

Data Section

PROTON-INDUCED THICK-TARGET GAMMA-RAY YIELDS FOR THE ELEMENTAL ANALYSIS OF THE $Z = 3-9, 11-21$ ELEMENTS

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A systematic study of the relative thick-target yields of prompt γ -rays following proton bombardment has been carried out at $E_p = 1, 1.7$ and 2.4 MeV for the elements $Z = 3-9, 11-21$. The relevant spectra for each element are depicted and a table of the most suitable γ -rays for elemental analysis are given. Depending on the strength of the reaction cross section, the sensitivity limits of the detection vary from ppm to a few percent under practical measuring arrangements. Particular aspects of the measuring techniques are discussed.

Introduction

The applicability of low energy accelerators for elemental analysis has frequently proved successful. In particular, proton-induced X-ray emission (PIXE) due to the increased resolving power of the X-ray detectors has been one of the most often applied methods in elemental analysis. The advantage of PIXE is that all elements with $Z \geq 15$ can be measured in one measurement with high sensitivity. On the other hand, a serious disadvantage of PIXE is that the detection of light elements is not possible. This would be very desirable, as the major part of the earth's crust consists of light elements (the elements with $Z \leq 15$ correspond to 95 total at.%) and consequently the samples include, without exception, light elements. The complementary method to PIXE is proton-induced gamma-ray emission (PIGE). PIGE is very sensitive to the elements having low abundances in nature such as Li, B and F, but insensitive to the dominating elements such as O, Si and C. As a result, in studying "natural" samples, all induced γ -ray peaks are the same order of magnitude in spite of their different abundances. In spite of the clear advantage of PIGE, it is not commonly used. One evident reason is that up till now no systematic study has been performed, although for many individual elements PIGE studies

have been reported.¹⁻⁸ The aim of this work is to rectify this state of affairs by performing the required systematic study for all possible light elements and to present the results in a practical form.

Experimental

Experimental arrangements

The proton beam was obtained from the 2.5 MV van de Graaff accelerator at Helsinki University. The proton beam passed through adjustable slits and a 40 cm liquid nitrogen cold trap before striking the target, which could be cooled with water or liquid nitrogen. The angle between the proton beam and the target normal was 45°. The γ -radiation was detected with a Princeton 110 cm³ Ge(Li) detector with an energy resolution of 1.9 keV at $E_\gamma = 1.33$ MeV and 3.0 keV at $E_\gamma = 2.61$ MeV and with an efficiency of 21.8%. The γ -ray spectra were stored in the 4k memory of a Nuclear Data analyzer, after which the spectra were treated with the PDP-9 and Burroughs 6700 computers. In all measurements the detection was at an angle of $\Theta = 55^\circ$ relative to the beam direction at a distance of 4 cm from the target. The diameter of the beam spot on the target was collimated to about 2 mm. The beam intensity, which was adjusted according to the counting rate, varied from 1 nA to 1 μ A.

The Be-, C-, Mg-, Al- and Si-targets were 1 \times 1 cm² plates with thickness approximately 1 mm. In other cases the samples were prepared from the powdered compounds by pressing them into pills, 1 mm thick and 6 mm in diameter.

Measurements

The measurements were performed on all $Z \leq 21$ elements, except for hydrogen, helium and neon. In the helium case the Q-value of -5 MeV is too low. In the hydrogen case the $d(p, \gamma)^3\text{He}$ reaction is possible, but it is weak and no separate γ -rays occur, only a non-resonant background. Neon has strong resonances, but in the elemental analysis of non-gaseous samples it is of no great importance. Instead, an illustrative spectrum was taken for argon gas using the external beam arrangement, because in that arrangement the argon produces a background radiation.

The γ -ray spectra were taken at $E_p = 1, 1.7$ and 2.4 MeV using gains of 0-3 MeV/4 kch and 0-13 MeV/4 kch. When the samples were in compound form, such as S in PbS, the relevant spectra were taken from the other element. In order to restrict the otherwise considerable number of spectra to be presented, only those regarded as relevant for the use of elemental analysis are shown in Figs 1-18. Due to the difficulties in pictorial representation, the spectra have been condensed into 2000 channels. For clarity, the background or impurity peaks, when they

