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ABSTRACT

A lithium-drifted germanium gamma-ray spectrometer has been utilized for the non-destructive analysis of aluminum by the method of neutron activation. Because of the much higher resolving power of these semi-conductor detectors in comparison to the widely used sodium iodide scintillators, a marked simplification is achieved in the analysis of samples yielding complex gamma-ray spectra. In this work, fractional parts-per-million concentrations of Mn, Sc, Hf, and Cr were readily detected and analyzed non-destructively in 99.9999% aluminum. A comparison is made with the results of other non-destructive analyses of aluminum.

INTRODUCTION

In recent years, the technique of activation analysis utilizing gamma-ray detection has received considerable attention and has been shown to have important applications to a wide variety of analytical problems. Of the many features tending to make the technique attractive, perhaps the most important are: very high sensitivity for many elements, elimination of need for reagent blanks common to many other analytical techniques, and lack of interference from neighboring elements (since the decay properties of radioactive isotopes are unrelated to their chemical properties). With the development of large sodium iodide scintillation detectors and lower-cost multichannel pulse-height analyzers, the technique has been put within reach of most laboratories.

However, in many practical situations, the use of activation analysis has not been attractive because of the laborious procedures that are required, for example, for the simultaneous determination of several elements in the same sample. Practical samples containing a number of readily activated elements generally yield complicated gamma-ray spectra, because of the production of several radioactive isotopes each of which may have a number of gamma-rays in its characteristic spectrum. Because of the poor intrinsic resolving power of sodium iodide scintillation detectors, there results a considerable overlap of gamma lines in the spectrum. In order to sort out and identify the component gamma-ray lines, it is necessary either to employ elaborate and time consuming chemical separations or to resort to indirect methods such as the "synthetic analysis" of the spectrum with use of complex computer programs (2).

Recently, a significant advance in the field of gamma-ray spectroscopy has taken place, with the development of semiconductor detectors that have very much higher resolving power than the widely-used NaI scintillators and yet are moderately sensitive to gamma rays. It is possible with the use of these lithium-

drifted germanium (Ge(Li)) detectors to distinguish gamma rays differing in energy by as little as 2-4 keV in complex gamma-ray spectra, and to determine their absolute energies to better than 0.5 keV. Because of the high resolution, individual photopeaks stand out more distinctly over background radiations, and thus it is possible to detect relatively weaker gamma lines in a spectrum than can be done with scintillation detectors.

These properties have aroused our interest in the application of Ge(Li) detectors to problems in activation analysis, especially to non-destructive analysis, where the high available resolution would appear to allow wider application of the technique as well as an improvement in sensitivity.

To investigate these possibilities, we have considered the analysis of high-purity aluminum by neutron activation, a problem that has been given considerable attention. For a review of previous activation analyses of high-purity aluminum, the reader is referred to the paper by Chinaglia and Malvano (3) on a non-destructive analysis and that of Gaittet and Albert (5) on a destructive analysis. In this report we discuss and compare the results of our non-destructive analysis using Ge(Li) detectors with previously reported non-destructive analyses.

EXPERIMENTAL

The detector used in the present study was prepared in this laboratory and has dimensions 6 cm^2 × 9 mm (active thickness). The detector is operated in vacuum at approximately 77°K, with a bias voltage of 720 volts. For a comprehensive description of the characteristics and fabrication of lithium-drifted germanium detector systems, the reader is referred to the reports of Ewan and Tavendale (4), Goulding (6), Goulding and Hansen (7), Hansen and Jarrett (9), and Miner (12).

A sectional view of a typical detector assembly is shown in Figure 1 and a picture is reproduced in Figure 2. The detector is mounted on a copper plate that makes thermal contact with a liquid nitrogen reservoir cryostat. A Varian VacIon pump is used to provide a pressure of approximately 2×10^{-5} microns in the detector chamber. The front window of the detector chamber is aluminum, of thickness 0.020 in. (137 mg/cm^2). The associated electronics consists of a low-noise, low-capacity preamplifier and biased amplifier system designed by Goulding and Landis (8) and constructed at this Laboratory. Pulses from this system are routed to an RIDL 400 channel pulse-height analyzer for sorting.

The photopeak efficiency function of the detector for gamma rays of various energies was obtained by counting standardized sources of Hg^{203}, Na^{22}, Na^{24}, and Au^{198} under the experimental conditions used for the activation analysis samples. The absolute disintegration rates of these standard sources were obtained by a coincidence method (1). The resulting experimental photoelectric efficiency curve is shown in Figure 3 along with the corresponding curve for a 3" × 3" (diam.) NaI(Tl) crystal. The latter curve was constructed from the data given by Heath (10). In the case of the Hg^{203} 279-keV line, the efficiency of the Ge(Li) detector relative to that of the NaI(Tl) detector (with the source

located at a distance of approximately 2.5 cm from the face of the detector) was found to be 1.3×10^{-2}.

In Figure 4 are shown curves relating the observed line widths of gamma rays as a function of gamma-ray energy for a Ge(Li) detector of dimensions 2 cm^2 × 7 mm (active layer) and a 3" × 3" (diam.) NaI(Tl) cyrstal. The larger Ge(Li) detector used in the present work showed a line width of about 4 keV (full width at half maximum) for the 122-keV gamma ray of Co^{57}, as compared to about 2 keV for the smaller detector. These line widths are to be compared with a width of about 20 keV typical of the response of NaI(Tl) detectors at this energy.

