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QUANTITATIVE ANALYSIS OF ALUMINIUM BY PROMPT NUCLEAR REACTIONS

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A new physical method of analysis of samples containing small quantities of aluminium is described. The sample is bombarded with fast protons and the resulting γ-rays are analysed by the Ge(Li) technique. The high selectivity of these detectors allows identification of the nuclei responsible for the γ-ray emission.

A careful analysis has been made of the different nuclear reactions involved in the production of γ-rays in the bombardment of aluminium. Four γ-rays have been observed with sufficient intensities for rapid determination: 843 keV, 1 013 keV, 1 368 keV and 1 778 keV. Thick-target excitation yields are presented and discussed in view of their use in analysis. A complete tabulation of these reactions is also presented. The method allows the determination of the aluminium concentration in every solid matrix in the 100 ppm range. In some cases concentrations as low as 10 ppm can be observed. All these determinations are quantitative. Lower concentrations can be detected qualitatively. Examples of the application of the method to different substances are the following: stainless steel, inorganic compounds, crystals, evaporated layers, etc. The resonance pattern observed in the intensity curves can be used to measure the homogeneity and the thickness of thin layers containing aluminium (0.2 to 4 μm). In most cases the method can be considered non-destructive and there is no residual radioactivity. Analysis of a sample of a total weight not exceeding 0.1 mg can be achieved.

Introduction

The aim of the present project is to apply some particular types of non-destructive methods to the analysis of aluminium, using the known functional dependence of the intensity of γ-rays on the energy of protons producing these radiations during the bombardment of Al.

To determine the best approach to this analysis, we intend to study the nuclear reactions induced by the bombardment of Al by protons, select the useful reactions, and tabulate the values measured. This is the aim of the first part.

In the second part we establish the measuring procedure. In order that advantage may be taken of this research, practical instructions are formulated, and the region of applicability and the limits of the method are clearly stated.

The third part will be devoted to the applications.

Physical aspects of the analytical problem, production and selection of the γ-radiation

Production of γ-radiation by the bombardment of Al with protons

In order to determine the most appropriate measuring conditions in each instance, a systematic study of the reactions leading to the emission of γ-radiation and a measurement of the intensities as a function of the energy of acceleration of the protons have been made.

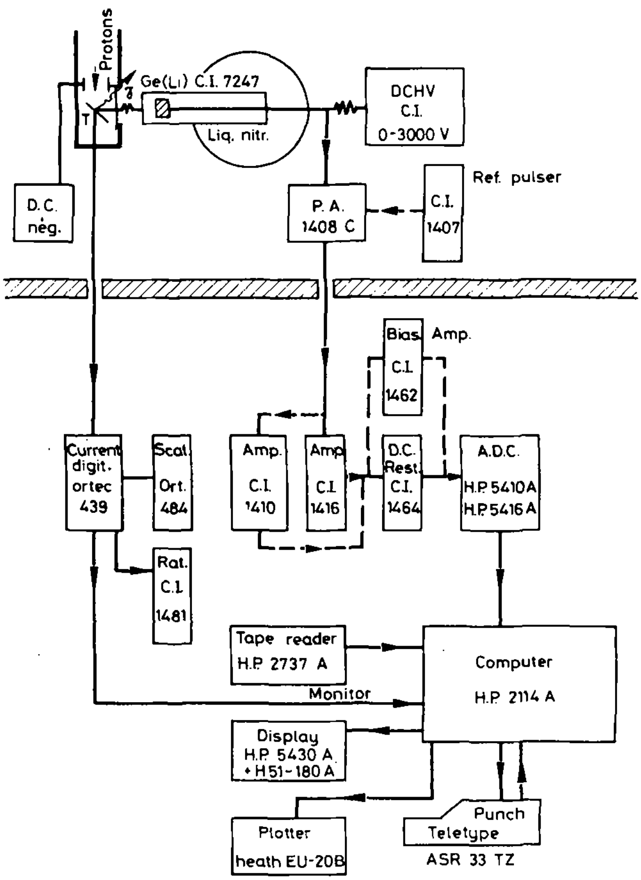

Fig. 1. Sketch of the experimental set-up

A target of pure aluminium of 1 mm thickness was bombarded by protons from the AN-2500 Van de Graaff accelerator of LARN.[1] The emitted γ-radiation was detected by a calibrated and standardized Ge(Li) detector.[2]

The spectra of the radiations emitted by the pure Al target bombarded with protons of energy varying between 500 and 2 500 keV were recorded by the experimental apparatus described elsewhere[1] and are shown schematically in Fig. 1. Fig. 2 gives the spectra generated by 1 000, 1 700 and 1 950 keV protons, for the same number of μC incident on the target (note the difference in scale along the ordinate).

