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NONDESTRUCTIVE IDENTIFICATION OF CUSIL BRAZE MATERIAL BY NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

Neutron activation analysis was used as a nondestructive technique to positively distinguish between cusil (28% Cu, 72% Ag) and silver braze material bonding electrical leads to the substrate of an LSI. The SLL californium-252 source was used to activate LSI samples and a small volume Ge(Li) spectrometer was used to observe the characteristic radiations. Based on these results, it is concluded that an exposure of the braze material for twenty-four hours to a thermal neutron flux of 10^7 neutrons/cm^2/sec will produce sufficient activation to positively identify the cusil braze parts. Thermal neutron fluxes of this order, and large exposure areas, are available at nuclear reactor facilities. Using a large volume Ge(Li) gamma-ray spectrometer to observe the characteristic radiations from copper-64, the counting interval per part would be approximately 100 sec. The neutron sensitive LSI chips can be shielded with cadmium foil to reduce the thermal neutron fluence to an insignificant level.

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Introduction

A nondestructive technique was developed to positively identify the braze material bonding electrical leads to the substrate of an LSI (Large Scale Integration) circuit. LSI's that were bonded with cusil braze material are not acceptable because the braze does not meet temperature and humidity requirements, while parts with pure silver brazes are acceptable. An LSI part and a schematic cross-sectional view of the braze joint are shown in Figure). Kovar leads (53% iron, 29% nickel, 17% cobalt, 0.3% maganese, and 0.2% silicon by weight) are bonded to a tungsten pad on the LSI substrate with either cusil (28% copper and 72% silver) or silver (100%) braze material. The braze joint is electroplated with nickel and then with gold. Visual inspection does not always positively distinguish between cusil and silver braze parts because of the electroplated surface layers covering the braze materials. Because the LSI chips cannot be salvaged once they are bonded to the substrate, a nondestructive technique was required that would positively distinguish between the acceptable and unacceptable parts. We have used thermal neutron activation analysis to differentiate between cusil and silver braze parts by detecting the presence of copper in the cusil braze material.

Basic Concepts

Neutron activation analysis is a sensitive nondestructive method of measuring elemental constituents, either qualitatively or quantitatively, by measuring the characteristic radiations emitted by radioactive nuclides resulting from selected nuclear transformations. Gamma-ray spectroscopy provides a measure of the energies and intensities of gamma emissions from the radioactive products or daughter isotopes. The gamma emissions result in a unique signature allowing identification of the stable constituents, or parent isotopes, in the sample material. Since the number of emitted gamma rays is proportional to the number of atoms in the sample, an accurate measure of the fractional composition of the material is possible.

An element lends itself to routine neutron activation analysis when one of its isotopes undergoes a capture gamma, (n, γ), reaction with thermal neutrons to form a radioactive daughter isotope. There are approximately seventy-four elements that are routinely addressed in this manner. Additional elements may be addressed by fast neutron activation analysis where the daughter isotopes are formed through (n, α), (n, p), and $(n, 2n)$ reactions where neutron energies are above a given threshold energy.

The sensitivity of the method depends on a number of variables including nuclear reaction cross section, neutron flux, irradiation time, radioactive half-life, and fractional gamma-ray yield. The resolution and efficiency of the gamma-ray spectrometer are also important factors. The advent of the large volume lithium-drifted germanium, Ge(Li), detector with a resolution of a few keV and efficiency of greater than 10% at 1 MeV has dramatically increased the applications of this technique in the past few years. Gamma rays interact with this detector primarily through photoelectric interactions (total energy absorption), resulting in discrete photopeak, and Compton interactions (partial absorption), resulting in a continuous spectral distribution (e.g., the Compton distribution). The photopeaks in the activation spectra provide unique signatures for identifying and quantifying the elemental composition of a material. Interference free signatures of the element of interest are obtained by appropriate choices of neutron irradiation time and time interval between end of irradiation and gamma-ray measurements, considering the half-lives and characteristic radiations of the radioactive products.