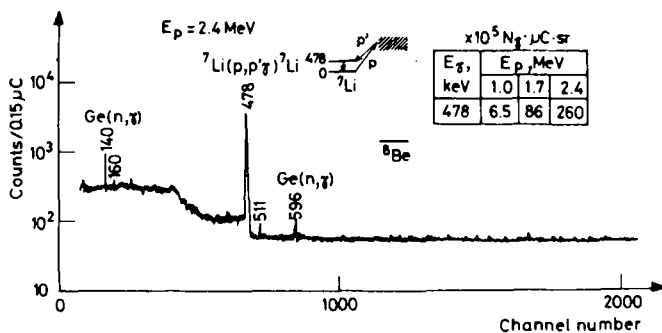


Fig. 1. Gamma-ray spectrum of lithium

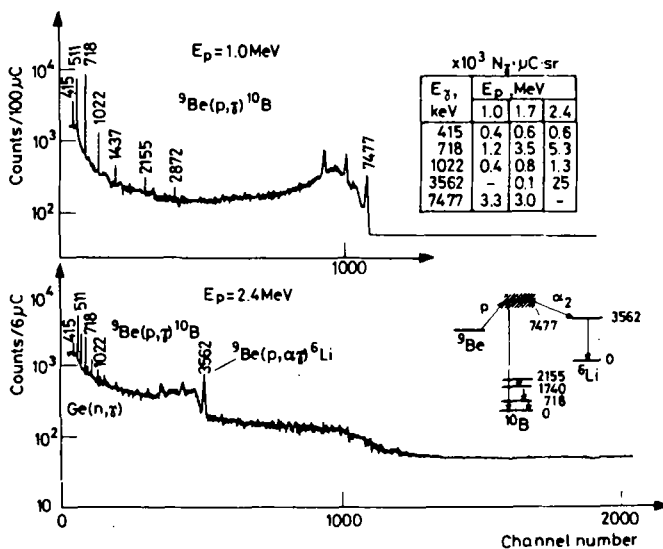


Fig. 2. Gamma-ray spectra of beryllium

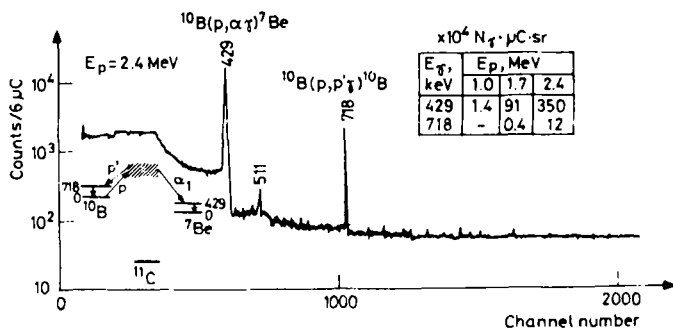


Fig. 3. Gamma-ray spectrum of boron

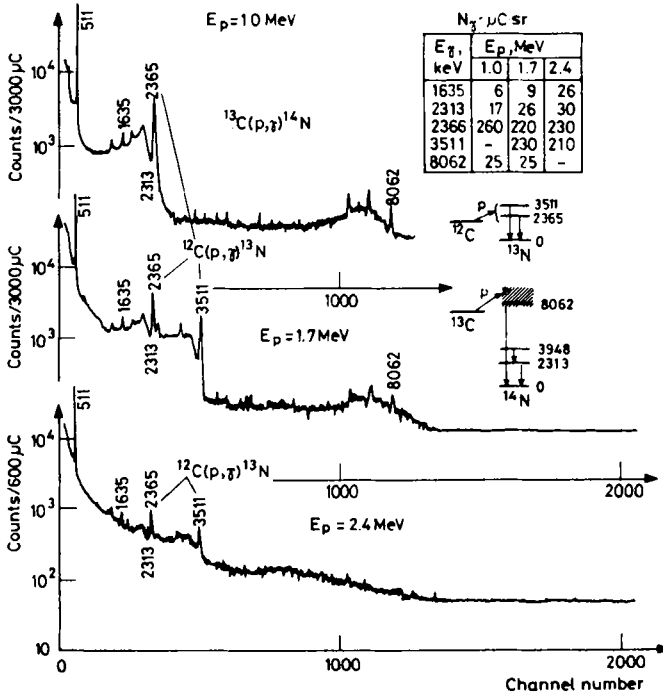


Fig. 4. Gamma-ray spectra of carbon

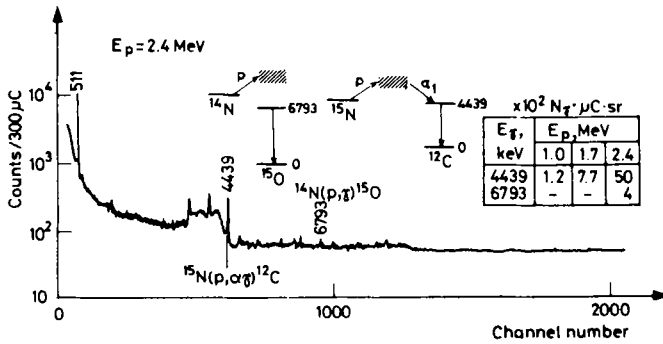


Fig. 5. Gamma-ray spectrum of nitrogen

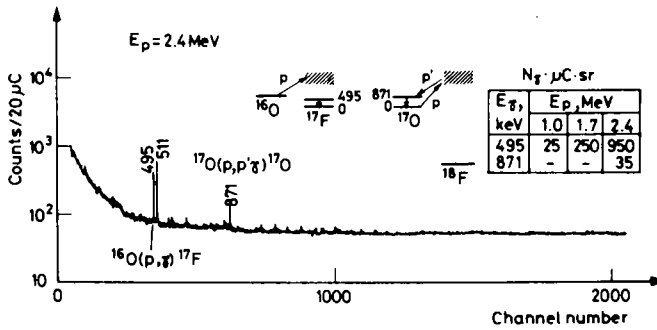


Fig. 6. Gamma-ray spectrum of oxygen

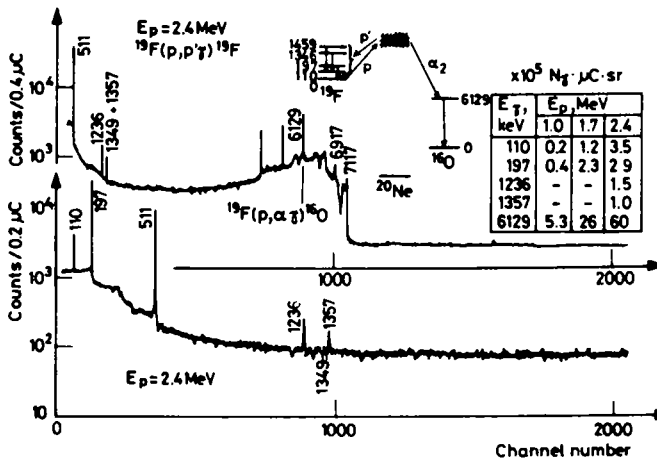


Fig. 7. Gamma-ray spectra of fluorine

occur in the spectra, have been subtracted or otherwise accounted for. On the other hand, the spectra include peaks generated by neutron irradiation. The intensities of the strongest γ -rays are given in the insert tables of the figures. These intensities correspond to those obtained from the pure natural element. The origin of the γ -ray peaks is also shown in the decay schemes drawn in the figures. The origin of the relevant, strong γ -ray peaks was solved in all spectra except for the calcium case, where the peaks at 121, 131, 520 and 776 keV are probably due to Coulomb excitation of a heavier impurity element. The energy values assigned in the figures and the table are taken from the latest compilations.^{9,10}