The aluminum samples, which ranged from aluminum wire of unspecified purity to 99.9999% aluminum ingots, were prepared for irradiation by etching in concentrated HCl to remove surface contamination. The samples were then packaged in polyethylene film or sealed in quartz tubes along with the appropriate standards. Neutron irradiations were carried out in the Livermore LPTR reactor. Irradiation periods ranged from 2 hours to 90 hours. After irradiation the samples were again cleaned by etching in concentrated HCl and then mounted on aluminum planchets for counting. Samples were generally available for counting within 3 hours after the end of irradiation. In order to prevent the detection of beta rays and internal conversion electrons, the samples were counted through a 675 mg/cm^2 aluminum absorber.

The pertinent characteristics of the reactor irradiation positions used in these studies are given in Table I.

RESULTS AND DISCUSSION

Short Irradiations: Analysis of Copper, Manganese, and Gallium in Aluminum. In order to determine inpurities in the aluminum giving rise to short-lived activities, several samples of aluminum of different purities were irradiated for 2-hour periods in the LPTR reactor. The gamma-ray spectra of these samples indicated the presence of Cu^{64}, Mn^{56}, Ga^{72}, and Na^{24}.

Examples of gamma-ray spectra obtained from the 2-hour irradiation of aluminum wire of unspecified purity in position S-1 of the reactor are shown in Figure 5. Spectra A and B were obtained with the Ge(Li) detector and spectrum C with a good 3" × 3" (diam.) NaI(Tl) detector.

The energy range used in the spectra of Figure 5 is 2500 keV. Although most of the gamma rays are well resolved it is important to note that the full resolving power of the detector is not apparent because of this large energy range. In particular, it appears that the 834-keV line from Ga^{72} is not resolved from the 845-keV line from Mn^{56}; that the detector is capable of resolving these lines is demonstrated in the insert to this figure in which a smaller energy interval is analyzed. This illustrates the practical point that although a 400-channel analyzer provides a sufficient number of channels for the low-resolution sodium iodide spectrum of an energy range as great as 2500 keV, it is not adequate for a high-resolution spectrum. We normally use a maximum energy increment of 1.0 keV per channel with germanium systems in order to take full advantage of the available detector resolution.

Note also that the relatively weak line from Mn^{56} at 1815 keV is cleanly resolved from the 1729 keV "double escape peak" from Na^{24} in the Ge(Li) spectrum. The many resolved lines of Ga^{72}, although weak, illustrate the benefits of the improved resolution.

The results of the analysis of copper, manganese, and gallium in aluminum samples of four different grades are given in Table II. These were obtained by comparison of the intensities of the 511-keV line (Cu), 834-keV line (Ga), and the 849-keV line (Mn) in the spectra of the aluminum samples with the corresponding intensities obtained from standards that were irradiated simultaneously. Included in the table are the apparent concentrations of sodium impurity in two of the aluminum samples, as determined from the induced Na^{24} activity. In this case a major fraction of the observed Na^{24} is actually due to the secondary reaction, $Al^{27}(n,\alpha)Na^{24}$. In the case of the sample of 99.9999% aluminum, this reaction accounts for more than 90% of the observed Na^{24}.

Long Irradiations: Analysis of Iron, Cobalt, Chromium, Hafnium, and Scandium in Aluminum. Samples of the aluminum wire and 99.9999% aluminum were irradiated for 90-hour periods in position S-1 of the LPTR reactor to enhance the longer-lived activities induced in the aluminum. After a decay period of about 10 days essentially all of the Na^{24}, Cu^{64}, and Ga^{72} had decayed and it was possible to observe gamma rays from Fe^{59}, Co^{60}, Cr^{51}, Hf^{181}, and Sc^{46} in the activated aluminum wire. The gamma-ray spectrum of the wire sample, taken two weeks after the end of irradiation, is shown in Figure 6. The spectrum shown in the upper part of this figure was taken with an analyzer setting of 3.6 keV per channel. For more detail, the various energy regions were also examined with a setting of 0.8-1.0 keV per channel; two such regions are shown in the lower part of the figure.

The gamma-ray spectra of the wire sample obtained with the smaller energy interval per channel permitted the precise determination of the photon energies. These values are compared with literature values in Table III. Also

apparent in the expanded spectra were a number of weak lines whose presence aided in the qualitative identification of several isotopes. Thus the 55.3-keV line (Ta K x-ray) and 133.4-keV line, as well as the prominent lines at 345.3 and 481.2 keV, were readily assigned to the decay of Hf^{181} from their energies and relative intensities. Similarly, in the case of Fe^{59}, the assignments of the 1095-keV and 1292-keV lines to the decay of this isotope were confirmed by the observation of the weaker lines at 143.0 and 192.5 keV with the correct relative intensities. In addition to the impurities notes above, a weak line at 412 keV was observed in the earlier spectra and was assigned to the decay of Au^{198}. The gamma-ray spectra of the 99.9999% aluminum sample showed the presence of Cr^{51}, Hf^{181}, Au^{198}, and Sc^{46}. In Table IV we give the concentrations of the observed impurities calculated from the data described above.