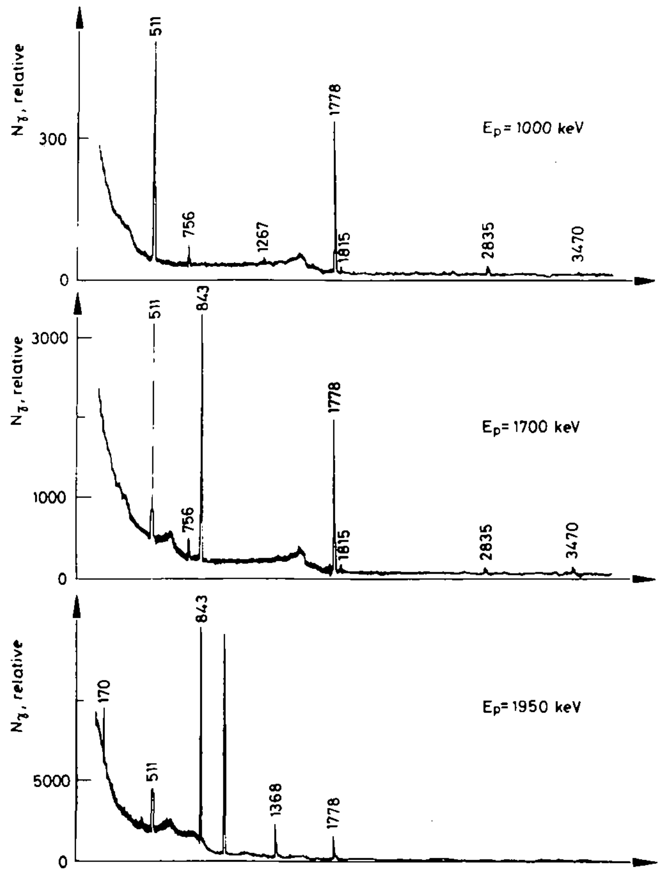

Fig. 2. Typical spectra of emitted γ-rays under bombardment with 1 000, 1 700 and 1 950 keV protons of a thick target of pure aluminium

The analysis permits the identification of the characteristic γ-rays of the reactions of protons on Al. Only the most intense characteristic peaks will be considered. The numbering of the γ-rays together with their identified origins and their intensities as measured by a Ge(Li) detector[2] of 26 cm^3 are given in Table 1. The symbol (n) indicates that the γ-rays cannot be distinguished from the background noise.

Table 1

Characteristic γ-rays from the reactions of proton on aluminium

E_γ (observed), keV	E_γ (emitted), keV	Reaction	Relative intensities at E_p, keV		
			1 000	1 700	1 950
170	170	$^{27}Al(p, p'\gamma)^{27}Al$ 1 043 → 643	0	0	5 000
511	511	annihilation	600	3 000	3 500
756 (2esc)	1 778	$^{27}Al(p, \gamma)^{28}Si$ 1 778 → 0	80	450	(n)
843	843	$^{27}Al(p, p'\gamma)^{27}Al$ 843 → 0	0	8 000	28 000
1 013	1 013	$^{27}Al(p, p'\gamma)^{27}Al$ 1 013 → 0	0	700	23 000
1 267 (1esc)	1 778	$^{27}Al(p, \gamma)^{28}Si$ 1 778 → 0	60	(n)	(n)
1 368	1 368	$^{27}Al(p, \alpha\gamma)^{24}Mg$ 1 368 → 0	0	300	4 900
1 778	1 778	$^{27}Al(p, \gamma)^{28}Si$ 1 778 → 0	510	3 000	3 500
1 815 (2esc)	2 835	$^{27}Al(p, \gamma)^{28}Si$ 4 610 → 1 778	25	150	(n)
2 835	2 835	$^{27}Al(p, \gamma)^{28}Si$ 4 610 → 1 778	30	180	(n)
3 470 (2esc)	4 490	$^{27}Al(p, \gamma)^{28}Si$ 6 270 → 1 778	20	80	(n)

The intensities of the following γ-rays were measured systematically: 1 778 keV for the reaction $^{27}Al(p, \gamma)^{28}Si$; 843 and 1 013 keV for the reaction $^{27}Al(p, p'\gamma)^{27}Al$; and 1 368 keV for the reaction $^{27}Al(p, \alpha\gamma)^{24}Mg$.

A critical analysis of the results with a view to a better choice of the proton acceleration energy and the energy of the γ-ray is contained in the following four sections.