The photopeak counting rate, R_p (counts/sec), is given by:

$$R_p = N_a \phi \sigma e^{-\lambda t_1}(1 - e^{-\lambda t_2})F$$

where

N_a = number of atoms of isotope a in the sample

ϕ = neutron flux (neutrons/cm^2/sec)

σ = neutron cross section (cm^2/atom)

λ = decay constant of radioactive daughter isotope

t_1 = time elapsed from end of neutron irradiation to mid-point of counting interval

t_2 = irradiation time

F = constant relating disintegration rate to count rate (includes geometry factors, detector efficiency, and fractional yield of gamma rays)

The median sensitivity of the elements routinely addressed by neutron activation analysis is approximately 10^{-9} g on an interference free basis, and the range of sensitivities is from approximately 10^{-12} g (Dy, In) to 10^{-6} g (P, S, Fe). By increasing neutron irradiation times from a routine 30 to 60 min, and increasing counting times to hours instead of minutes, half-lives permitting, these routine sensitivities can be enhanced significantly.

Technique and Results

The amount of copper in the cusil braze joint of the LSI was estimated to be of the order of 100 micrograms which makes the samples amenable to neutron activation analysis (see section on "Basic Concepts"). The nuclear reaction of interest is the (n, γ) reaction with copper-63 (69% abundart) to form the radioactive isotope copper-64 (12.8 hour half-life). The decay scheme for this isotope is given in Figure 2. Copper-64 decays 62% of the time to stable nickel-64 by either electron capture (43%) or positron emission (19%). Each positron emission results in annihilation radiation of energy 0.51 MeV, while a 1.34 MeV gamma emission follows electron capture to the first excited state of nickel-64 (0.5%). Copper-64 also decays by negatron emission to the ground state of stable zinc-64 (38%) without emission of a characteristic gamma ray. The other stable copper isotope, copper-65, also absorbs thermal neutrons to form radioactive copper-66 (see Figure 2). However, the short half-life of this isotope, 5.1 min, makes it less desirable for use in this application of neutron activation analysis. A summary of the radioactive isotopes that are formed by neutron irradiation of the materials near the braze joint is given in Table I together with thermal neutron activation cross sections, half-lives, and characteristic radiations.

LSI samples were irradiated with neutrons from the SLL californium-252 source (Figure 3). The samples were masked with cadmium foil so that the braze material was exposed to the neutron flux while the sensitive LSI chip and a majority of the electrical lead material was shielded (see Figure 1.b). *A cadmium foil 0.1 cm (0.04 in) thick reduces the thermal neutron flux by a* factor of 10^6. The braze material was exposed to a thermal neutron fluence of 2 x 10^{11} neutrons/cm^2. Total irradiation time with the californium-252 source was 71 hours.

Gamma-ray spectra from the activated samples were recorded with a small volume (0.4 cm^3) Ge(Li) spectrometer. Measured gamma-ray spectra from cusil and silver braze samples taken three hours after irradiation are shown in Figure 4. The counting interval to obtain these results was 4000 sec. The 0.51 MeV annihilation radiation from copper-64 is clearly evident in the spectrum from the cusil sample and absent from that of the silver sample. In addition to copper-64, other isotopes activated in the samples were tungsten-187 and gold-198 as indicated in Figure 4. If a large volume (40 cm^3) Ge(Li) detector had been available to us, we would have recorded additional higher energy peaks due to the increased detection efficiency. These higher energy peaks were recorded, although they were not resolved, with a 100 cm^3 sodium iodide, NaI, spectrometer as shown in Figure 5. In

the NaI record the presence of the 1.34 MeV gamma-ray peak is indicated, although it is not resolved from iron-59, nickel-65, and silver-110 gamma-ray peaks near 1.3 MeV. Similarly, the 0.51 MeV copper-64 radiation is not resolved from the intense 0.41 MeV gold-198 gamma ray. However, with a large volume Ge(Li) detector the presence 1.34 MeV copper-64 gamma ray in addition to the 0.51 MeV radiation should be observed, giving additional confirmation of the copper content of a cusil sample.

The californium-252 source has a fast neutron component that cannot be attenuated to protect the radiation sensitive LSI chip without significant reduction in thermal neutron intensity. It is suggested that an essentially pure thermal neutron source be used for activation of the braze joint with adequate shielding provided to protect the LSI chip. The LLL Pool Type Reactor, for instance, has a thermal neutron column that provides a large exposure area to a thermal flux of about 10^7 neutrons/cm^2/sec. An irradiation time of 24 hours at this facility and a counting interval of approximately 100 sec with a large volume Ge(Li) spectrometer should be sufficient to positively identify cusil braze parts.

