Radon and Thoron Interference in the Determination of Thorium and Uranium in Materials at sub-ng/g to a few ng/g level and Potassium at a few ppm level by direct γ-ray counting

P. Jagam, J.J. Simpson and E.D. Hallman*
Department of Physics, University of Guelph, Guelph, Ont., Canada, N1G 2W1
* Department of Physics and Astronomy, Laurentian University, Sudbury, Ont., Canada, P3E 2C6

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Introduction

Thorium, uranium and potassium are frequently determined in various materials by directly counting the γ-ray emission from these materials with a shielded γ-ray detector. High resolution germanium detectors (1.8 keV full width half maximum at 1332 keV) are used for this purpose. Large volume germanium detectors are readily available from commercial sources with detection efficiencies of 50% or more relative to a 7.62 cm x 7.62 cm NaI(Tl) detector. These high resolution high efficiency germanium detectors are also available at reasonable cost in ultra-low background (ULB) configurations giving 0.01 counts per second in the energy interval 40 keV to 4 MeV from radioactive contamination intrinsic to the detector assembly and the shielding materials. Lead and copper shields are used to minimize γ rays from Th, U, and K in the environment. It is also essential to shield the detector from cosmic rays by locating it at an underground site in order to reduce this contribution to the background to below that from the radioactivity contribution intrinsic to the detector assembly. At this point, radioactivity from radon in the air around the detector becomes a serious problem in the determination of Th, U and K by direct γ-ray counting.

Three radioactive isotopes of radon (Rn) are often present in air. ^{222}Rn (commonly called radon) occurs in the uranium decay chain and has a half-life of 3.82 d. ^{220}Rn (commonly known as thoron) occurs in the thorium decay chain and has a half-life of 55.6 s, and is generally less abundant than radon. ^{219}Rn is much less abundant than the previous two isotopes and is not considered here. The word radon is used to refer to the element radon representing all the isotopes or contextually the isotope in the uranium decay chain. Although radon and thoron themselves do not contribute to γ-ray background, as gases they can distribute solid phase decay products which tend to "plate-out " on nearby surfaces.

The presence of radon is evident in the comparison of typical spectra shown in figures 1 and 2 recorded with two shielded detectors operated in basement laboratories at two different locations. Both detectors are ULB quality detectors with active volumes within 10% of each other, and with passive shielding comparable to each other. The counting cavity inside the shield around the end-cap is also of comparable size in each case. In spite of the close characteristics of the detectors, the spectrum in figure 1 does not exhibit as prominently the full energy peaks corresponding to the γ rays emitted by the radon decay products as the spectrum in figure 2 does. Although these peaks are also present whenever uranium and its decay products are present, the peaks in figure 2 are attributed to the presence of radon around the shielded end-cap of the detector and not to decay products of uranium in the sample, because of the absence of the characteristic peak at 186 keV from ^{226}Ra or ^{235}U. Thoron can also be a significant interference in a similar manner as discussed later in this report.

The concentration of radon in the air at a given location depends on several factors. A source dependent factor is proportional to the concentration of Th and U in the environment near the detector. A ventilation dependent factor varies with the air change rate and the amount of air circulation. Ventilation inside the shield can govern the amount of radon that potentially exists around the counting assembly. Additional measures can be implemented to minimize or eliminate radon inside the shielded counting cavity around the detector end-cap to eliminate interference from radon in Th, U and K determinations by direct γ-ray counting. The present work reports on the identification of the radon problem and possible remedies to reduce or eliminate it.

Characteristics of the detectors and description of locations

Data were collected with three different detectors in the present work. Two of the detectors (Guelph ULB and Laurentian PGT) are single crystal high purity germanium detectors which are close to each other in their detection efficiencies. The third one (Guelph ULBT) has three crystals in one cryostat. The cryostats are of the J-configuration type which enable shielding to be provided all around the end-cap without line-of-sight leakage paths directly into the germanium crystals. The end-cap of the detectors is shielded by 5 or 10 cm thickness of copper surrounded by 15 or 25 cm of lead depending on the location. A 6 mm Hg shield all around the end-cap followed by 15 cm of Pb is also used routinely with the ULB detector at Guelph. The characteristics are given in table 1.

The detectors were operated at different locations. The ULB was run in a basement laboratory and at a depth of 300 m in a salt mine. The PGT was run in a second basement laboratory, and at a depth of 1400 m in a nickel mine. The ULBT was run in the basement laboratory at Guelph and Sudbury, in the salt mine, and in the nickel mine. The characteristics of the locations are given in table 2.

Measurements

The observed counting rates of the γ rays from thorium, uranium and potassium with an unshielded detector at the different locations are proportional to the concentrations of these elements in the environment at those locations and the placement of the detector in the rooms, and are given in table 3.

Table 1. Characteristics of the detectors

	Guelph ULB	Guelph ULB	Laurentian PGT
crystal dimensions: dia. x length	64mm x 72 mm	2 of 60mm x 70 mm 1 of 64 mm x 72mm	63mm x 67mm
Efficiency*	48%	80%^	55%
Resolution**	2.7	4.5	1.8
Shielding	6mmHg+15cmPb or 10cmCu+15cmPb	10cmCu+15cmPb	5cmCu+25cmPb
End-cap:			
diameter	83 mm	165 mm	83 mm
material	Al***	Cu	Cu#

* relative to a 7.62 cm dia. x 7.62cm NaI(Tl) detector for 1332 keV γ rays from a ^{60}Co source 25 cm from the face of the crystal
** full-width-half-maximum (keV)
*** zone refined aluminum
^ three crystals taken together
# Electroformed copper

From the Guelph ULB data it can be seen how remarkably low are the Th, U and K abundances in the salt mine compared to a normal university laboratory. It also appears that Th, U, and K are generally higher at location 3 compared to location 1. The count rates determine the minimum amount of shielding necessary at each location to achieve the required attenuation of the environmental photon flux incident on the detector. In addition, the presence of high uranium and thorium in a location will create a high ambient radon and thoron level though ventilation factors may reduce the levels present in air.