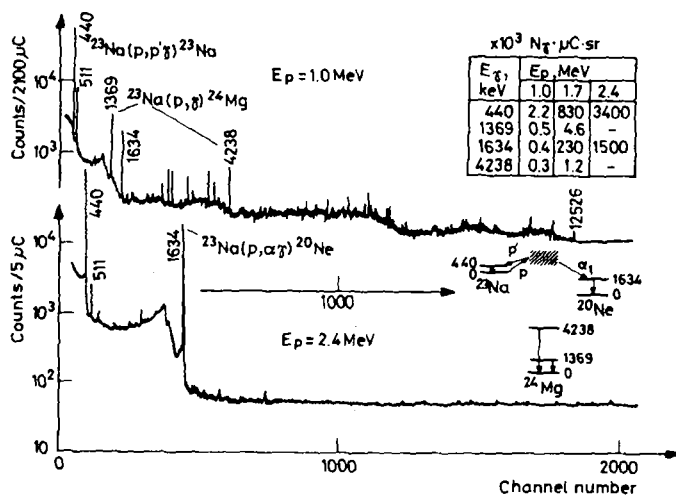


Fig. 8. Gamma-ray spectra of sodium

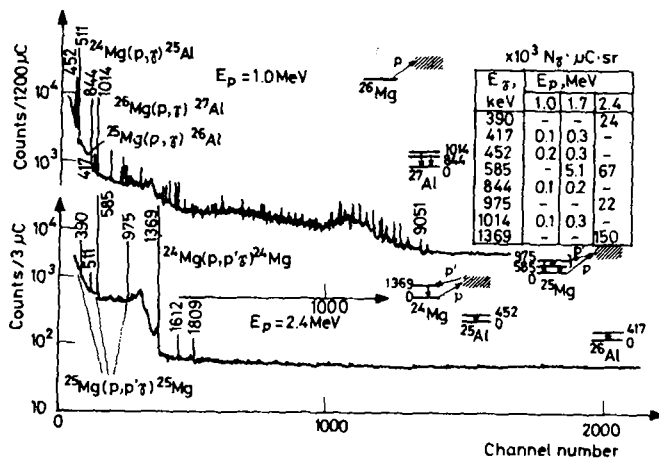


Fig. 9. Gamma-ray spectra of magnesium

All results have been collected in Table 1. For the values given in Table 1 no error limits are quoted. However, the main source of error comes from the stopping power, which can be as much as 20% in the compound cases.

However, the accuracy of the data presented here is not of essential importance, since for accurate elemental determinations the standard spectra should be taken in the applied geometry in order to avoid uncertainties arising from the geometry, the detection efficiency and absorption effects. In addition, one serious error

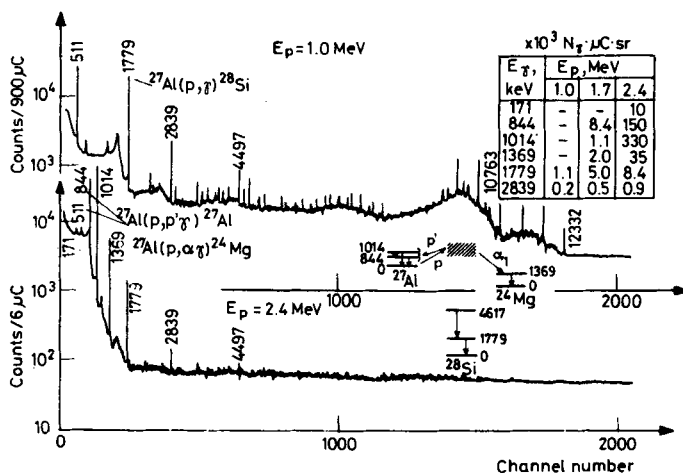


Fig. 10. Gamma-ray spectra of aluminum

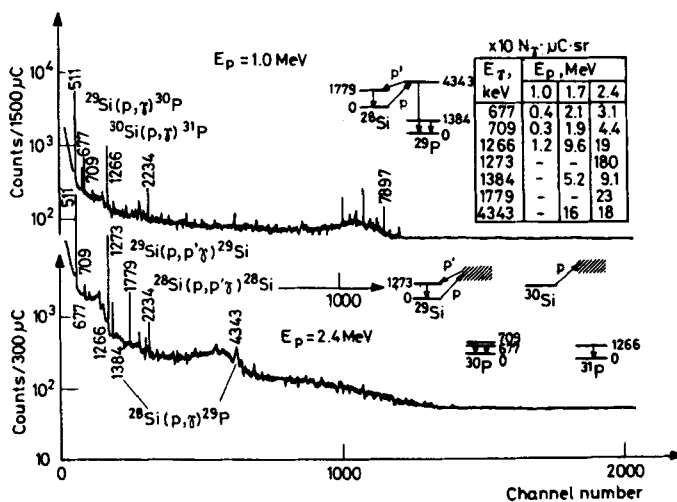


Fig. 11. Gamma-ray spectra of silicon

source which should be kept in mind is the dead time correction due to the high counting rates commonly occurring in γ -yield measurements.

Due to the short lifetimes of the de-exciting state and the high recoil of the light nucleus, a clear Doppler-broadening occurs in the peaks of $E_\gamma = 478$ keV (Li), 3562 (Be), 429 (B), 4439 (N) and 1634 (Na). Because of the large resonance width, the γ -peaks of 2365 and 3511 keV (C) and 4343 (Si) are broader than the experimental width of the peak. In cases where overlap occurs the broadening can be used to help identify the origin of the peak.