It is interesting to note here a problem associated with the early use of the new Ge(Li) detectors that, from the point of view of analysis, is somewhat troublesome. Due to the high resolution one often observes gamma-ray lines that have not been reported previously because of their low intensities or because they were not resolved from other lines. In the experiment reported here we have observed lines at 73.4, 311.8, and 1220 keV which at present are unassigned.

Sensitivity Limits. It would naturally be of interest to place on a quantitative basis the increase in sensitivity gained by use of Ge(Li) detectors in activation analysis. Limits of detection were not however indicated in the papers whose results we have quoted and, even if they had been given, such comparisons would not be justified because of possible differences in experimental conditions in the various studies (sample preparation, irradiation

conditions, etc.). This is particularly true in the case of aluminum since the detectable limits of Cu^{64}, Mn^{56}, and Ga^{72} are dependent upon the level of Na^{24} activity induced by the reaction $Al^{27}(n,\alpha)Na^{24}$. Since the threshold energy for this reaction is 3.3 MeV, variations in the ratio of fast neutrons ($E_n > 3.3$ MeV) to thermal neutrons in the different reactors can significantly alter the sensitivity limits for these elements.

For the present purpose it suffices to compare, in Table V, the lowest levels of copper, manganese, and gallium actually detected and measured in the several non-destructive analyses of aluminum. We also include in this table the estimated sensitivity limits for the irradiation and decay conditions of our experiment.

These data show clearly the lower levels of these impurities detected in this work and are an indication of the enhancement in sensitivity that may be attained with the use of Ge(Li) detectors.

CONCLUSIONS

The results of our analyses of high-purity aluminum demonstrate the power of lithium-drifted germanium gamma-ray detectors as a tool in activation analysis. Their high resolution relative to that of NaI(Tl) scintillators is particularly significant for non-destructive analysis. Because the need for extensive chemical separations is reduced when analysis of many elements in the same sample is required, the use of the non-destructive techniques can be extended to a greater variety of systems. In those systems presently studied by non-destructive analyses, the high resolution significantly improves the detection sensitivity and may also permit the determination of more elements. The ease with which gamma-ray energies can be measured precisely and the enhanced

ability to observe weak spectral lines facilitates the qualitative identification of radioactive isotopes, as shown here in the cases of Fe^{59} and Hf^{181}. The tedious procedure of decomposition and analysis of complex photopeaks, common to the scintillation technique, is generally unnecessary with the use of germanium detectors.

Although the experiments reported here were performed on a matrix that does not of itself produce interfering long-lived activities, the arguments presented here should be valid in most experimental situations. In some cases it may still be necessary to perform a primary separation from the bulk material, but there should be no need for individual separations of all elements of interest. The analyses of minerals and rare-earth element mixtures are particularly interesting in this regard, and experiments are now in progress to investigate these systems.

Acknowledgments

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Table I. Characteristics of LPTR Reactor Irradiation Positions

Position	Thermal flux	Cadmium ratio	Flux, $E_n > 3.3$ MeV
S-1	5.1×10^{12} n/cm^2 sec	11	1×10^{11} n/cm^2 sec
S-2	3.4×10^{12}	8.3	$2\text{-}3 \times 10^{10}$

Table II. Results of Non-Destructive Activation Analysis for Copper, Manganese, and Gallium in Four Grades of Aluminum

Sample	Sample Weight	Irradiation Position	Copper µg	Copper ppm	Manganese µg	Manganese ppm	Gallium µg	Gallium ppm	Sodium µg	Sodium ppm
Al wire[d]	0.0714g	S-1	68	950[b]	0.26	3.7	14	200	15	210[a]
99.99%Al[e]	0.133	S-2	1.7	13[b]	0.029	0.22		< 1.4[c]		-[f]
	0.5050	S-2	5.2	10[b]	0.12	0.25		< 3.4[c]		-[f]
99.999%Al[e]	0.6918	S-2	0.79	1.1[b]	0.22	0.32		< 0.14[c]	11	16[a]
	0.3706	S-2	0.39	1.1[b]	0.080	0.22		< 0.19[c]	7.4	20[a]
99.9999%Al[e]	0.6072	S-2		< 0.30[c]	0.13	0.22		< 0.14[c]		-[f]
	0.5024	S-2		< 0.40[c]	0.084	0.17		-[f]		-[f]

[a] Sodium concentrations are uncorrected for contribution from the reaction $Al^{27}(n,\alpha)Na^{24}$.

[b] Calculation of copper concentrations have been corrected for contribution to the 511-keV photopeak from Na^{24}.

[c] Upper limits correspond to the maximum concentration allowed by statistics (2σ limits) of the total counts in the region of the analyzed photopeak.

[d] Sample of unspecified purity.

[e] Obtained with spectrographic analysis in the form of ingots from Cominco Products, Inc., Spokane, Washington.

[f] Not determined.

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Table III. Gamma-Ray Energies and Isotope Assignments

Isotope	E_γ(exp)(keV)	E_γ(literature)(keV)
Ta K x-ray	55.3	55.8
Hf^{181}	133.4[a]	133.0
	345.3	345.8
	481.2	482.0
Fe^{59}	143.0	145
	192.5	192
	1095	1100
	1292	1290
Cr^{51}	319.0	319.8[b]
Sc^{46}	1117	1119
	892	885-892
Co^{60}	1172	1173
	1333	1333

[a]All values have been taken from the Nuclear Data Sheets (13) unless otherwise noted.

