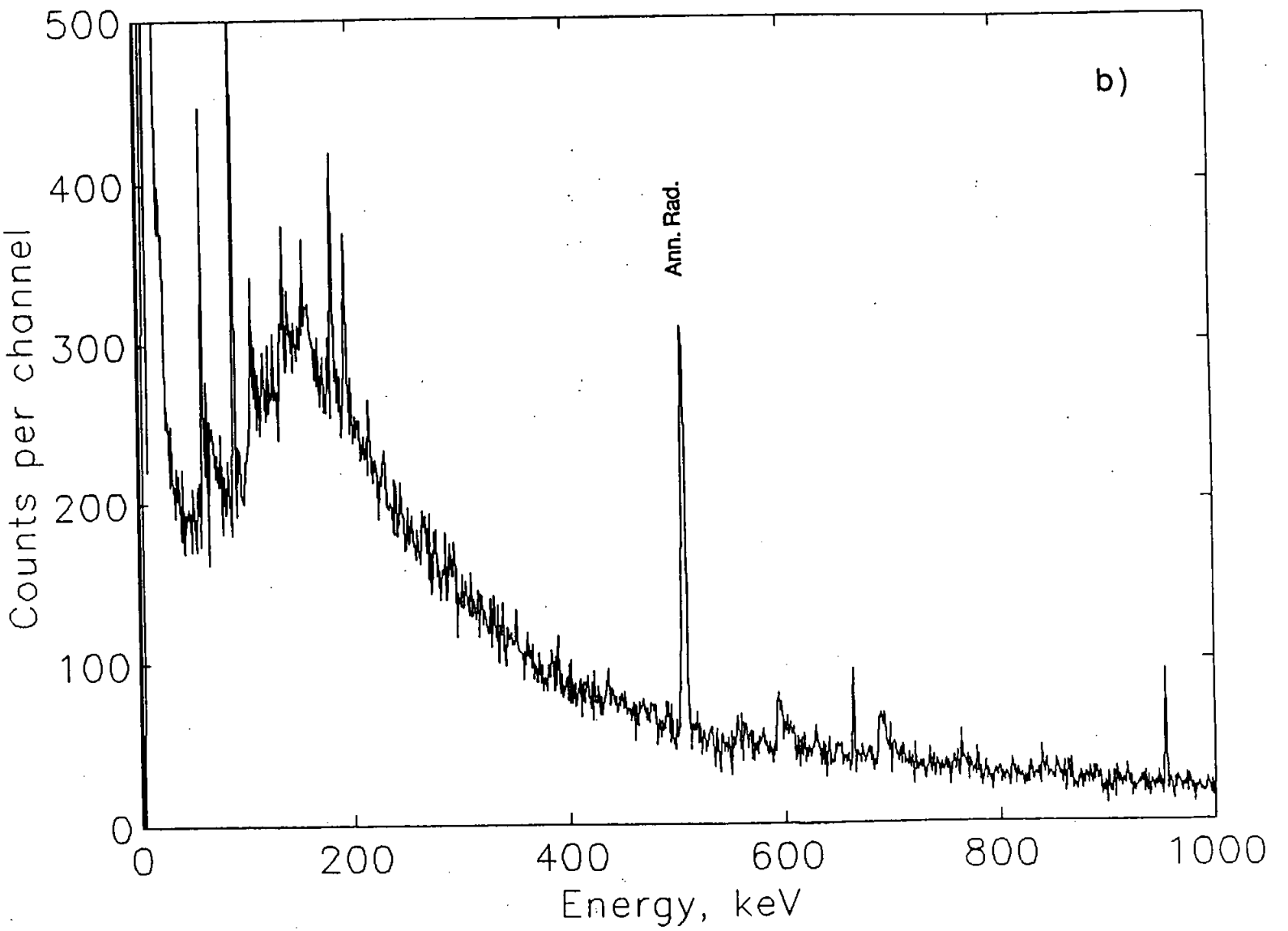