It should be noted that X-ray fluorescence analysis was also attempted as a means of identifying copper in the cusil braze. Direct radiation from a 20 millicurie americium-241 source, and fluorescence radiation from selenium (11.2 keV) were both used independently to excite the 8.9 keV fluorescence radiation of copper. Fluorescence spectra from the samples were recorded with a lithium drifted silicon, Si(Li), X-ray spectrometer. The copper fluorescence was too weak to be observed above the background and scattered radiation, although gold, tungsten, silver, nickel, and iron fluorescence peaks were observed. The fact that the copper fluorescence was not observed is attributed to the small quantity of copper in the total part and attenuation of the copper fluorescence radiation in the nickel and gold plating that covers the braze material.

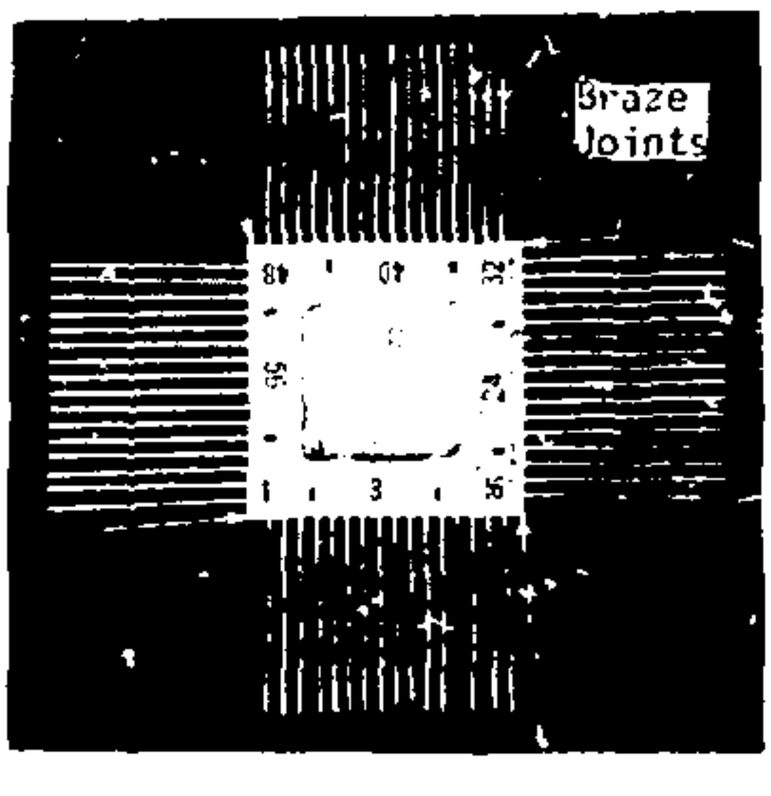
Conclusions

Neutron activation analysis was found to be a feasible nondestructive inspection technique to positively identify cusil as the braze material bonding kovar leads to an LSI substrate. A small volume Ge(Li) detector used here recorded the characteristic 0.51 MeV annihilation gamma radiation from copper-64 after an LSI part with cusil braze was exposed to a fluence of 2 x 10^{11} thermal neutrons/cm^2. This characteristic radiation was absent from the spectrum of a pure silver braze LSI part that was exposed to the same neutron fluence. From these results, it is estimated that a 24-hour exposure to a flux of 10^7 neutrons/cm^2/sec, available at reactor facilities, would activate the parts to a desirable level. A counting period of approximately 100 sec per part with a large volume Ge(Li) spectrometer would then result in a positive identification of cusil braze parts. The sensitive LSI chips can be shielded from the thermal neutron flux with cadmium foil to reduce the neutron fluence to an insignificant low level. An attempt to identify the parts by an alternate method, X-ray fluorescence analysis, was unsuccessful because of the small quantity of copper in the total part, in addition to attenuation of the copper fluorescence radiation in the nickel and gold plating that covers the braze material.