[b]Reference 14.

Table IV. Concentrations of Impurity Elements in Aluminum Giving Rise to Long-Lived Activities

Sample	Sample wt.	Concentrations in ppm Fe	Sc	Hf	Co	Cr
Al wire	0.1216g	5300	0.58	2.6	0.88	57
99.9999% Al	1.029	--	0.17	0.48	--	0.47

Table V. Comparison of concentrations of Cu, Mn, and Ga Observed by Non-destructive Activation Analyses of High-Purity Aluminum

	Type of Al	Concentration (ppm) Cu	Mn	Ga
Chinaglia and Malvano (3)	zone refined	5.7	0.96	--
Jervis and Mackintosh (11)	99.99%	18	1.5	0.5
Yakovlev et al. (15)	zone refined	8	0.4	--
Present work	99.999%	1.1	0.27	--
	99.9999%	--	0.20	--
Estimated lower limit observable with Ge(Li) detector	99.9999%	0.5	0.05	0.3

FIGURE CAPTIONS

Fig. 1. Schematic diagram of Ge(Li) detector assembly.

Fig. 2. Photograph of Ge(Li) detector assembly.

Fig. 3. Photoelectric efficiency curves for the Ge(Li) gamma-ray detector and a 3" × 3" (diam.) NaI(Tl) scintillator.

Fig. 4. Comparison of gamma-ray line widths as a function of gamma-ray energy for a Ge(Li) detector and a 3" × 3" NaI(Tl) detector.

Fig. 5. Gamma-ray spectra of activated aluminum wire. Spectra A and B were obtained with the Ge(Li) detector and spectrum C with a 3" × 3" (diam.) NaI(Tl) scintillator. The spectra were taken at the following times after a 2-hour irradiation: A = 5.2 hr; B = 54.7 hr; C = 5.7 hr.

Fig. 6. Gamma-ray spectra of the activated aluminum wire showing long-lived activities induced in the sample. The spectra were obtained with the Ge(Li) detector 16.4 days after the end of a 90-hour irradiation.