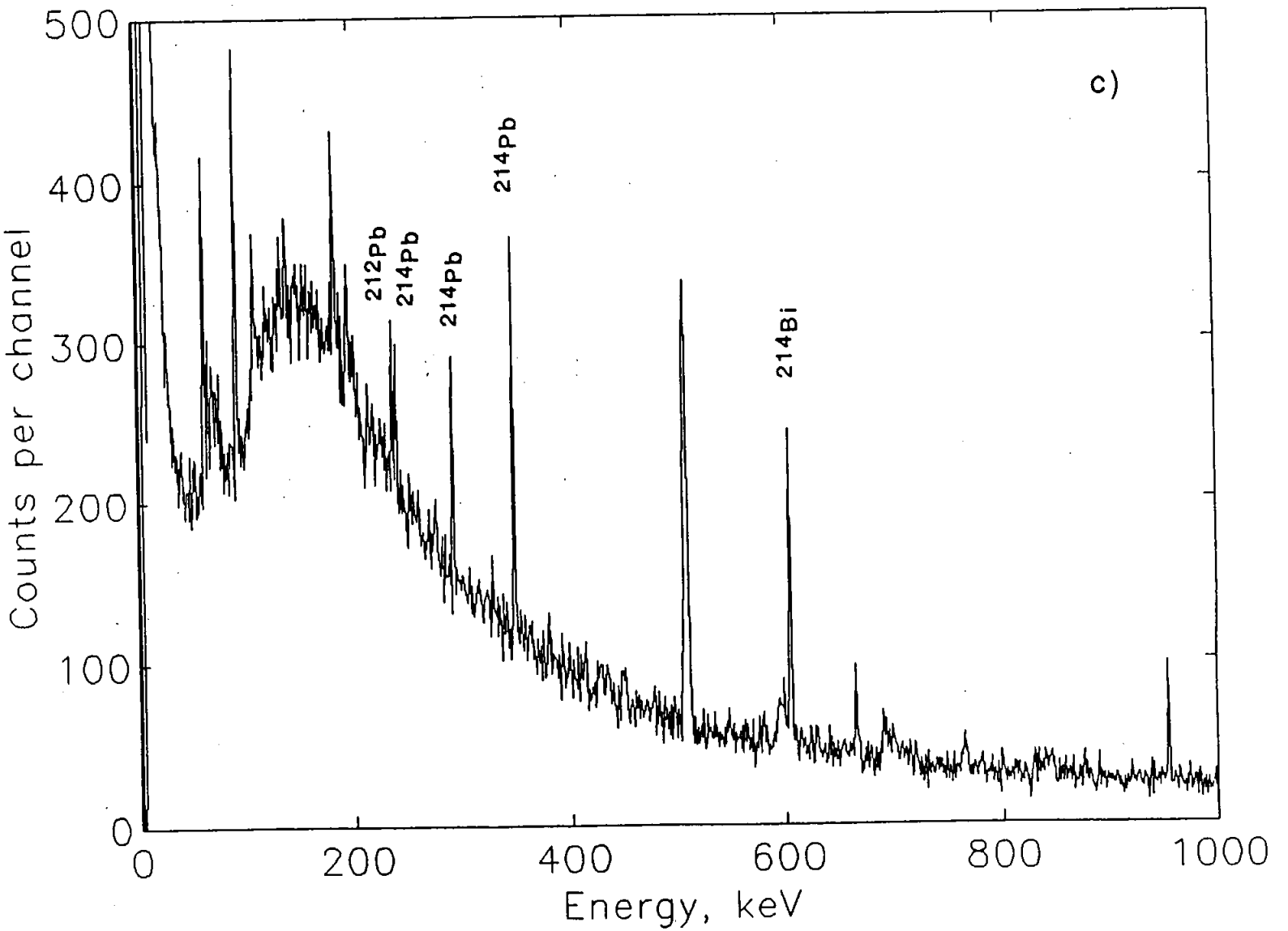
ENERGY, keV