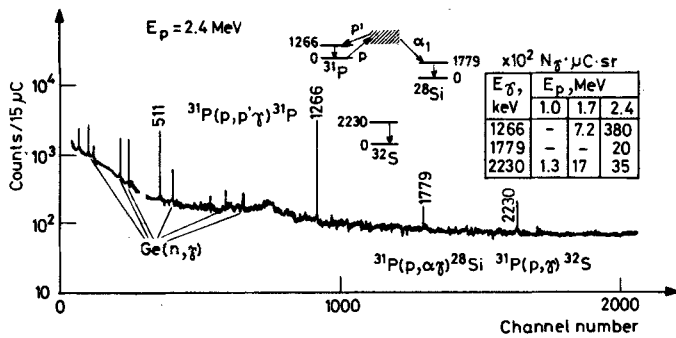


Fig. 12. Gamma-ray spectrum of phosphorus

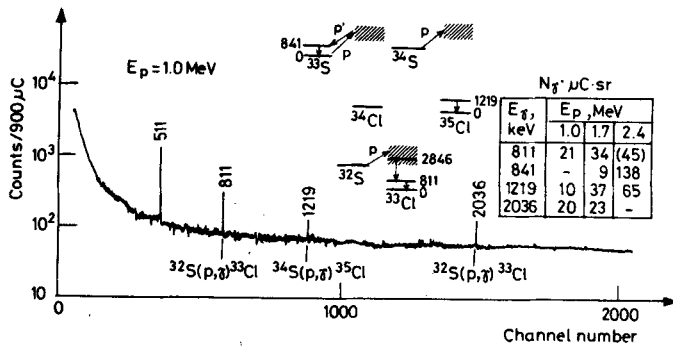


Fig. 13. Gamma-ray spectrum of sulfur

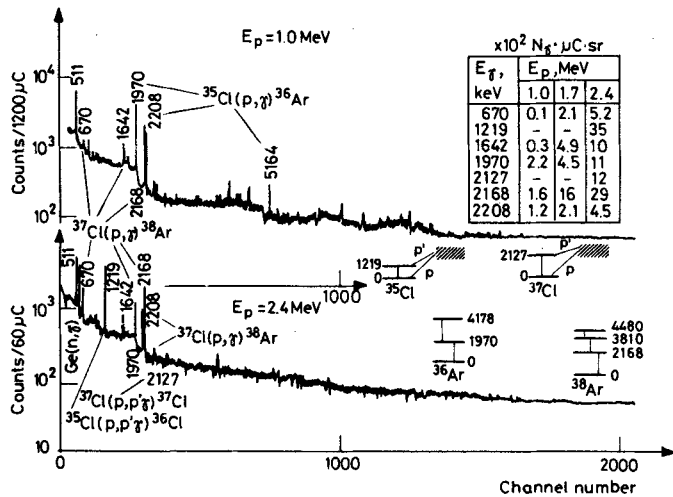


Fig. 14. Gamma-ray spectra of chlorine

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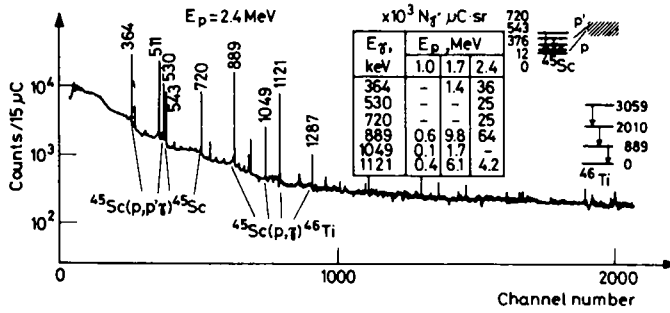