The reaction $^{27}Al(p, \gamma)^{28}Si$ (E_γ = 1 778 keV)

The intensity of the γ-rays for this reaction was measured absolutely between 500 and 1 800 keV in steps of 1.5 keV, and between 1 800 and 2 500 keV in steps of 20 keV for $\Theta_\gamma = 0°$ and $\Theta_\gamma = 90°$. For the measurements made at 0°, the γ-rays cross the sample before reaching the detector; a fraction of the rays is there-

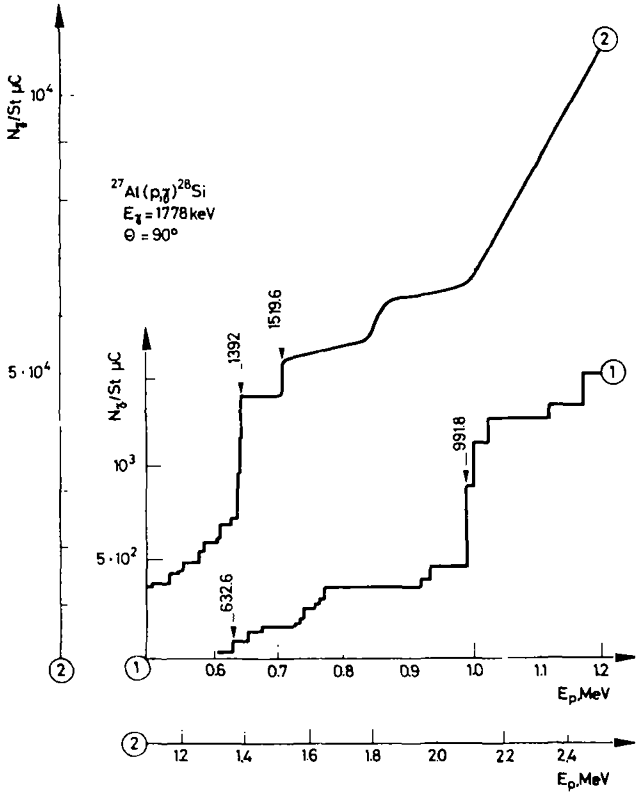

Fig. 3. Absolute intensities of the 1 778 keV γ-rays from the reaction $^{27}Al(p, \gamma)^{28}Si$. The photons are detected at 90° with respect to the direction of the incident proton beam

fore autoabsorbed. Measurements performed at 90° will be most often used in analysis, since in this case the flux of γ-rays resulting from the surface bombardment is detected without first being attenuated by the sample.

The intensity curve $N_\gamma(E_p)$ of the emitted γ-rays as a function of the proton energy expresses an intensity increase by a factor 1 200 between 500 and 2 500 keV. The intensity increases in the beginning in a stepwise manner. A jump in the intensity corresponds every time to the appearance of a resonance in the reaction $^{27}Al(p, \gamma)^{28}Si$. The presence of these level stretches indicates that γ-rays are not emitted except at the resonance energies (cf. Ref.[1] p. 8). Beyond 2 MeV the intensity increases monotonically (Fig. 3).

The γ-ray intensities measured at $\Theta_\gamma = 90°$ are summarized in Table 2.

The most outstanding and often used regions for the analysis of Al in the sample surface are situated at resonance energies of 632 and 991.82 keV.

Table 2

Absolute intensities of the 1 778 keV γ-rays emitted under bombardment by protons from
in the relative intensities are less than 5%. Intermediate values can be obtained

E_p, keV	$\frac{N\gamma}{\mu C \cdot st}$	E_p, keV	$\frac{N\gamma}{\mu C \cdot st}$	E_p, keV	$\frac{N\gamma}{\mu C \cdot st}$	E_p, keV	$\frac{N\gamma}{\mu C \cdot st}$
500	7	695	170	835	375	1 003	1 130
504	7	700	170	840	375	1 005	1 130
*504.8	11	705	170	845	375	1 010	1 130
505	14	710	170	850	375	1 015	1 130
*506.9	17	715	170	855	375	1 020	1 130
508	19	720	170	860	375	1 024	1 130
510	19	725	170	865	375	*1 025	1 185
520	19	730	170	870	375	1 026	1 245
530	19	731	170	875	375	1 030	1 245
540	19	*731.3	176	880	375	1 035	1 245
550	19	732	182	*885	375	1 040	1 245
560	19	735	182	890	375	1 045	1 245
570	19	736	182	895	375	1 050	1 245
580	19	*736.3	193	900	375	1 055	1 245
590	19	737	204	905	375	1 060	1 245
600	19	740	204	910	375	1 065	1 245
605	19	742	204	915	375	1 070	1 245
610	19	*742.3	237	920	375	1 075	1 245
611	19	743	265	922	375	1 080	1 245
*612.1	22	745	265	*922.6	396	1 085	1 245
613	28	750	265	923	418	1 089	1 245
615	28	755	265	925	418	*1 089.8	1 245
620	28	759	265	930	418	1 091	1 245
625	28	*760	275	935	418	1 095	1 245
630	28	761	286	937	418	1 097	1 245
632	28	764	286	*937.2	452	*1 097.6	1 245
632.6	60	767	286	938	485	1 098	1 245
633	93	*767.9	300	940	485	1 099	1 245
635	93	769	314	945	485	1 100	1 245
640	93	770	314	950	485	1 105	1 245
645	93	773	314	955	485	1 110	1 245
650	93	*773.7	344	960	485	1 115	1 245
654	93	774	375	965	485	1 117	1 245
*654.9	117	775	375	970	485	*1 118.4	1 280
656	142	780	375	975	485	1 120	1 310
660	142	785	375	980	485	1 125	1 310
665	142	790	375	985	485	1 130	1 310
670	142	795	375	990	485	1 135	1 310
675	142	800	375	991	485	1 140	1 310
678	142	805	375	*991.822	670	1 145	1 310
*678.6	157	810	375	992	904	1 150	1 310
679	170	815	375	995	904	1 155	1 310
680	170	820	375	1 000	904	1 160	1 310
685	170	825	375	1 001	904	1 165	1 310
690	170	830	375	*1 002.1	1 020	1 170	1 310