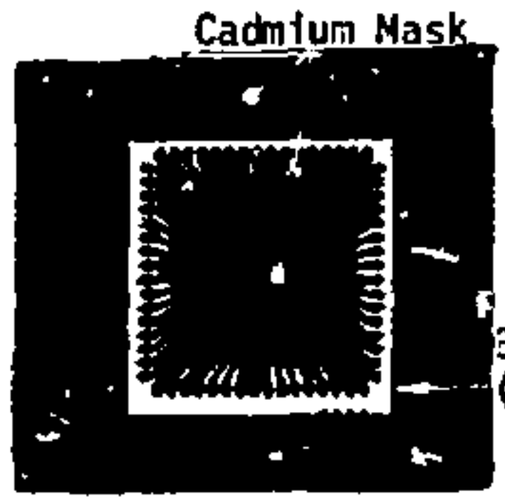
Table 1 - Major radiation isotopes formed by neutron activation of LSI part.

Parent Isotope (% Abundance)	Daughter Isotope	Cross Section[1] (Barns)	Half-Life[2]	Major Gamma Rays (MeV)
Co-59 (100)	Co-60 m	19	10.5 m	1.33
Co-59 (100)	Co-60	18	5.26 y	1.17, 1.33
Ni-64 (1.2)	Ni-65	1.7	2.6 h	0.37, 1.12, 1.48
Cu-63 (69)	Cu-64	4.7	12.8 h	0.51, 1.35
Cu-65 (31)	Cu-66	0.05	5.1 m	1.04
Ag-109 (48)	Ag-110	4	253 d	0.66, 0.76, 1.48
W-184 (31)	W-185	1.8	75 d	0.13
W-186 (28)	W-187	36	24 h	0.69, 1.34
Au-197 (100)	Au-198	99	2.7 d	0.41, 0.68

1) Thermal neutrons (1 barn = 10^{-24} cm^2/atom)
2) minutes, hours, days, years



(a)



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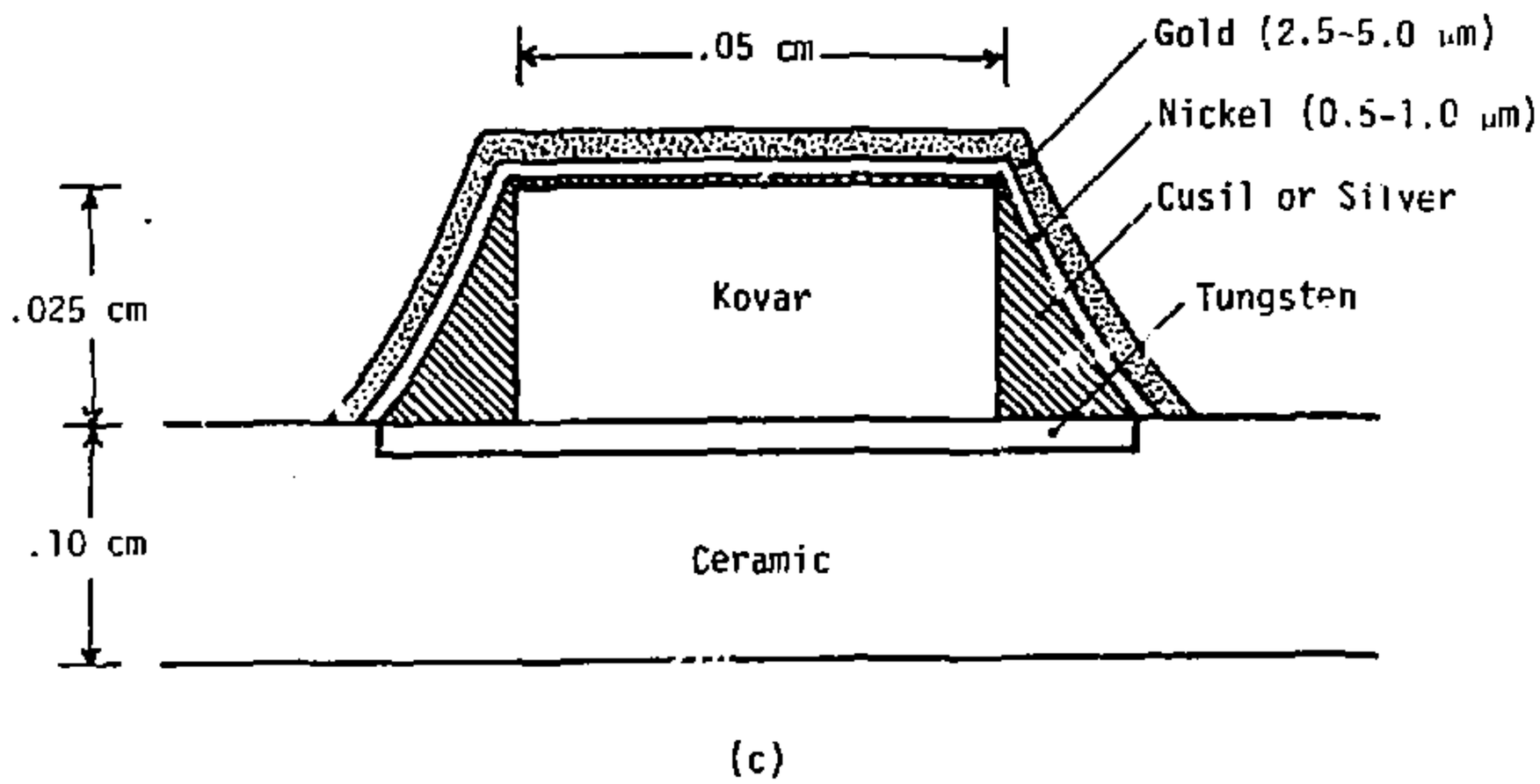