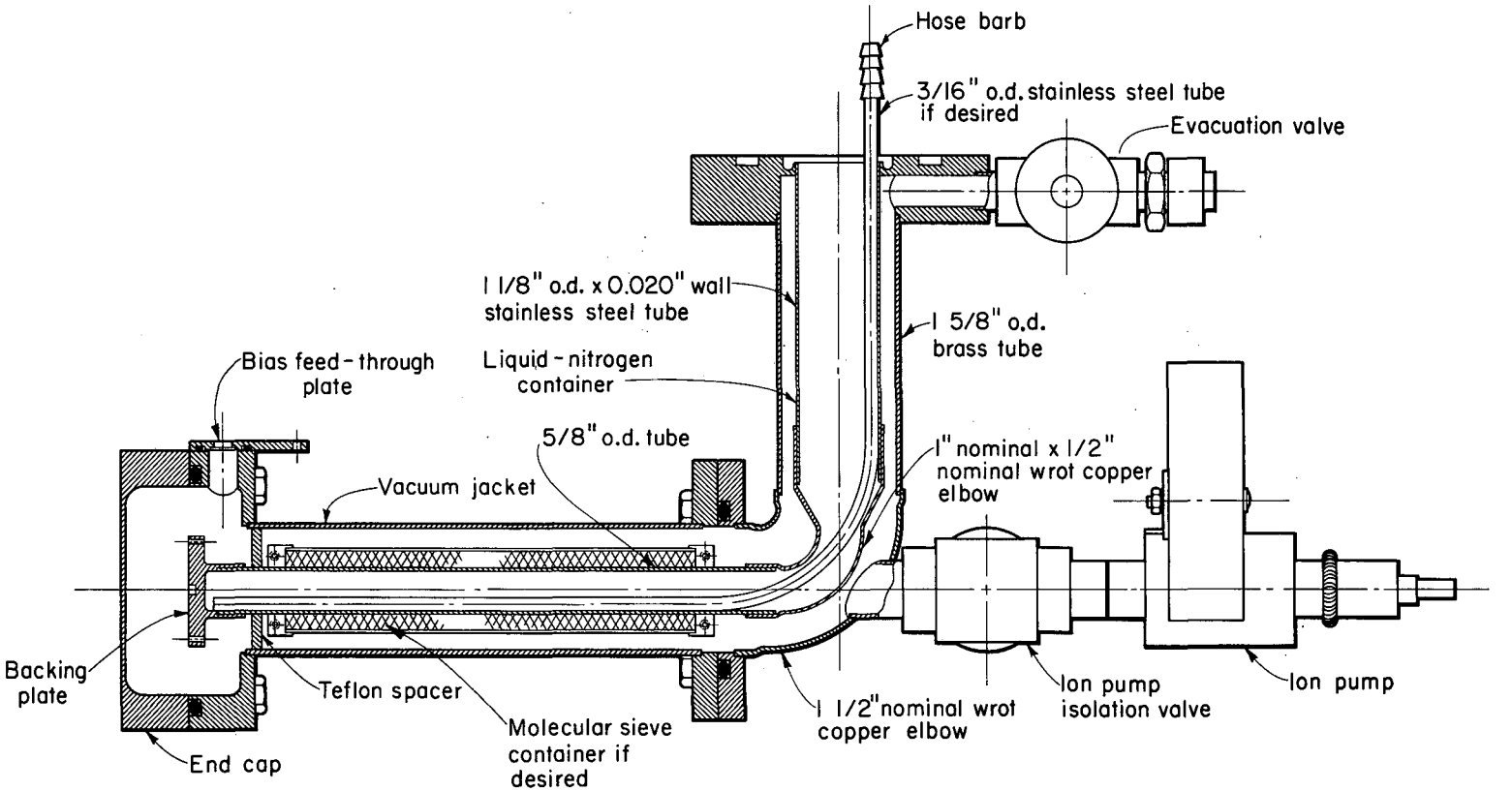
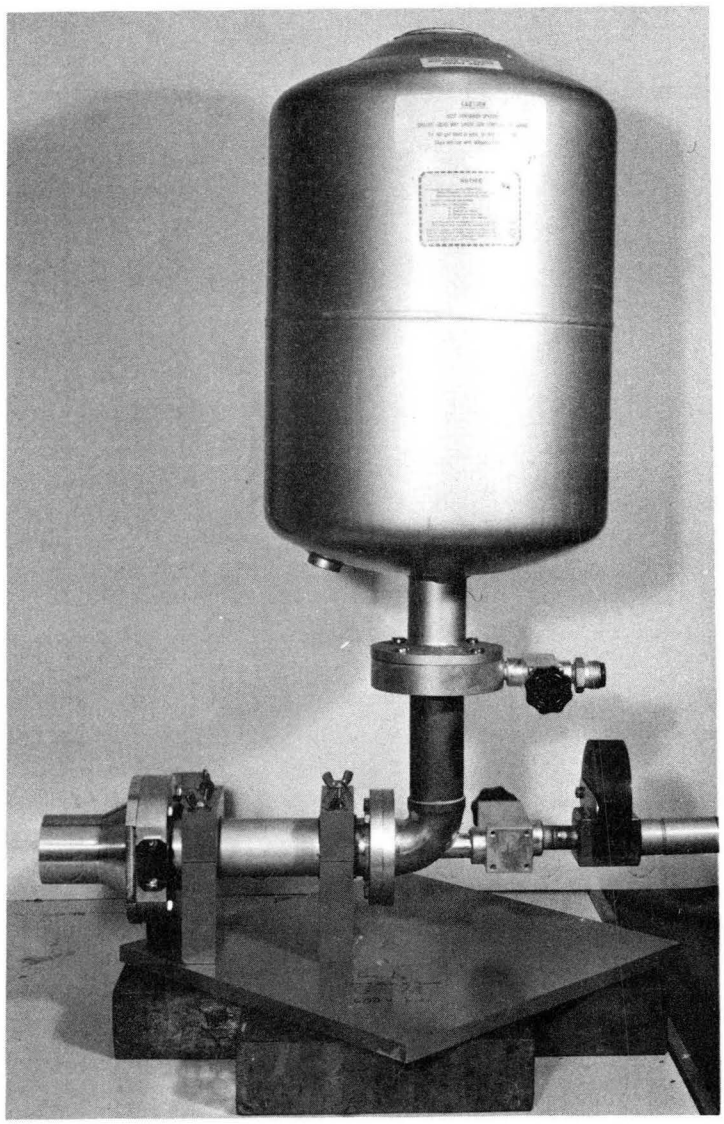