a thick target of pure Al. The errors in the absolute values are less than 15%, and thc errors by linear interpolation; * indicates the positions of the expected resonances

E_p, keV	$\frac{N\gamma}{\mu C \cdot st}$	E_p, keV	$\frac{N\gamma}{\mu C \cdot st}$	E_p, keV	$\frac{N\gamma}{\mu C \cdot st}$	E_p, keV	$\frac{N\gamma}{\mu C \cdot st}$
1 171	1 310	1 317	2 080	1 465	4 560	1 760	5 460
*1 171.9	1 395	1 320	2 080	1 475	4 560	1 770	5 470
1 173	1 475	1 325	2 080	1 475	4 560	1 780	5 490
1 175	1 475	1 327	2 080	1 480	4 560	1 790	5 555
1 180	1 475	*1 328.1	2 195	1 485	4 560	1 797	5 605
1 181	1 475	1 329	2 310	1 490	4 560	1 799.9	5 630
*1 183.3	1 475	1 330	2 310	1 500	4 560	1 800	5 635
1 185	1 475	1 335	2 310	1 502.3	4 560	1 802	5 655
1 190	1 475	1 340	2 310	1 510	4 560	1 810	5 745
1 195	1 475	1 345	2 310	1 518	4 560	1 820	5 960
*1 199.4	1 490	1 350	2 310	* 1519.6	4 920	1 830	6 130
1 201	1 510	1 355	2 310	1 521	5 120	*1 841.5	6.180
1 205	1 510	1 360	2 310	1 530	5 150	1 850	6.190
1 210	1 510	1 363	2 310	1 540	5 175	7.860	6 203
1 212	1 510	*1 363.7	2 445	1 550	5 195	1 870	6.220
*1 213	1 595	1 365	2 590	1 560	5 220	1 880	6 235
1 214	1 675	1 370	2 590	*1 565.5	5 225	1 890	6.250
1 215	1 675	1 375	2 590	1 570	5 230	*1 899.1	6 255
1 220	1 675	1 380	2 590	*1 577.9	5 235	1 900	6 255
1 225	1 675	*1 381.3	2 900	1 580	5 240	1 909.9	6.270
1 230	1 675	1 382	3 215	*1 588.2	5 250	1 920	6.280
1 235	1 675	1 385	3 215	1 590	5 250	1 940	6.300
1 240	1 675	1 388	3 215	1 600	5 260	1 960	6 235
1 245	1 675	*1 388.4	3.510	1 610	5 275	*1 968.6	6 340
1 250	1 675	1 389	3 800	1 620	5 285	1 980	6 345
1 255	1 675	1 390	3 800	1 630	5 300	2 000	6 365
1 260	1 675	1 392	3 800	1 640	5 315	2 020	6 390
1 261	1 675	*1 392	4 180	*1 647.4	5 325	2 040	6 410
*1 262.2	1 770	1 393	4 560	1 650	5 330	2 060	6 435
1 263	1 885	1 395	4 560	1 660	5 340	2 080	6 455
1 265	1 885	1 400	4 560	*1 662.2	5 345	2 100	6 520
1 270	1 885	1 405	4 560	*1 663	5 345	2 120	6 695
1 275	1 885	1 410	4 560	1 670	5 350	2 140	6 890
*1 276	1 950	1 415	4 560	1 680	5 360	2 160	7 115
1 277	2 015	*1 416.8	4 560	*1 683.9	5 365	2 180	7.330
1 280	2 015	1 420	4 560	1 690	5 375	2 200	7 485
1 285	2 015	1 425	4 560	1 700	5 395	2 250	8 035
1 290	2 015	1 430	4 560	*1 705.6	5 400	2 300	8 545
1 295	2 015	1 435	4 560	1 710	5 405	2 350	9 050
1 300	2 015	1 440	4 560	1 720	5 415	2 400	9 510
1 305	2 015	1 445	4 560	*1 724.4	5 420	2 450	10 005
1 310	2 015	1 450	4 560	1 730	5 425	2 500	10 490
1 315	2 015	1 455	4 560	1 740	5 435		
1 316	2 015	*1 457.3	4 560	*1 749	5 445		
*1 316.8	2 050	1 460	4 560	1 750	5 445		