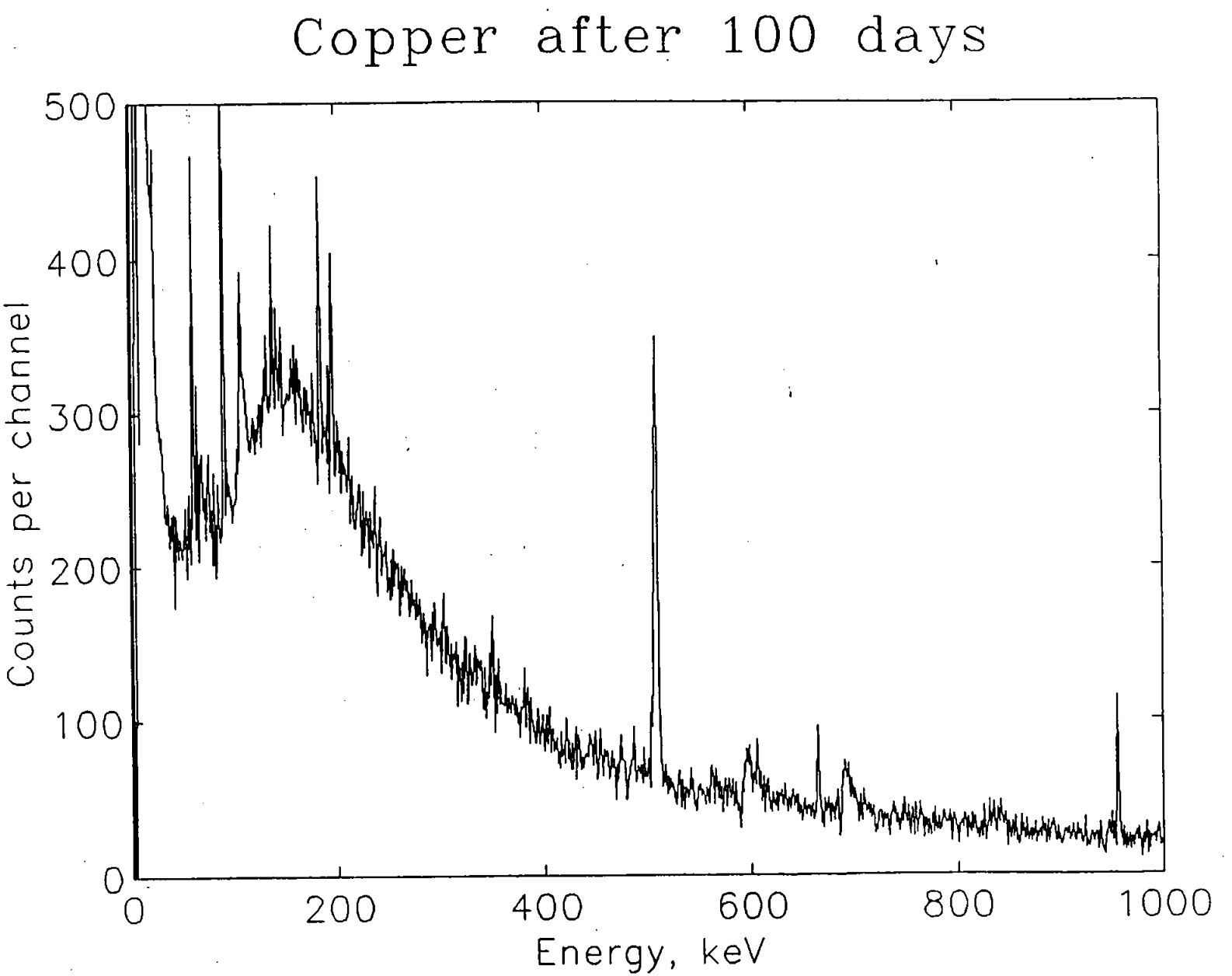

Counts/keV/124 Days
Energy in keV
122.06 57Co
143.59 57Co
238.40 212Pb
511.00
661.66 137Cs
810.79 58Co
817.90 58Co
834.83 54Mn
1115.52 65Zn
1124.50 65Zn
1238.32 56Co
1460.75 40K


Counts/keV/124 Days
Energy in keV


a)
Counts per channel
Energy, keV
0
2000
4000
6000
8000
10000
12000
0
200
400
600
800
1000
212Pb
208Tl
212Pb
208Tl
208Tl
208Tl


b)
Ann. Rad.
Counts per channel
Energy, keV
0
100
200
300
400
500
0
200
400
600
800
1000


c)
212Pb
214Pb
214Pb
214Pb
214Bi
Counts per channel
Energy, keV
0
100
200
300
400
500
0
200
400
600
800
1000


Copper after 100 days
Counts per channel
0
100
200
300
400
500
0
200
400
600
800
1000
Energy, keV