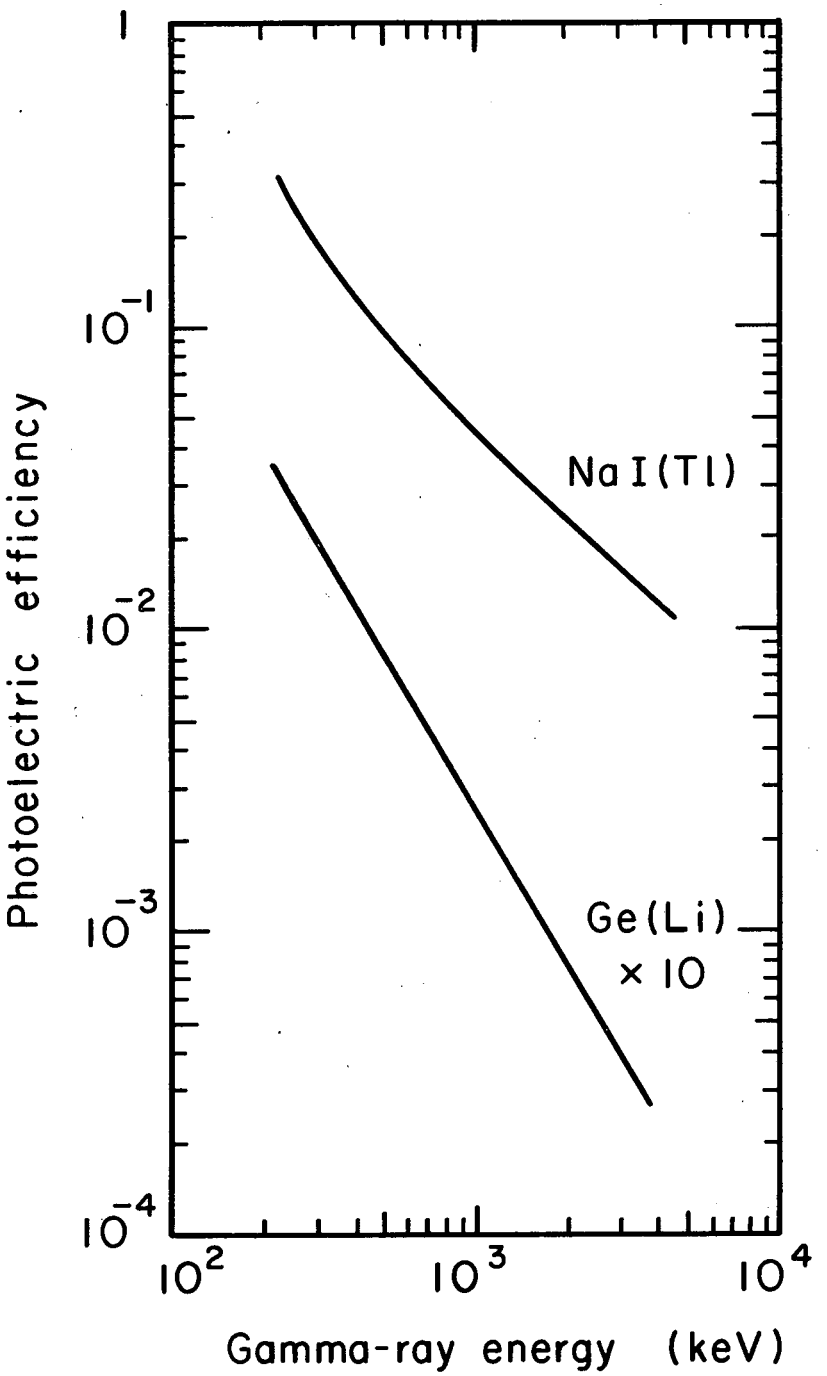