These resonances are characterized by:

(1) a considerable increase in the relative intensity of the emitted γ-rays (intense resonance);

(2) long plateau on both sides of the resonance (isolated resonance).

For the analysis of Al to a quite considerable depth (10 μm), protons of 2.5 MeV will be used which produce an intensity ten times as big as those of 1 MeV.

The energy region between 1 370 and 1 400 keV was scanned in steps of 0.3 keV in order to obtain the best description of the intensity behaviour $N_\gamma(E_p)$. A resonance not quoted in the literature was observed at 1 392±0.5 keV.

The vast majority of the other known resonances were observed in our measurements. Exact resonance values were not measured in the course of these experiments; they are contained in the literature.[3,4] Positions located in our experiments correspond to the values published in these references. Of the resonances quoted in Ref.[4] only those situated at 1 519 and 1 800 keV are clearly visible.

Table 3

Absolute intensities of the 843 keV γ-rays emitted under bombardment by protons from a thick target of pure Al. The errors in the absolute values are less than 15%, and the errors in the relative intensities are less than 5%. Intermediate values can be obtained by linear interpolation; * indicates the positions of the expected resonances

E_p, keV	N_γ / μC · st	E_p, keV	N_γ / μC · st	E_p, keV	N_γ / μC · st	E_p, keV	N_γ / μC · st
1 500	186	*1 662.2	3 330	1 790	13 935	1 967	23 535
*1 502.3	186	*1 663	3 640	1 798	14 300	*1 968.6	24 695
1 510	186	1 664	3 915	*1 799.9	17 700	1 970	25 930
1 518	186	1 670	3 915	1 803	19 805	1 980	26 155
*1 519.6	1 490	1 680	3 915	1 810	20 515	1 990	26 245
1 521	2 890	1 683	3 915	1 820	20 585	2 000	26 280
1 530	2 890	*1 683.9	6 125	1 830	20 655	2 050	27 625
1 540	2 890	1 685	7 105	1 840	20 685	2 100	28 636
1 550	2 890	1 690	7 920	*1 841.5	20 735	2 150	29 985
1 560	2 890	1 700	7 920	1 850	20 780	2 200	31 000
*1 565.5	2 890	*1 705.6	7 920	1 860	20 825	2 250	34 370
1 570	2 890	1 710	7 920	1 870	20 860	2 300	15 115
*1 577.9	2 890	1 720	7 920	1 880	20 895	2 350	67 315
*1 588.2	2 890	1 723	7 920	1 890	20 960	2 400	102 400
1 590	2 890	*1 724.4	8 665	*1 899.1	20 965	2 450	148 225
1 600	2 890	1 726	9 315	1 900	21 135	2 500	225 150
1 610	2 890	1 730	9 315	1 908	21 180	2 600	577 250
1 620	2 890	1 740	9 315	*1 909.9	21 430	2 700	913 800
1 630	2 890	1 747	9 315	1 911	22 025	2 800	1 086 000
1 640	2 890	*1 749	10 895	1 920	22 080	2 900	1 384 000
*1 647.7	2 890	1 751	10 970	1 930	22 380	3 000	1 880 000
1 650	2 890	1 760	13 140	1 940	22 830		
1 660	2 890	1 770	13 420	1 950	23 145		
1 661	2 890	1 780	13 885	1 960	23 480		

The reaction $^{27}Al(p, p'\gamma)^{27}Al$ (E_γ = 843 keV)

The intensity of the reaction was measured from E_p = 1 500 to 2 500 keV. Fig. 4 shows the results for $\Theta_\gamma = 90°$. The numerical values are listed in Table 3.