(c)

Figure 1 - (a) Photograph of LSI part with electrical leads attached. Locations of braze joints are indicated. (b) X-radiograph at 28 kV of LSI part showing cadmium mask and unshielded thermal neutron activation region (Note: electrical leads are not seen in positive print of radiograph because of inherent low sensitivity of positive print). (c) Illustrated cross-sectional view of braze joint indicating materials, thicknesses, and size.

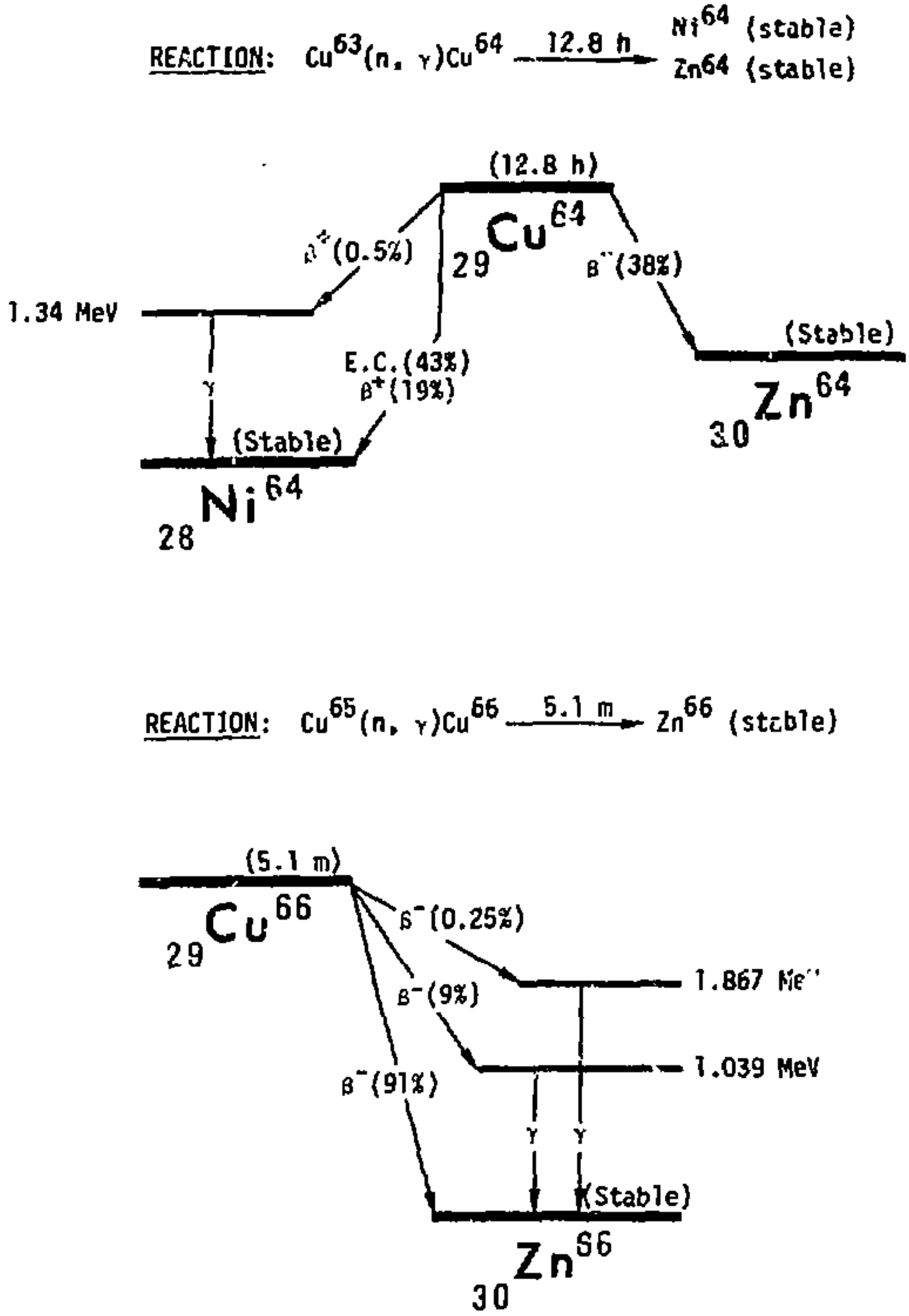

Figure 2 - Decay schemes of thermal neutron activated copper isotopes.