Hose barb
3/16" o.d. stainless steel tube if desired
Evacuation valve
1 1/8" o.d. x 0.020" wall stainless steel tube
1 5/8" o.d. brass tube
Bias feed-through plate
Liquid-nitrogen container
5/8" o.d. tube
1" nominal x 1/2" nominal wrot copper elbow
Vacuum jacket
Backing plate
Teflon spacer
Molecular sieve container if desired
End cap
1 1/2" nominal wrot copper elbow
Ion pump isolation valve
Ion pump
MUB-5549

Fig. 1



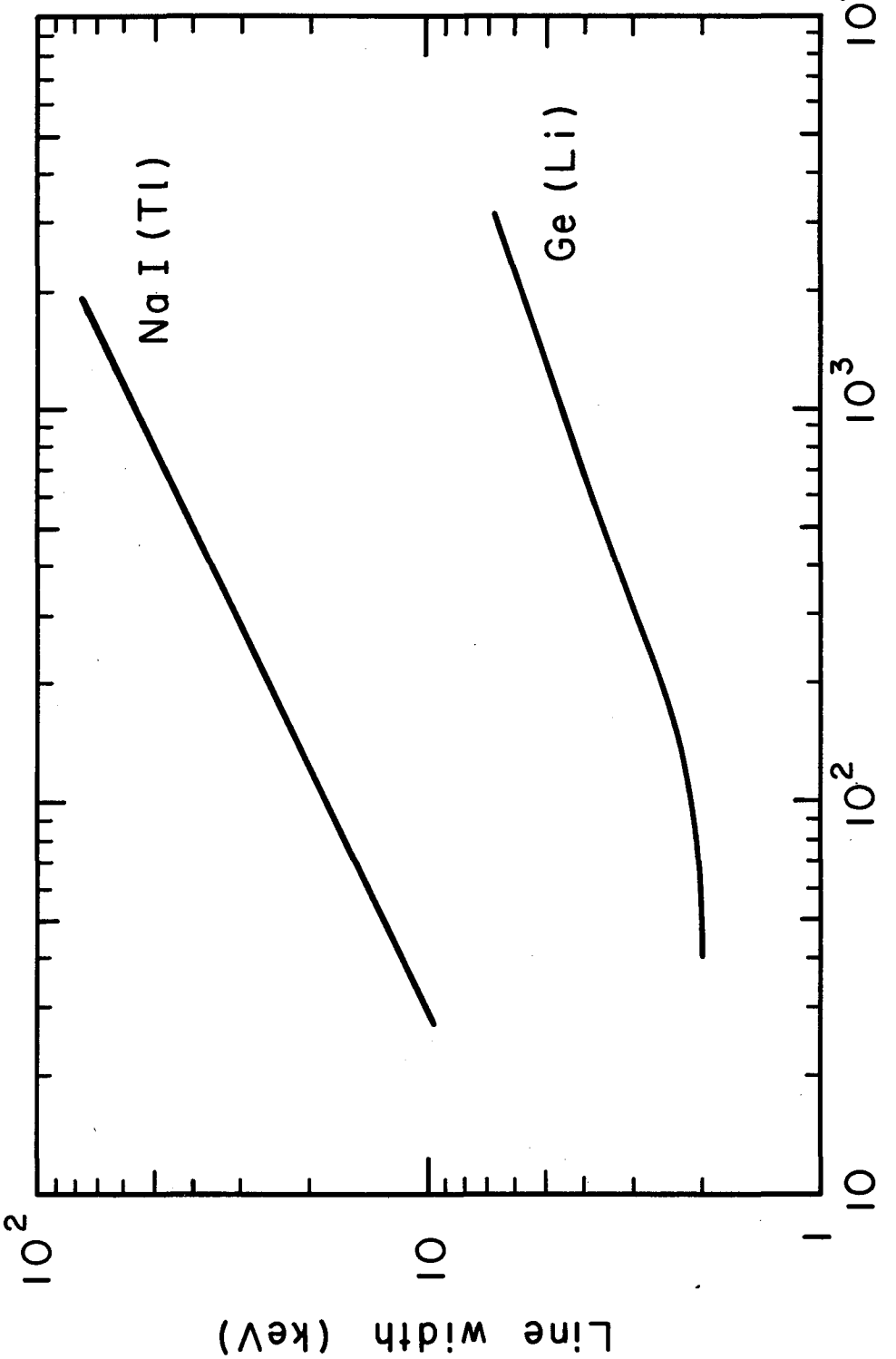
ZN-4854

Fig. 2



MUB-5743

Fig. 3



MUB-5744

Fig. 4

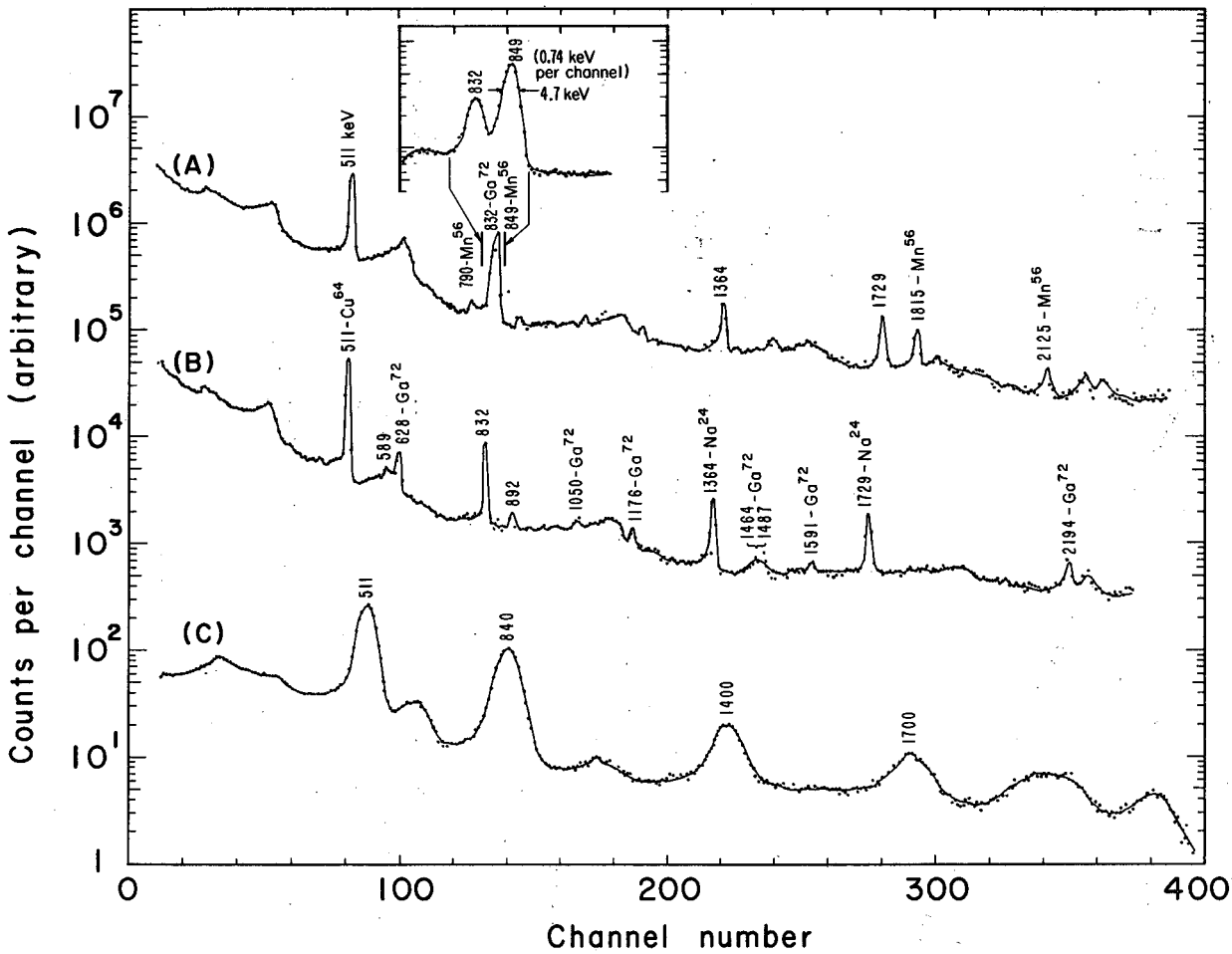

Counts per channel (arbitrary)
Channel number
(A)
(B)
(C)
511 keV
(0.74 keV per channel)
4.7 keV
832
849
790-Mn56
832-Ga72
849-Mn56
1364
1729
1815 - Mn56
2125 - Mn56
511-Cu64
589
628 - Ga72
832
892
1050-Ga72
1176-Ga72
1364 - Na24
1464-Ga72
1487
1591 - Ga72
1729 - Na24
2194 - Ga72
511
840
1400
1700
MUB-5746