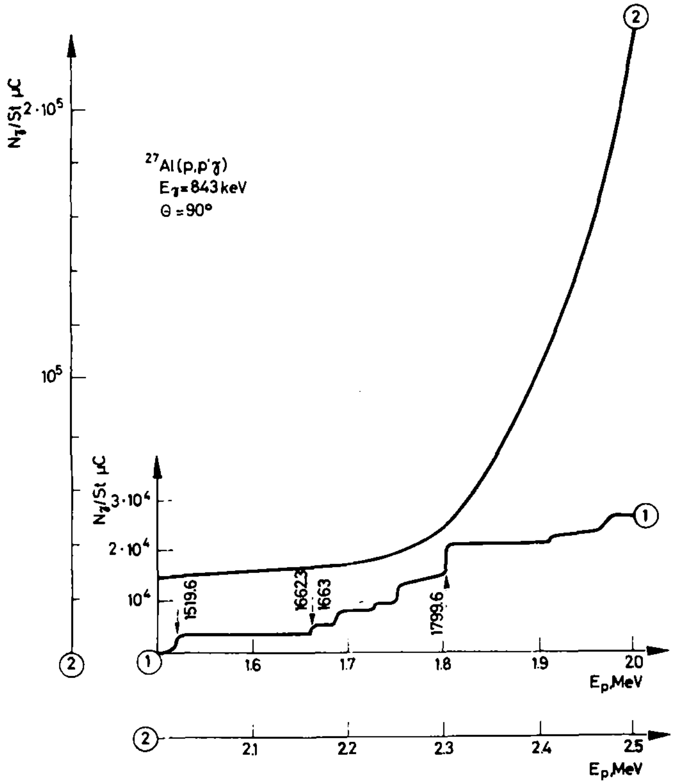

Fig. 4. Absolute intensities of the 843 keV γ-rays from the reaction $^{27}Al(p, p'\gamma)^{27}Al$. The photons are detected at 90° with respect to the direction of the incident proton beam

The intensity approaches zero for E_p < 1 520 keV. Beyond this energy it suddenly increases to a level stretch between 1 520 and 1 660 keV. Next, several resonances (quoted in Ref.[4]) can be perceived at 1 662.2, 1 683.9, 1 724.4, 1 749, 1 799.9, 1 899.1, 1 909.9 and 1 968.6 keV.

The most considerable intensity increases are situated at E_p = 1 520, 1 684 and 1 800 keV.

The reaction $^{27}Al(p, p'\gamma)^{27}Al$ (E_γ = 1 013 keV)

This reaction does not produce any appreciable intensities below E_p = 1 600 keV. The intensity curve also displays stepwise increases, indicating the presence of

Table 4

Absolute intensities of the 1 013 keV γ-rays emitted under bombardment by protons from a thick target of pure Al. The errors in the absolute values are less than 15%, and the errors in the relative intensities are less than 5%. Intermediate values can be obtained by linear interpolation; * indicates the positions of the expected resonances

E_p, keV	$\frac{N\gamma}{\mu C \cdot st}$	E_p, keV	$\frac{N\gamma}{\mu C \cdot st}$	E_p, keV	$\frac{N\gamma}{\mu C \cdot st}$	E_p, keV	$\frac{N\gamma}{\mu C \cdot st}$
1 660	280	*1 799.9	4 032	1 960	22 500	2 250	109 000
*1 662.2	213	1 802	5 060	1 965	24 335	2 300	152 200
*1 663	320	1 820	5 455	*1 968.6	30 000	2 350	222 000
1 680	462	1 840	6 000	1 970	34 370	2 400	297 000
1 700	657	*1 841.5	6 085	1 980	36 575	2 450	372 100
*1 705.6	1 030	1 860	6 565	2 000	40 135	2 500	445 000
1 720	1 500	1 880	7 125	2 050	43 200	2 600	661 300
*1 724.4	1 680	1 895	8 525	2 100	52 600	2 700	874 300
1 740	2 530	*1 899.1	11 250	2 120	62 030	2 800	1 669 000
*1 749	2 905	*1 909.9	15 940	2 140	68 560	2 900	2 360 000
1 760	3 280	1 912	16 520	2 160	71 135	3 000	3 472 000
1 780	3 470	1 920	17 450	2 180	75 090		
1 798	3 505	1 940	19 890	2 200	79 010		

resonances. It is interesting to note that between 1 895 and 1 915 keV the intensity of this reaction increases by a factor of 2.

The measured intensity values are exhibited in Fig. 5 and Table 4.

Beyond 1 900 keV the intensity of this reaction exceeds those of all the others.