Fig. 18. Gamma-ray spectrum of scandium

Table 1
Thick target γ -ray yields

Element	E _γ , keV	Yield · $\mu\text{C} \cdot \text{sr}$		
		E _p = 1.0 MeV	1.7 MeV	2.4 MeV
Li	478	6.5	86	260 · 10 ⁵
Be	415	0.4	0.6	0.6 · 10 ³
	718	1.2	3.5	5.3
	1022	0.4	0.8	1.3
	3562	-	0.1	25
	7477	3.3	3.0	-
B	429	1.4	91	350 · 10 ⁴
	718	-	0.4	12
C	1635	6	9	26
	2313	17	26	30
	2365	260	220	230
	3511	-	230	210
	8062	25	25	-
N	4439	1.2	7.7	50 · 10 ²
	6793	-	-	4
O	495	25	250	950
	871	-	-	35
F	110	0.2	1.2	3.5 · 10 ⁵
	197	0.4	2.3	29
	1236	-	-	1.5
	1357	-	-	1.0
	6129	5.3	26	60
Na	440	2.2	830	3400 · 10 ³
	1369	0.5	4.6	-
	1634	0.4	230	1500
Mg	4238	0.3	1.2	-
	390	-	-	24 · 10 ³
	417	0.1	0.3	-
	452	0.2	0.3	-
	585	-	5.1	67
	844	0.1	0.2	-
	975	-	-	22

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Table 1 (cont.)

Element	E_{γ} , keV	Yield $\cdot \mu\text{C} \cdot \text{sr}$		
		$E_p = 1.0 \text{ MeV}$	1.7 MeV	2.4 MeV
Al	1014	0.1	0.3	—
	1369	—	—	150
	171	—	—	$10 \cdot 10^3$
	844	—	8.4	150
	1014	—	1.1	330
	1369	—	2.0	35
	1779	1.1	5.0	8.4
Si	2839	0.2	0.5	0.9
	677	0.4	2.1	$3.1 \cdot 10$
	709	0.3	1.9	4.4
	1266	1.2	9.6	19
	1273	—	—	180
	1384	—	5.2	9.1
	1779	—	—	23
P	4343	—	16	18
	1266	—	7.2	$380 \cdot 10^2$
	1779	—	—	20
	2230	1.3	17	35
S	811	21	34	45
	841	—	9	138
	1219	10	37	65
	2036	20	23	—
Cl	670	0.1	2.1	$5.2 \cdot 10^2$
	1219	—	—	35
	1642	0.3	4.9	10
	1970	2.2	4.5	11
	2127	—	—	12
	2168	1.6	16	29
	2208	1.2	2.1	4.5
K	313	0.4	5.6	$— \cdot 10$
	755	—	6.1	—
	899	0.7	11	25
	980	—	—	52
	1525	4.3	54	130
	2168	—	20	260
	364	—	43	240
Ca	373	—	32	870
	530	—	15	69
	543	—	12	46
	720	—	29	100
	Sc	364	—	1.4
530		—	—	25
720		—	—	25
889		0.6	9.8	64
1049		0.1	1.7	—
	1121	0.4	6.1	42

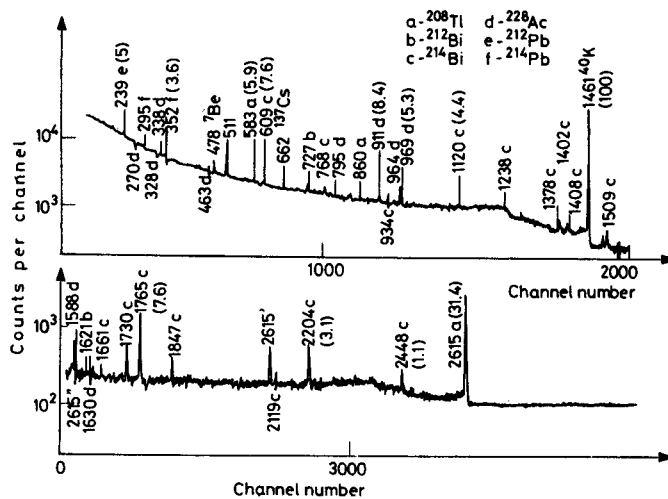


Fig. 19. Laboratory background

In Fig. 19 the background spectrum of the laboratory is shown and the energy, intensity and origin of the strongest peaks are denoted. Conventionally the background using well-shielded detectors is insignificant, but when measuring samples with a low γ -ray yield the existence of the background should be remembered and corrected for.