Table 2. Description of locations where the detectors were operated

Location ID	location 1 University of Guelph: basement room	location 2 salt mine Windsor,Ont.	location 3 Laurentian University, Sudbury,Ont	location 4 nickel mine: Sudbury,Ont.
Room/cavity size (m) detector location	10m x 15m 6m high centre of room	12.2m x 12.2m 6m high central in one quarter of room	3m x 7m 4 m high in one corner of room	4m x 5 m 3.5 m high central in one third of room
Ventilation	end of ventilation shaft, recirculated air with 10% fresh air mix	close to ventilation exhaust vent	limited ventilation	low ventilation

Table 3. Observed counts per day at γ-ray peaks of interest with the unshielded Guelph ULB and Laurentian PGT detectors operated at various locations

	Guelph ULB detector				Laurentian PGT detector			
E(keV)	Location 1		Location 2		Location 3*		Location 4	
	Net	2σ%	Net	2σ%	Net	2σ%	Net	2σ%
186	5845	18	117	136	20784	32	17460	8.1
239	34310	2.7	343	37	81312	6.8	88160	1.2
242	9126	7.7	432	34	28656	19	22000	4.6
295	15717	4.6	448	29	43584	12	56029	1.8
352	30814	2.1	1093	12	82728	5.7	106023	0.9
511	15010	3.9	103	83	27216	14	37968	2.0
583	18455	2.8	180	45	44184	7.3	65438	1.1
609	33887	1.5	985	10	92280	4.1	123438	0.6
911	14458	2.7	86	69	37752	7.2	56041	1.0
934	1871	13	85	74	6024	31	7496	4.5
1001	761	35	-5	987	1608	18	2263	15
1120	10052	3.3	229	29	27168	8.8	38280	1.3
1461	136261	0.6	4625	3.6	279768	1.9	352058	0.3
1764	9566	2.3	204	19	22632	7.0	38573	0.9
2204	2862	4.6	47	45	6720	15	11660	1.9
2448	832	10	14	81	1800	37	3576	4.3
2614	15081	1.7	79	29	41160	4.9	77356	0.6

* 5th floor laboratory

The observed counting rates with the PGT shielded detector configuration are given in table 4. The Cu-Pb shield around the detector was also enclosed in a PVC box at location 4 to isolate the shielded detector from the room air. In addition, the cavity inside the shield was also continuously flushed with evaporating nitrogen gas drawn from a liquid nitrogen storage dewar at a minimum rate of 4 l per minute . It can be seen that the counts at the energies corresponding to ^{214}Pb-Bi activities (242, 295, 352, 609, 934, 1120, 1764, 2204, 2448 keV) have all been eliminated with active flushing.

Results and discussion

A typical spectrum recorded at location 4 with the shielded PGT detector inside the PVC box employing active flushing using evaporating nitrogen gas drawn from a liquid nitrogen cylinder is shown in figure 3. The spectrum shown in figure 4 was recorded when the nitrogen flushing was interrupted. The count rate in the complete spectrum in

Table 4. Observed counts per day at γ-ray peaks of interest with shielded Sudbury PGT detector operated at various locations. The data at location 3 and initially at location 4 are collected without a sealed box.

E (keV)	Location 3		Location 4		Location 4* without flushing		Location 4* with flushing	
	net	2σ%	net	2σ%	net	2σ%	net	2σ%
186	35	165	0	7108	-3	253	-0.6	529
239	-8	256	72	25	6	197	4	71
242	139	34	116	17	85	19	-0.7	388
295	333	15	282	7.6	185	9.5	0.2	1513
352	528	8.2	494	5.1	297	6.7	-1.1	197
511	996	5.3	41	29	16	54	6.7	29
583	-4	265	37	27	-3	76	1.1	107
609	437	8.5	406	5.5	256	6.7	1.7	61
911	5	350	8	117	0	755	0.6	114
934	32	59	15	53	14	36	0	1500
1001	-17	51	-5	151	0	1789	0	8131
1120	92	21	81	14	53	16	0	1069
1461	9	120	66	15	8	52	10	16
1764	80	20	94	11	48	15	0.2	234
2204	22	45	23	25	13	29		
2448	6	165	9	39	5	51		
2614	2	422	54	14	4	52	1.0	50

* with a sealed PVC box enclosing the shield

the energy interval from 0 to 3 MeV changed from 0.017 cps with nitrogen flushing to 0.107 cps without nitrogen flushing. It can also be seen from figure 4 that the peaks corresponding to the radon daughter products reappeared in the shielded detector spectrum when the active flushing of the counting cavity with nitrogen gas was stopped. Thus, flushing inside the shield with nitrogen gas at the rate of 4 l/min is found to be a fairly effective means of reducing the radon problem, but clearly the surrounding air diffuses into the detector when this procedure is interrupted even briefly.