Table 5

Absolute intensities of the 1 368 keV γ-rays emitted under bombardment by protons from a thick target of pure Al. The errors in the absolute values are less than 15%, and the errors in the relative intensities are less than 5%. Intermediate values can be obtained by linear interpolation; * indicates the positions of the expected resonances

E_p, keV	$\frac{N\gamma}{\mu C \cdot st}$	E_p, keV	$\frac{N\gamma}{\mu C \cdot st}$	E_p, keV	$\frac{N\gamma}{\mu C \cdot st}$	E_p, keV	$\frac{N\gamma}{\mu C \cdot st}$
1 660	390	1 751	5 700	1 912	6 200	2 140	15 310
*1 662.3	410	1 755	5 525	1 920	6 370	2 160	17 550
*1 663	417	1 760	5 525	1 940	6 370	2 180	20 965
1 680	585	1 780	5 525	1 960	6 370	2 200	23 100
1 700	780	*1 799.9	5.525	*1 968.6	7 090	2 220	24 180
*1 705.6	845	1 820	5 525	1 980	8 255	2 240	24 865
1 710	930	*1 841.5	5 525	2 000	9 750	2 260	25 350
1 720	1 640	1 860	5 525	2 020	10 330	2 280	25 940
*1 724.4	2 665	1 880	5 525	2 040	11 010	2 300	26 325
1 730	3 995	1 890	5 525	2 060	11 800	2 350	28 730
1 740	4 030	1 895	5 525	2 080	12 580	2 400	33 150
1 747	4 065	*1 899.1	5 720	2 100	13 460	2 450	42 700
*1 749	4 745	*1 909.9	6 165	2 120	14 240	2 500	55 750

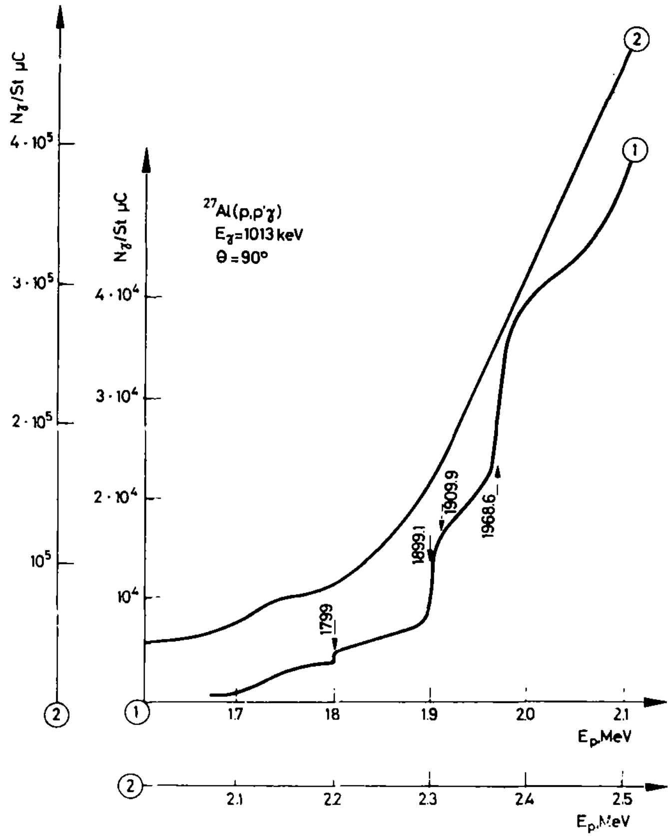

Fig. 5. Absolute intensities of the 1 013 keV γ-rays from the reaction $^{27}Al(p, p'\gamma)^{27}Al$. The photons are detected at 90° with respect to the direction of the incident proton beam

The reaction $^{27}Al(p, \alpha\gamma)^{24}Mg$ (E_γ = 1 368 keV)

The intensity of this reaction was measured between 1 660 and 2 500 keV. Below E_p = 1 600 keV, the intensity is unobservable. For the higher energies it reaches a value comparable to that of the reaction $^{27}Al(p, \gamma)^{28}Si$. We observed a flat region between 1 760 and 1 890 keV in the intensity curve.

Details are given in Fig. 6 and Table 5.

Interferences

The interest in this method of analysis is limited to proton energies less than 5 MeV. Beyond 5 MeV the damage to the sample may become considerable. In addition, because of the considerable emission of neutrons at these energies, a rapid destruction of the Ge(Li) detector is to be feared.