Discussion

On the basis of the γ -ray spectra obtained it seems that the neutron yield occurring in connection with some of the isotopes is significant, in that it increases the number of γ -ray peaks in the $E_\gamma \leq 1$ MeV region. For example, even with a dose of 15 μ C in the K case, many peaks originating from the neutron induced Ge-isotopes were observed. Germanium has five stable isotopes, each having a moderate cross-section for slow neutrons and evidently also for fast neutrons. Although no thorough study of the origin of all the peaks observed was made, we could in the potassium case identify at least 20 γ -rays originating from neutron induced reactions in germanium. The isotopes where the (p, n) reaction is possible are as follows (Q-value in MeV): ^6Li (-1.6), ^9Be (-1.8), ^{36}S (-1.9), ^{37}Cl (-1.6), ^{40}K (0.5), ^{41}K (-1.2) and ^{46}Ca (-2.2). However, in the S and Ca cases no significant neutron yield was observed. The neutron activation of the germanium depends strongly on the energy of the neutrons and, in addition, it is evident that the shielding of the detector affects the scattering of neutrons and the γ -spectrum due to neutrons is changing. It is therefore difficult to estimate neutron activation in advance. In all,

the neutron activation is no serious problem, but its existence should be kept in mind, especially if the major components of the sample produce neutrons.

The present γ -ray yield measurement was performed at the conventionally used angle of 55° , which produces the best average yield. In earlier papers relating to elemental analysis the angles of 90° and 135° were used, apparently on account of experimental arrangements. The measurement can actually be performed at any angle, if the standard measurements are also performed in the same geometry. However, because it is desirable to place the detector as close to the sample as possible, the Doppler broadening of the γ -ray peaks does have some significance, especially in the lightest nuclei. The broadening occurs when the lifetime of the de-exciting state is short ($\lesssim 100$ ps) and is strongest at an angle of 90° . The broadening is smallest at 0° , which is why the best resolving power for the peaks can in principle be achieved at this angle, one disadvantage is that in some cases at 0° the peak profile can be distorted due to Doppler shift attenuation.

In using PIGE for the quantitative analysis, the conventional technique is to compare the stopping power values and γ -ray yields of the sample and the pure material. However, as a rule, the composition of the sample is not known completely and therefore the accurate determination of its stopping power is difficult. In complicated cases it is reasonable to mix in small quantities of a material with known composition with the sample material. This method yields good results, if it is possible to prepare homogeneous mixtures. However, if powdered materials are used, the grain size of the sample and the known material should be much smaller than the range of the probing protons. Thus, when the sample material is rough and the added known material is fine, as often occurs in practice, concentration values which are too high are deduced.

The sensitivity of PIGE obviously depends on the reaction cross-section, but it depends also on many other factors, such as the resolving power and effectiveness of the detector, the beam intensity and the composition of the sample. Under favourable conditions a Li concentration, for example, of much below the ppm level in heavy metals can be measured using beam of tens of μA . In the practical case, e.g. the Li determination from the orchard leaves standard (NBS 1571) consisting over 40 elements, the concentration of 0.8 ppm Li is quite possible with a $100 \mu\text{C}$ measurement.¹¹ On the other hand, in low yield cases such as O, P, S, K, and Ca, lowest concentrations of only a few percent can be determined. Fortunately, P, S, K and Ca can generally be determined using PIXE, even below the ppm level. In the important case of oxygen, since the natural samples contain high oxygen concentrations, the sensitivity of PIGE is generally sufficient.

Conventionally the PIGE measurements are performed in vacuum. However, many samples are volatile in vacuum and therefore the external beam method should be

used. The simple method applied in our laboratory is to arrange the external beam as follows: one or more 0.1–0.3 mm holes were drilled in a tantalum plate, then covered with $\sim 1 \mu\text{m}$ gold diaphragm. The diaphragm was pressed by a tantalum plate on an o-ring. An additional advantage of the external beam is that the cooling of the sample can be made effective.

We have here shown that PIGE is a complementary method to PIXE. In principle, all elements except H and He can be detected by one or another of these methods. In addition, since the experimental arrangement of PIGE corresponds to that of PIXE, the combined use of these methods is favourable.

It is worth emphasizing that PIGE is also excellent for subsurface studies in cases where the distribution of light tracer ions in heavy backings is desired, although no details of this application are given in this report. Those natural elements which have two or more isotopes are seldom suitable for depth analysis. But, by using separation techniques, a suitable isotope can be selected. In our laboratory at Helsinki University the implantation technique has been used to study the distributions of the following isotopes: ^{13}C , ^{15}N , ^{19}F , ^{22}Ne , ^{23}Na , $^{24,26}\text{Mg}$, ^{27}Al , $^{29,30}\text{Si}$ and ^{34}S . These isotopes have been successfully measured in various backings.^{12–18}

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