Interference from radon in the air inside the counting cavity in the determination of Th U and K occurs primarily by the decrease in detection sensitivity by increasing the continuum count rates under the γ-ray peaks of interest. Radon also contributes through its decay products to most of the γ rays used in thorium and uranium determinations. For these reasons it is desirable that radon be not present in the counting cavity when the radioactivity in the sample is less than or equal to the radon activity in the air around the end cap of the detector. The ^{222}Rn activity was found to be between 0.2 and 0.7 Bq per litre of air at location 4.

The largest sensitivity for thorium and uranium determination is obtained using the 239 keV γ-ray for thorium and the 352 keV γ-ray for uranium. The counting sensitivity at these two energies with a one litre Marinelli sample geometry for the PGT detector is found to be 3.27 and 8.53 counts per day per μg respectively. When the radon is not present in the cavity, there are 4 +- 3 counts per day in the 239 keV peak and 0 +- 2 counts per day in the 352 keV peak. However, when the radon was present the same regions recorded 9 +- 10 counts per day and 491 +- 22 counts per day. The errors quoted are two sigma values. It appears that radon in the air is primarily ^{222}Rn (radon) although there may be some ^{220}Rn (thoron) as well.

To investigate the presence of thoron more accurately spectra were recorded for five days immediately from the time the counting cavity was closed. Sequential spectra in the energy interval 190 to 430 keV are shown in figures 5 - 8. Figure 5 shows the data in the first 2.74 h, figure 6 in the next 19 h, figure 7 the last 12 h of the five day period with figure 8 showing the sum of the data over four days without the initial one day of the five day period. The 239 keV peak from the ^{212}Pb activity is clearly seen to decay in intensity with an estimated half-life of ~ 9 h, consistent with the 10.6 h half-life of ^{212}Pb which produces the 239 keV γ-ray. This indicates that "plated out" thoron daughter activities may be present in a spectrum started soon after closing the shield.

The peaks at 242, 295 and 352 keV in figures 5 - 8 occur in the decay of the ^{214}Pb activity which is a daughter product of radon (^{222}Rn). Since the half-life of ^{214}Pb activity (26.8 m) is short compared to the half-life of the parent ^{222}Rn (3.82 d) they should be in equilibrium. The rate of increase of counts in the five day counting period, therefore, indicates that some radon is diffusing into the counting cavity after the cavity is closed. Since the room air contains a mixture of radon (^{222}Rn) and thoron (^{220}Rn)

activities this observation of radon diffusion over the counting period confirms that thoron contamination has to be taken into account while interpreting background and sample data over and above the plated out daughter activities.

Of particular interest in the materials selection for the SNO detector is the thorium value in several key components. From the above results it can be concluded that the values of thorium and uranium determined in samples with one litre Marinelli geometry are subject to errors whenever the nitrogen purge is insufficient or altogether interrupted and, in particular, values in the concentration range from 1 to 10 ppb are subject to these errors. In order to detect this type of error the ratio of Th to U found in nature may be used as a guide. The most common ratio of Th to U found in nature is about 3-5. Since ^{222}Rn is the dominant activity present in radon any situation where U values are higher than Th values need to be examined carefully.

For samples of materials with thorium and uranium content at or below a few ppb level, it is expected that increased signal to background ratio can be obtained by increasing the sample size from 1 l to 20 l and by using a lower background detector such as the Guelph ULBT. For the larger shielded counting cavity needed to accommodate the larger sample size it was found that a higher flushing rate of nitrogen gas, 7.5 l/min, is required to keep the radon out.

The counting sensitivity with a 21 l sample volume around the detector end-cap at 239 keV was found to be 1.85 counts per day per μg of Th. The background at the peak region without a sample and no radon was found to be 75 counts per day giving a one sigma detection limit of 4.7 μg of Th. With a 20 kg sample this is equal to a limit of 235 ppt. However, effects due to variation in attenuation at 239 keV because of differences between samples and standards may be more dramatic at these large sample sizes. Therefore, a higher energy γ-ray was chosen even though the counting sensitivity decreases from the 239 keV value. At 2614 keV the counting sensitivity with the ULBT detector was found to be 0.3 counts per day per microgram of Th with the 21 l Marinelli geometry. The background was found to be 0.37 counts per day. A spectrum recorded with a sample weighing 15 kg and containing 200 pg/g (=ppt) Th is estimated to give 19 counts as signal and 8 counts as background for a total of 27 counts at 2614 keV in a counting time of three weeks. This estimate shows that thorium can be determined at 200 ppt level with a statistical counting error of 36% at one sigma.

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Guelph 2beta Decay: TN170-18.S0