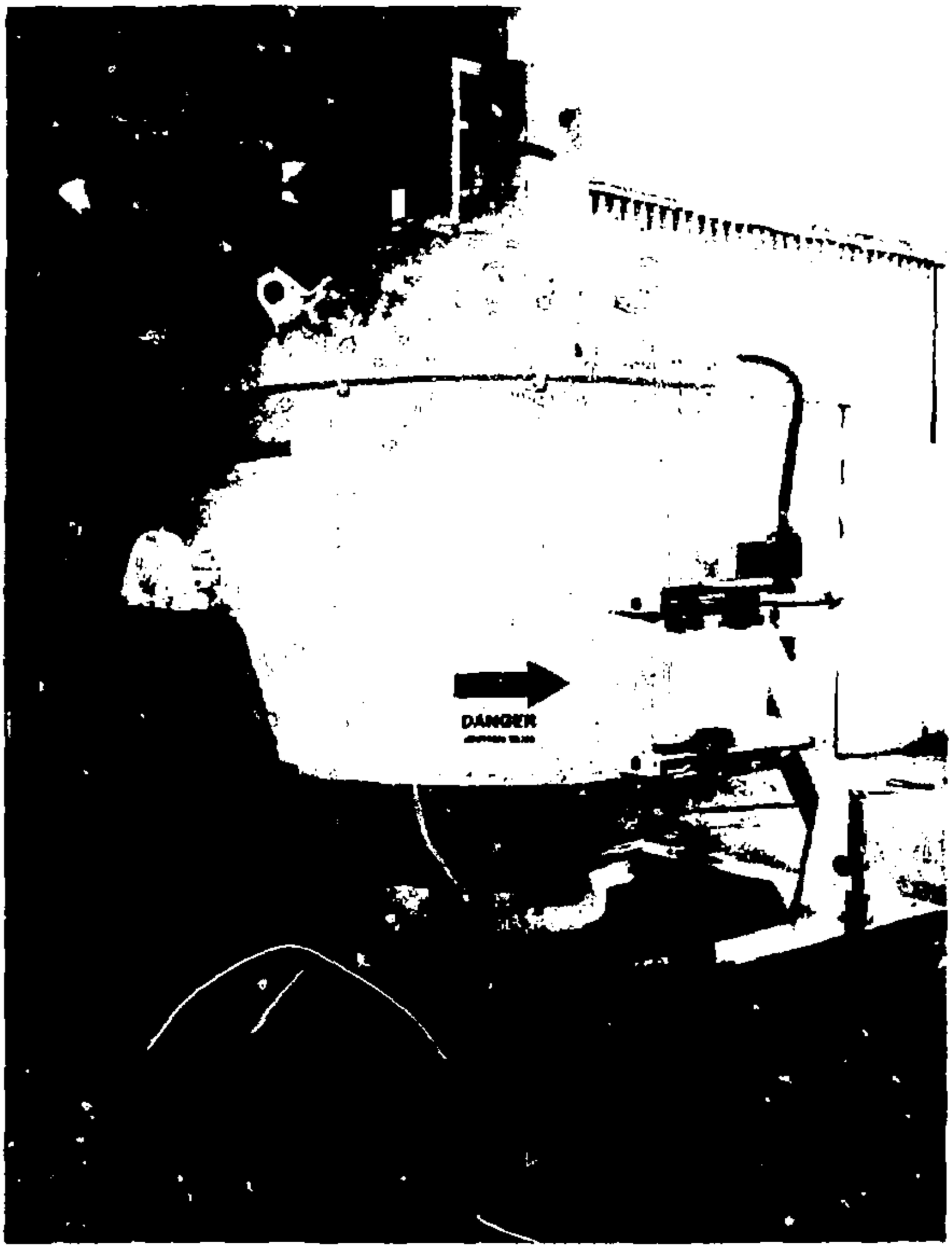

Figure 3 - Californium-252 Source Shield

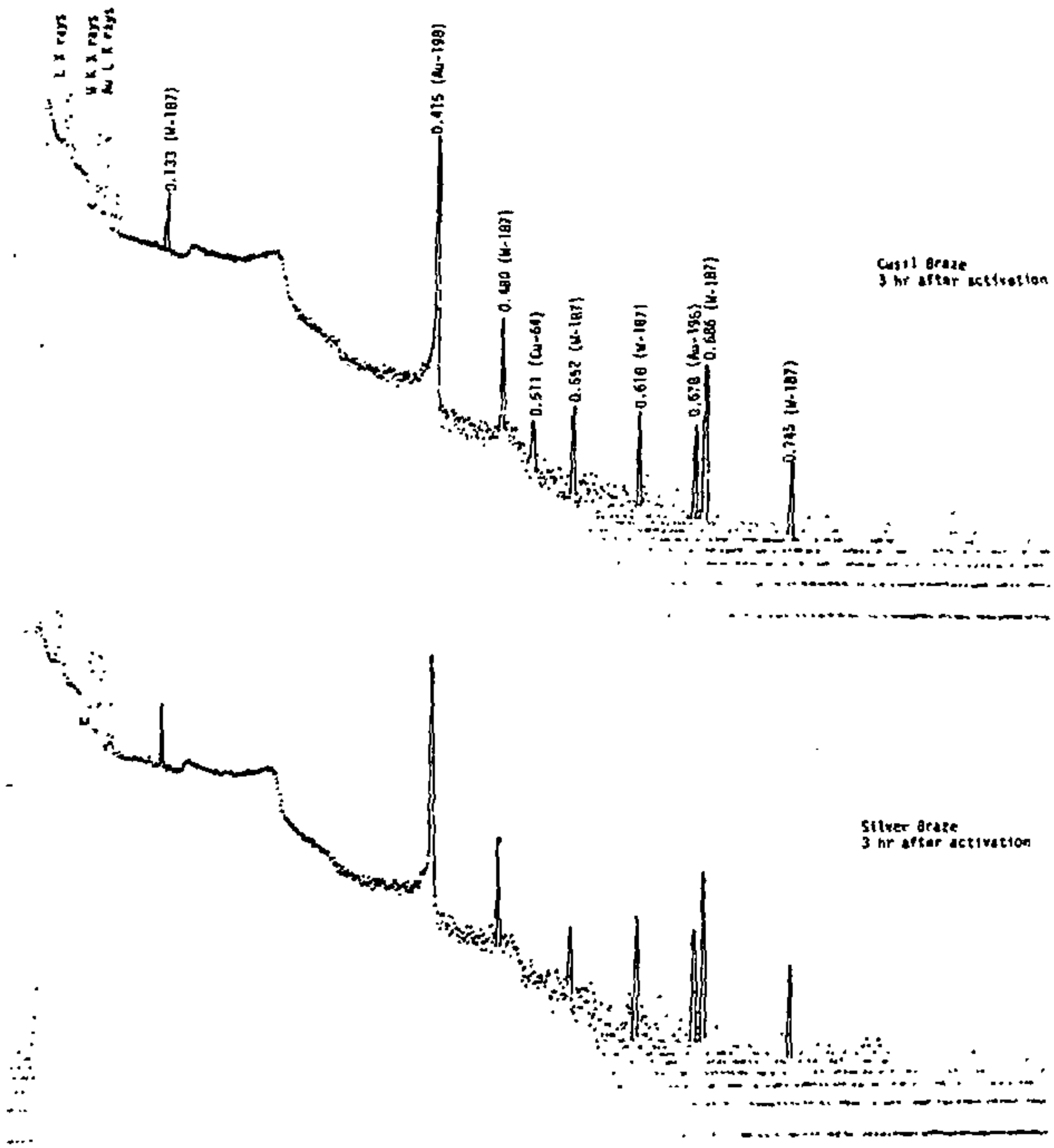

Figure 4 - Gamma-ray spectra from activated samples measured with a Ge(Li) spectrometer