Fig. 5

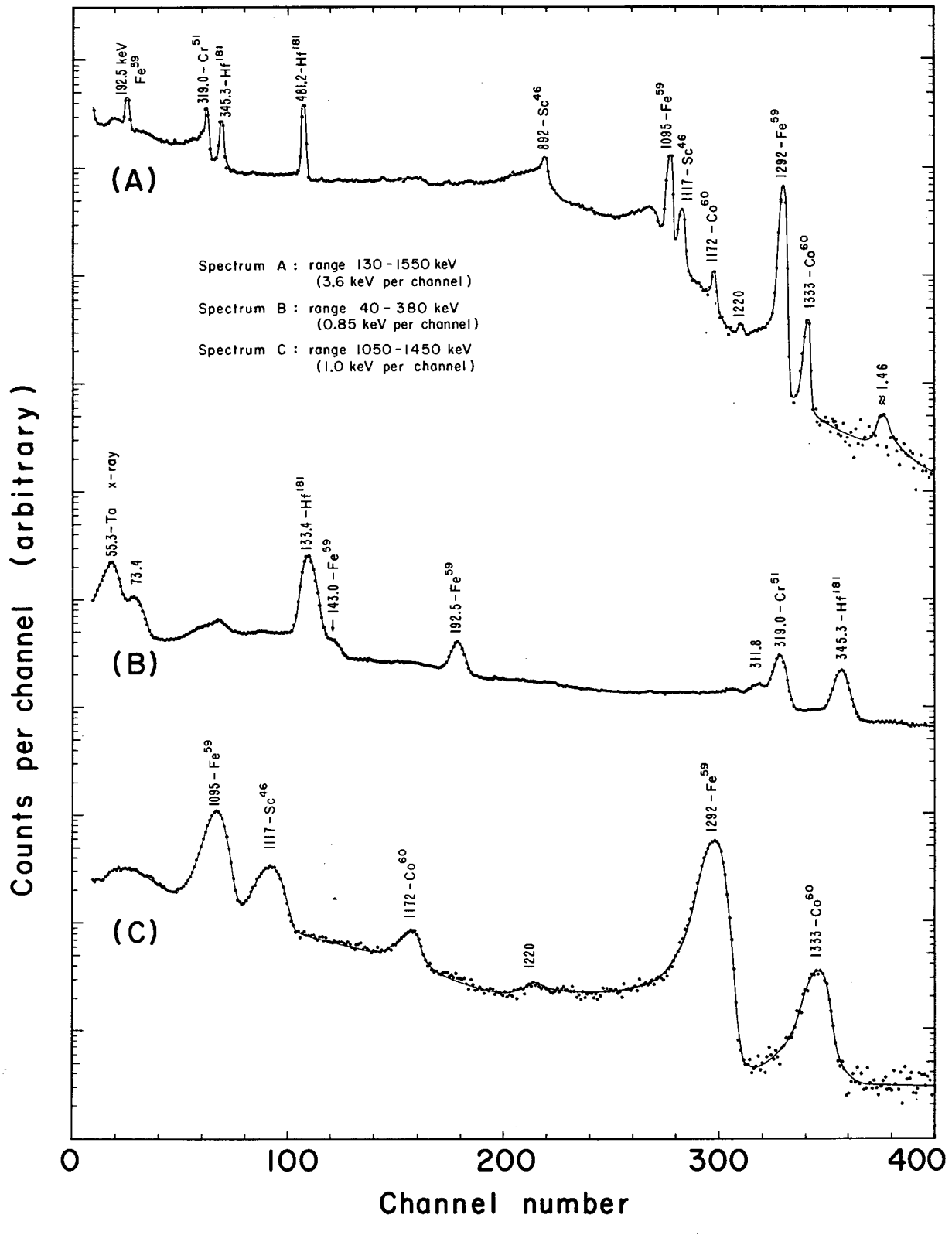

192.5 keV Fe59
319.0 - Cr51
345.3 - Hf181
481.2 - Hf181
892 - Sc46
1095 - Fe59
1117 - Sc46
1172 - Co60
1220
1292 - Fe59
1333 - Co60
≈ 1.46
(A)
Spectrum A : range 130 - 1550 keV
(3.6 keV per channel)
Spectrum B : range 40 - 380 keV
(0.85 keV per channel)
Spectrum C : range 1050 - 1450 keV
(1.0 keV per channel)
55.3 - Ta x-ray
73.4
133.4 - Hf181
← 143.0 - Fe59
192.5 - Fe59
311.8
319.0 - Cr51
345.3 - Hf181
(B)
1095 - Fe59
1117 - Sc46
1172 - Co60
1220
1292 - Fe59
1333 - Co60
(C)
Counts per channel (arbitrary)
0
100
200
300
400
Channel number
MUB-5745

Fig. 6