BG AC: 206.316H: 17887

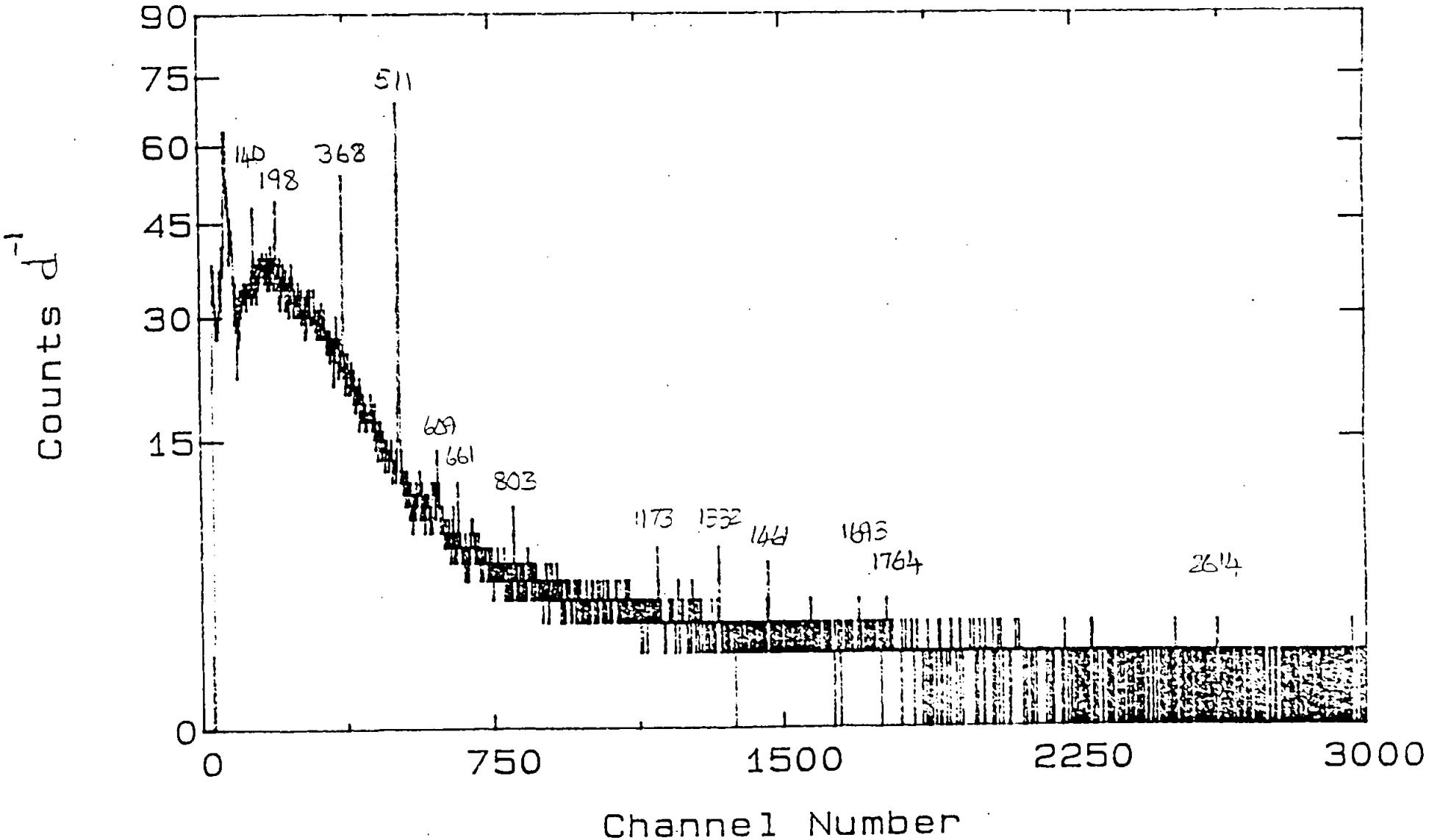
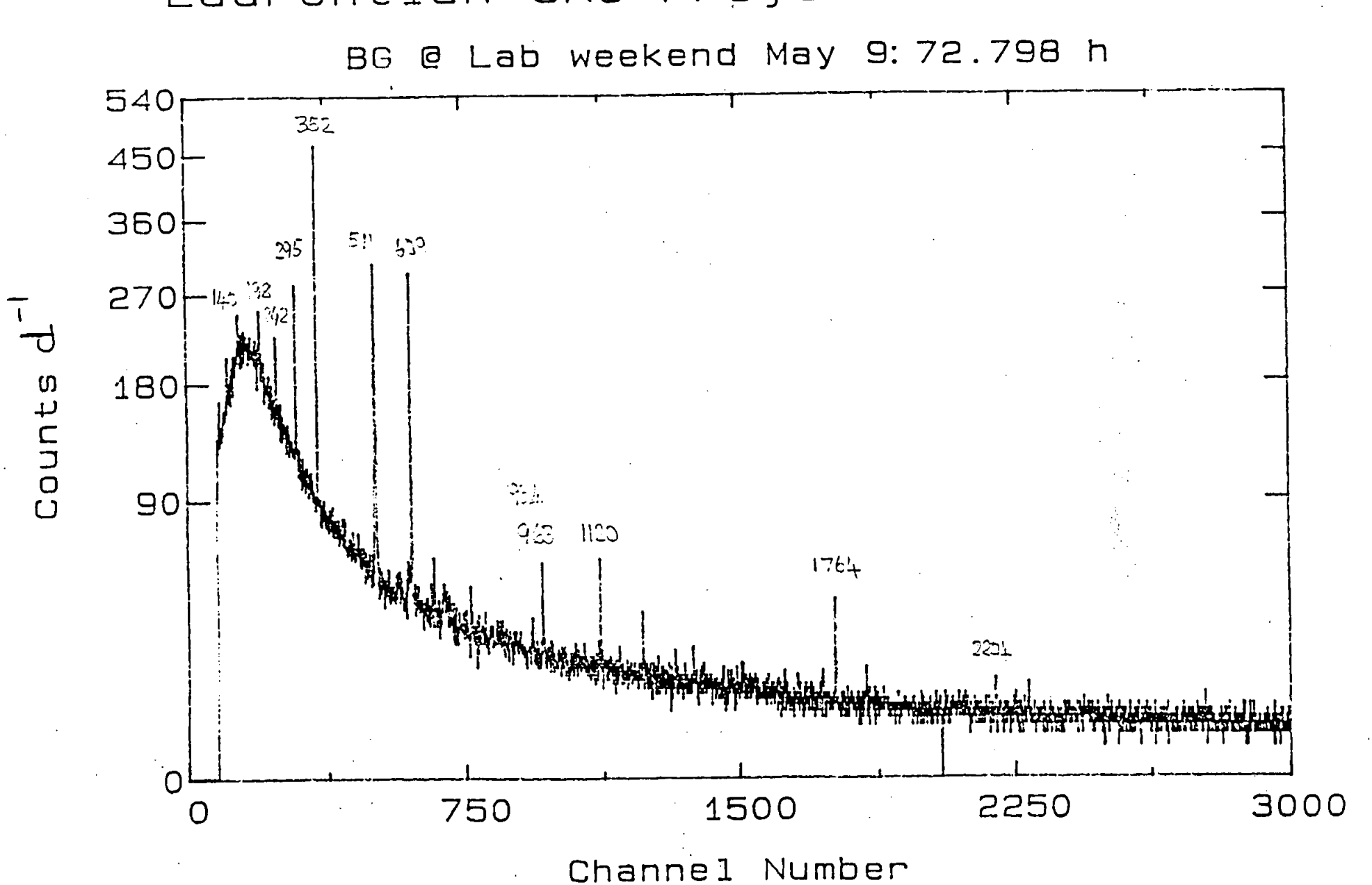