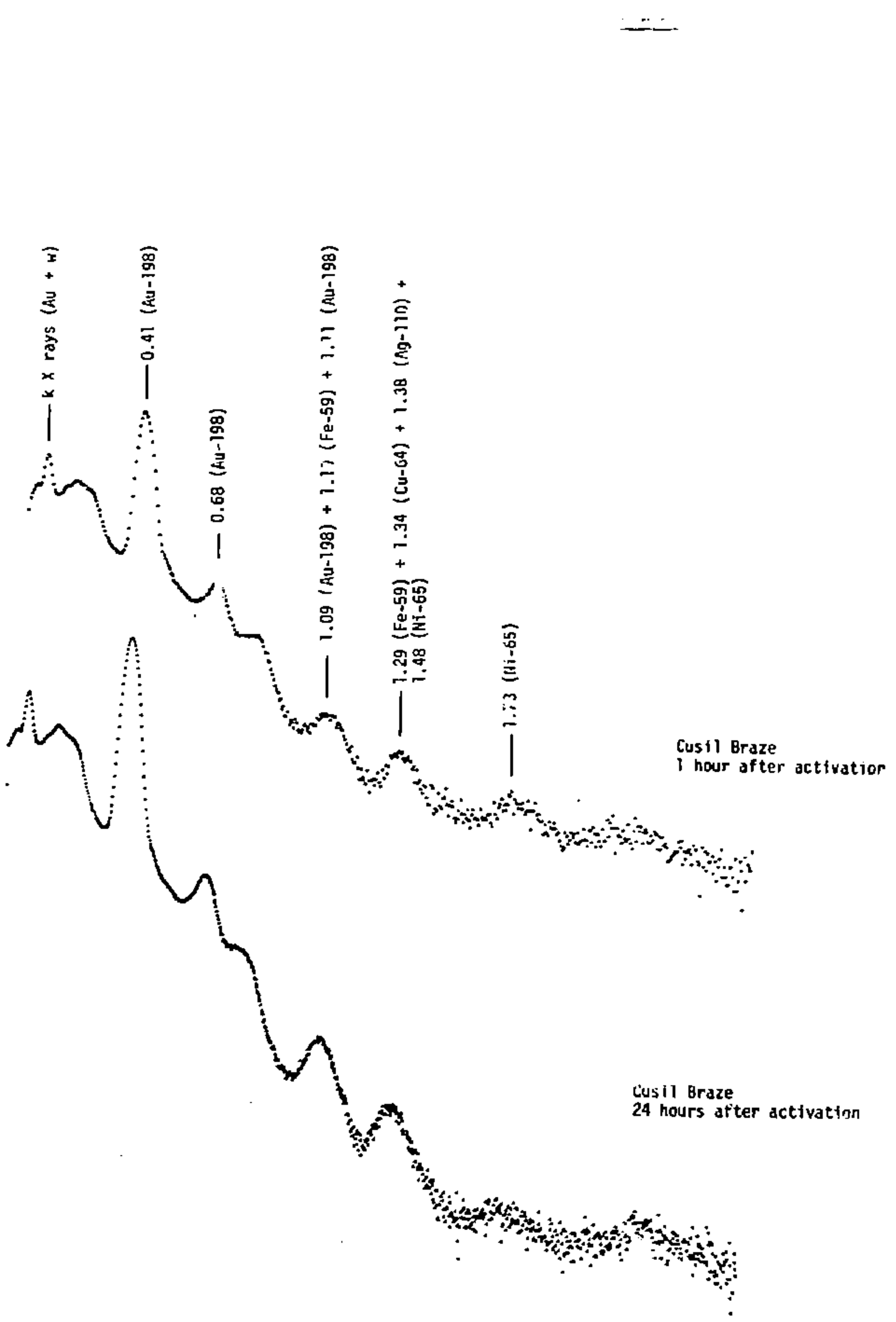

Figure 5 - Gamma-ray spectra from activated samples measured with a NaI spectrometer