FIGURE 1

Laurentian SNO Project: PGTBAC9.SO



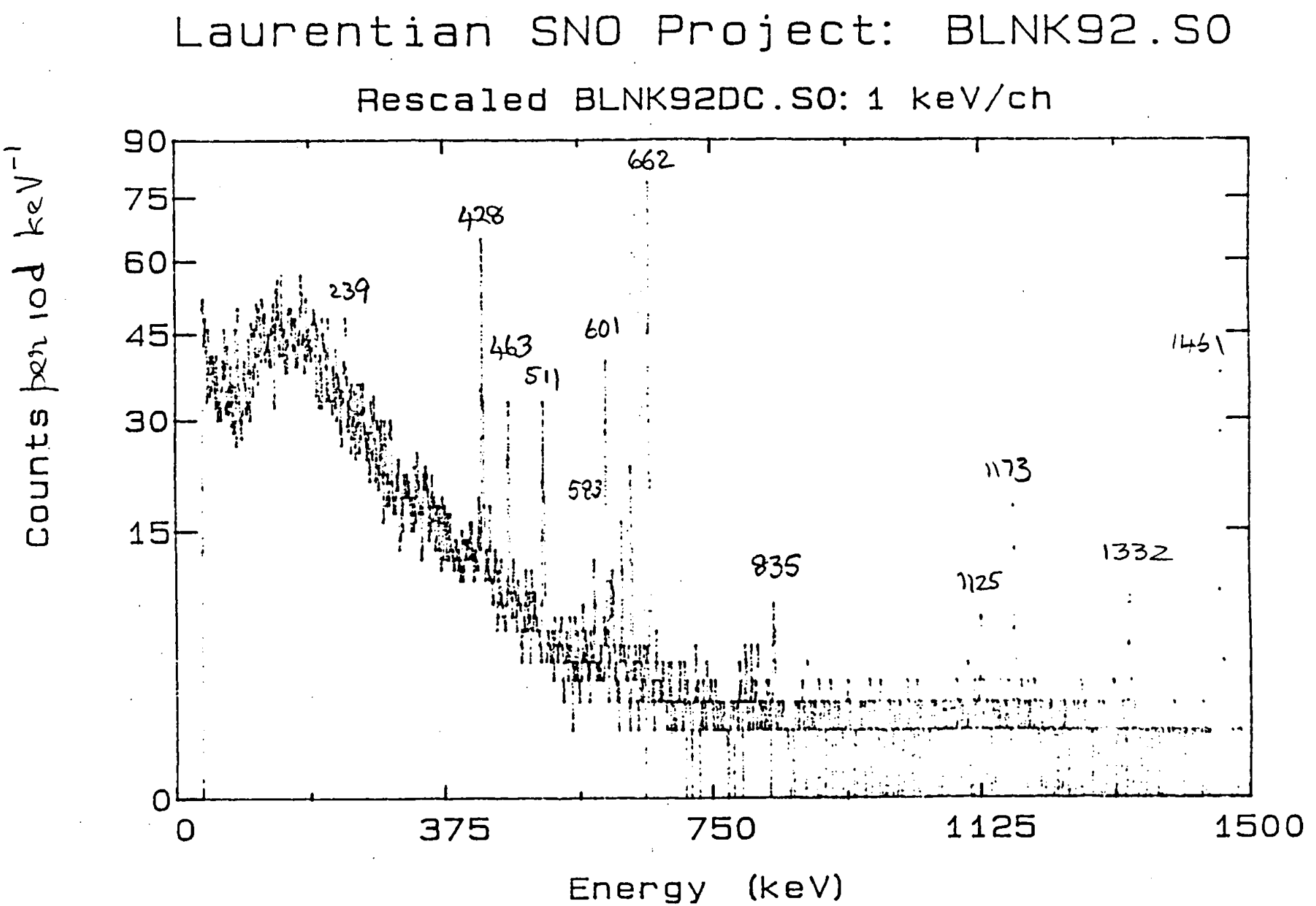

Laurentian SNO Project: BLNK92.SO
Rescaled BLNK92DC.SO: 1 keV/ch
Counts per 10d keV⁻¹
90
75
60
45
30
15
0
0
375
750
1125
1500
Energy (keV)
662
428
239
463
601
511
1461
583
1173
835
1332
1125

Fig 3

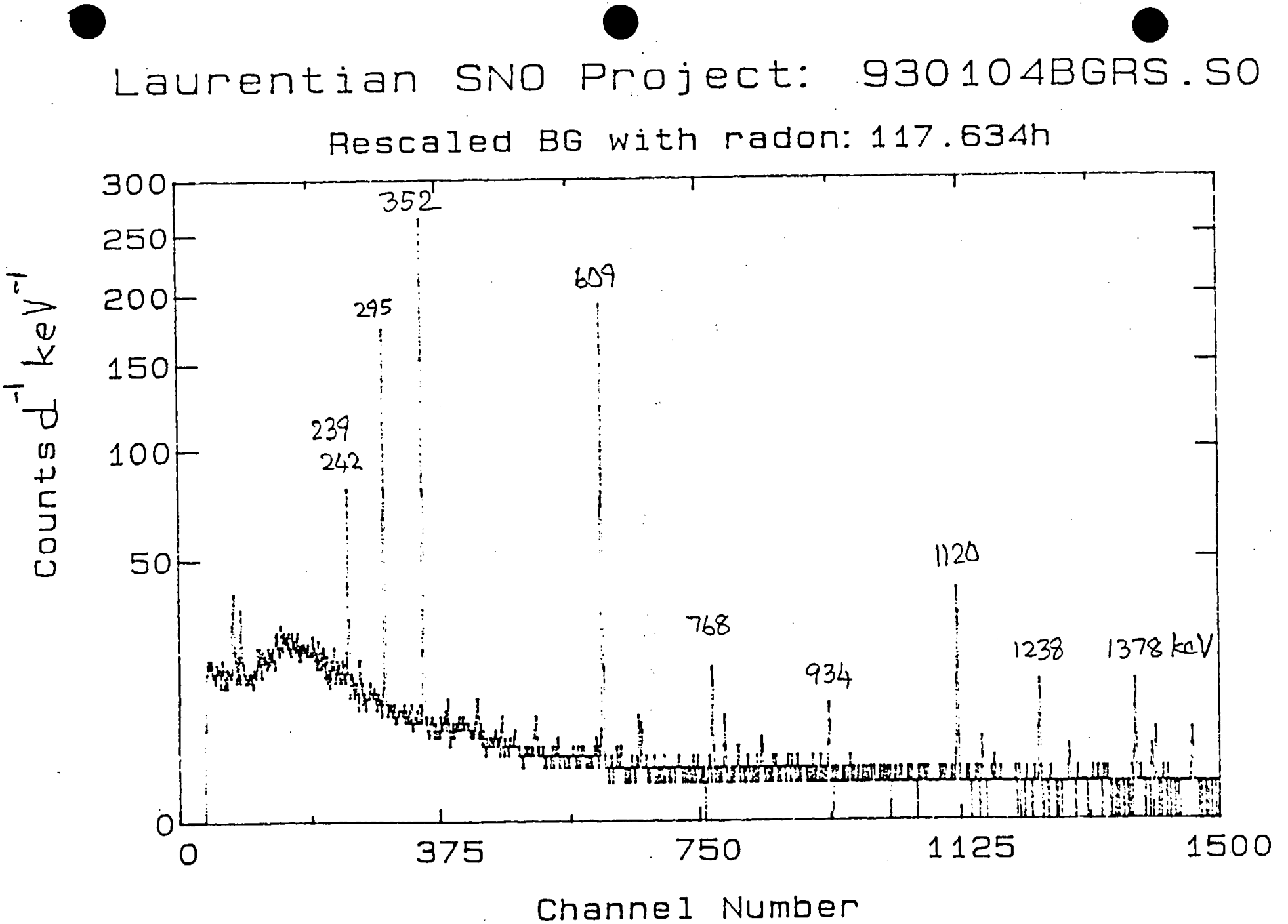
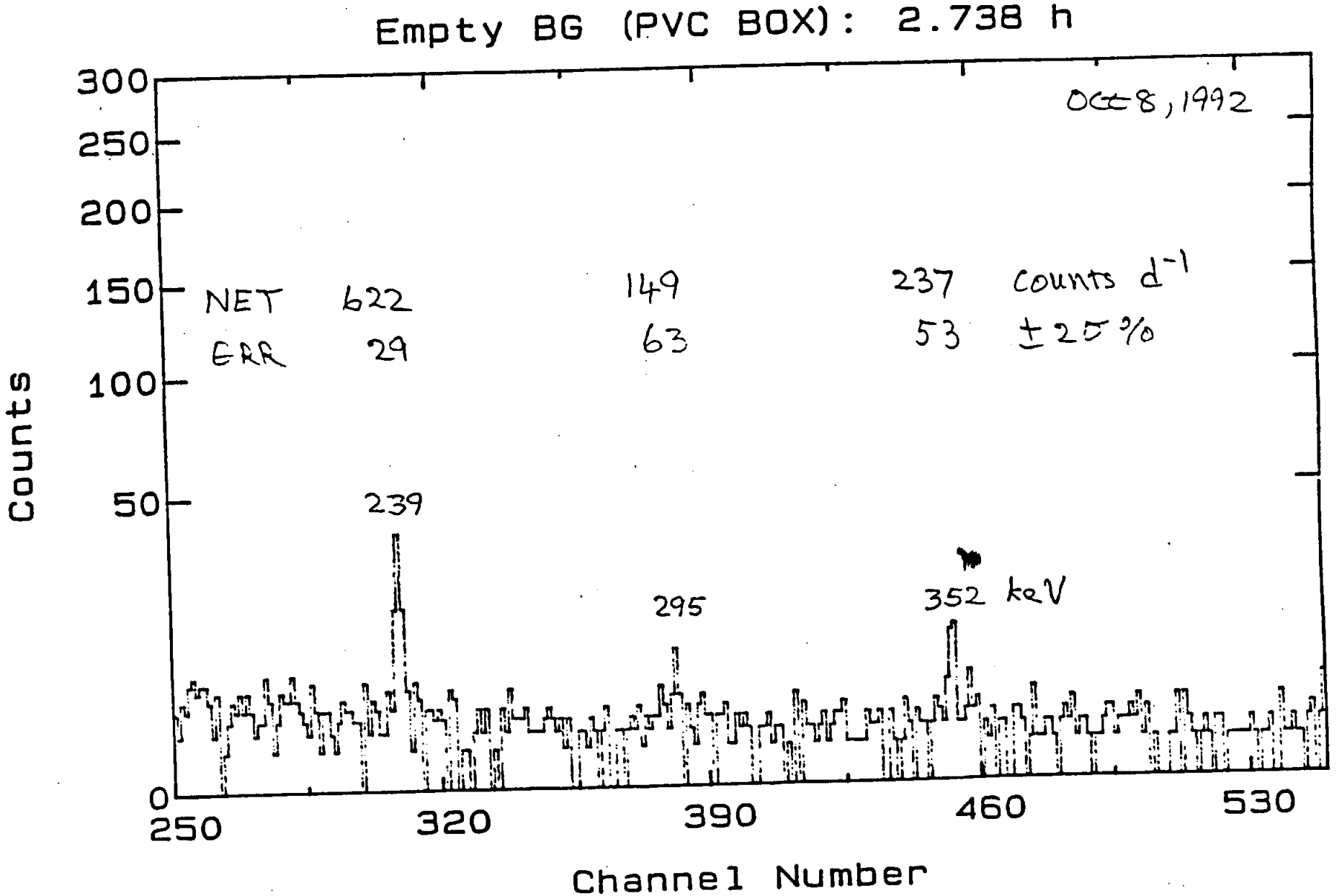
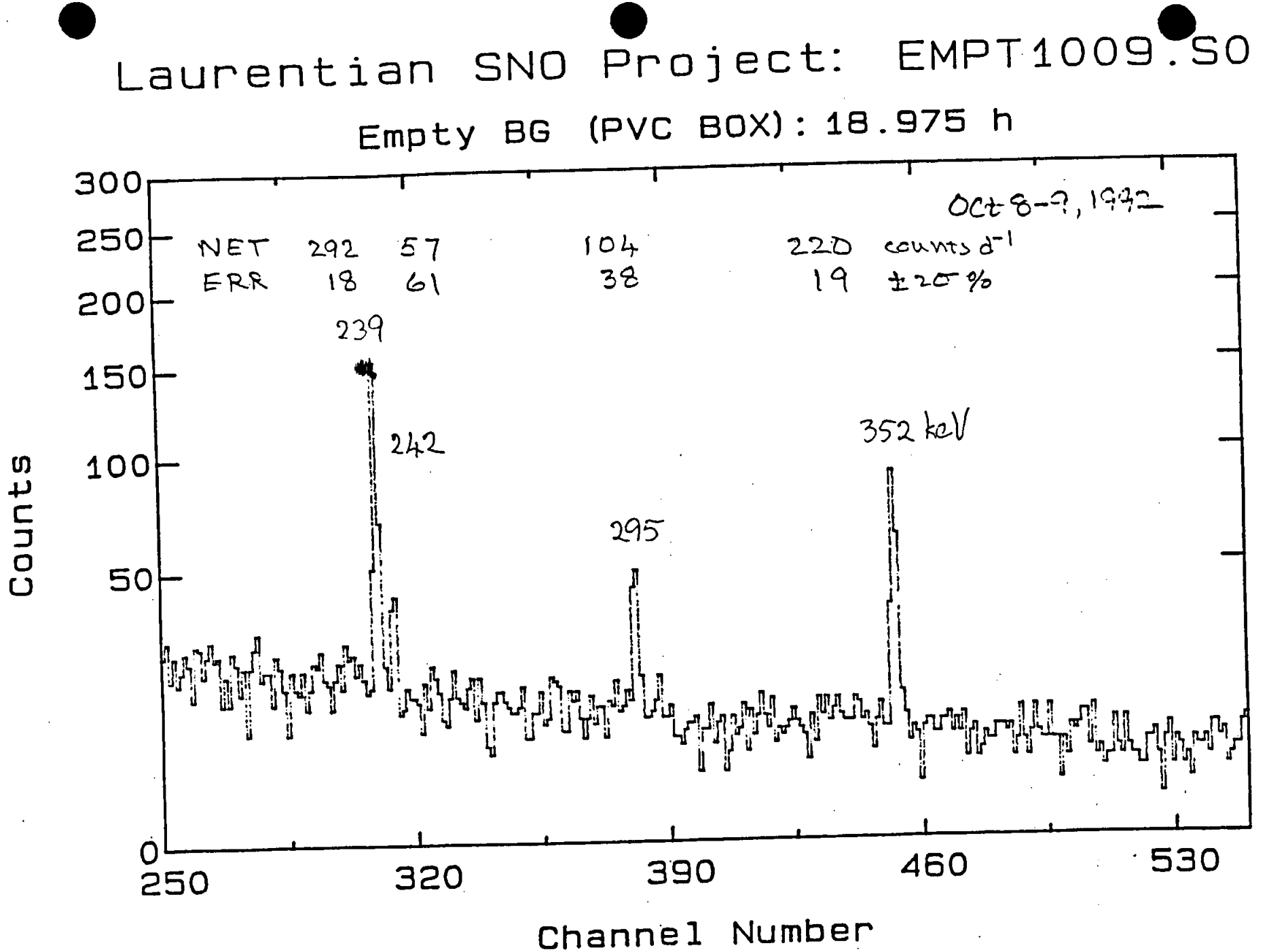
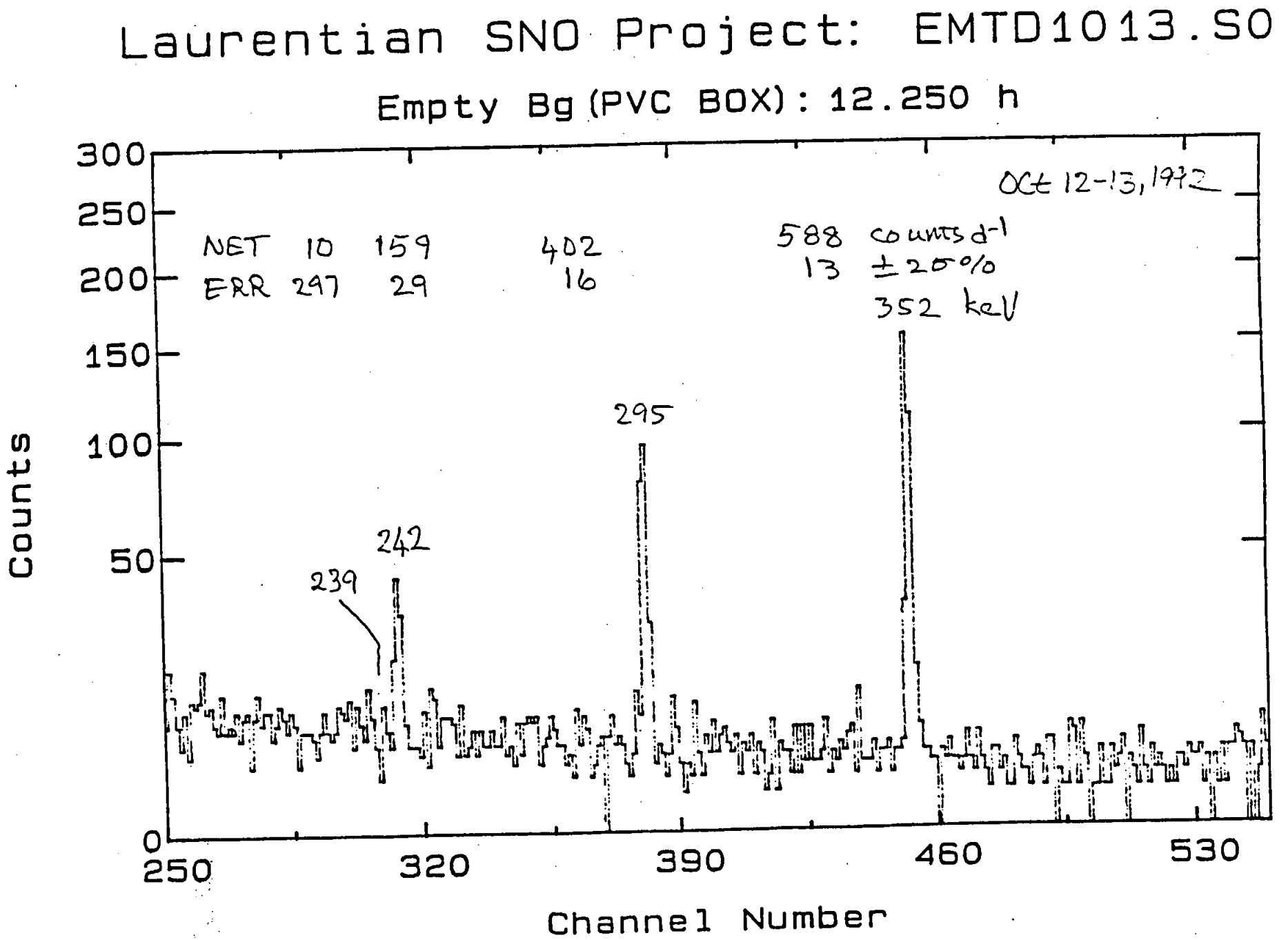

Laurentian SNO Project: 930104BGRS.SO
Rescaled BG with radon: 117.634h
Counts d^{-1} keV^{-1}
300
250
200
150
100
50
0
352
295
609
239
242
1120
768
934
1238
1378 keV
0
375
750
1125
1500
Channel Number

Fig 4

Laurentian SNO Project: EMPT1008.SO




Laurentian SNO Project: EMPT1009.SO
Empty BG (PVC BOX): 18.975 h
Oct 8-9, 1992
NET 292 57 104 220 counts d⁻¹
ERR 18 61 38 19 ±20%
239
242
295
352 keV
Counts
Channel Number
300
250
200
150
100
50
0
250
320
390
460
530


Laurentian SNO Project: EMTD1013.S0
Empty Bg (PVC BOX): 12.250 h
Oct 12-13, 1972
NET 10 159 402
ERR 297 29 16
588 counts d-1
13 ±20%
352 keV
295
242
239
Counts
300
250
200
150
100
50
0
250
320
390
460
530
Channel Number

Laurentian SNO Project: EMPT1013.S0