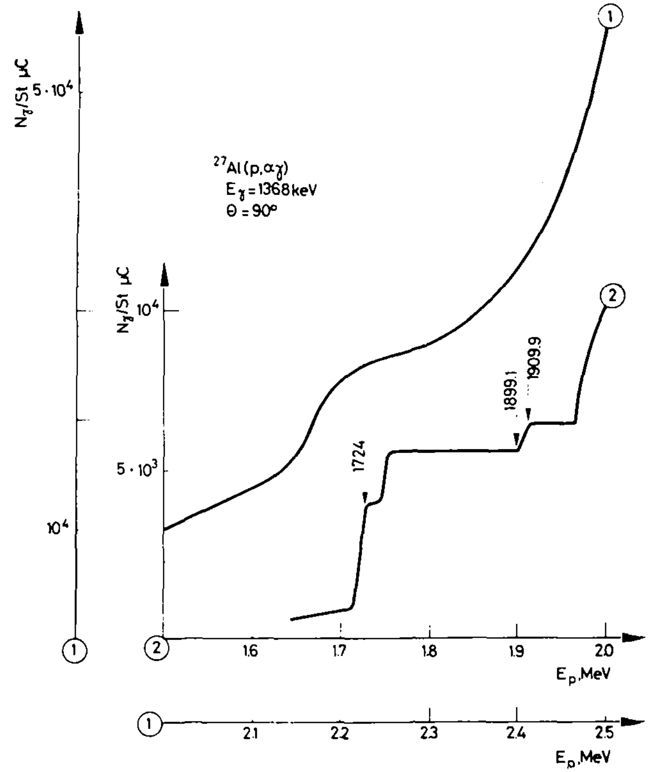

Fig. 6. Absolute intensities of the 1 368 keV γ-rays from the reaction $^{27}Al(p, \alpha\gamma)^{24}Mg$. The photons are detected at 90° with respect to the direction of the incident proton beam

A complete study of interferences will not be possible until all the intensities of the γ-rays emitted by the elements are known. Those which are described here are only the most important ones.

The γ-rays of 1 778 keV can be produced by inelastic scattering of protons on ^{28}Si and by the reaction $^{31}P(p, \alpha\gamma)^{28}Si$. The minimum energy required for the first reaction to be possible is 1 842 keV. The second has been extensively studied at LARN.[5]

The γ-rays of 843 and 1 013 keV can be produced by the reaction $^{26}Mg(p, \gamma)^{27}Al$ (reaction without threshold) and by the reaction $^{30}Si(p, \alpha\gamma)^{27}Al$ for proton energies greater than 3.3 MeV.

The γ-rays of 1 368 keV can be produced by inelastic scattering of protons on ^{24}Mg and by the reaction[6] $^{23}Na(p, \gamma)^{24}Mg$.

Other reactions on light nuclei which can produce these γ-rays have thresholds at energies greater than 5 MeV.

To avoid the possibility of interference it is sometimes possible to work with incident protons of energy less than the threshold energy, if any. Nevertheless, it is often more interesting to test the presence of interference nuclei by the following method.

When samples containing elements such as Na, Mg, P and Si are bombarded with 2.2 MeV protons, they emit γ-rays of an energy different from the characteristic ones of P. The relative intensities of the principal γ-rays emitted under the bombardment of these four nuclei are given in Table 6. The existence of one or more γ-rays of greater intensity than the interfering one allows rapid detection of the possibility of interference. The most useful γ-ray for discovering the possibility of interference in each case is underlined in Table 6.

Table 6

Intensities of the γ-rays emitted under bombardment with 2.2 MeV protons

Bombarded element		Possible interfering γ-rays		
Na	E_γ, keV	1 368		
	$N_\gamma/\mu C \cdot st$	300 ± 50		
	Reaction	$^{23}Na(p, \gamma)^{24}Mg$		
Mg	E_γ, keV	803	1 013	1 368
	$N_\gamma/\mu C \cdot st$	1 080 ± 200	1 670 ± 200	11 100 ± 500
	Reaction	$^{26}Mg(p, \gamma)^{27}Al$	$^{26}Mg(p, \gamma)^{27}Al$	$^{24}Mg(p, p'\gamma)^{24}Mg$
Si	E_γ, keV	1 778		
	$N_\gamma/\mu C \cdot st$	<10		
	Reaction	$^{28}Si(p, p'\gamma)^{28}Si$		
P	E_γ, keV	1 778		
	$N_\gamma/\mu C \cdot st$	400 ± 40		
	Reaction	$^{31}P(p, \alpha\gamma)^{28}Si$		
Bombarded element		**Other emitted γ-rays**		
Na	E_γ, keV	439	1 630	
	$N_\gamma/\mu C \cdot st$	1 900 000 ± 10 000	442 000 ± 5 000	
	Reaction	$^{23}Na(p, p'\gamma)^{23}Na$	$^{23}Na(p, \alpha\gamma)^{20}Ne$	
Mg	E_γ, keV	390	586	976
	$N_\gamma/\mu C \cdot st$	10 560 ± 500	48 400 ± 2 000	9 900 ± 500
	Reaction	$^{25}Mg(p, p'\gamma)^{25}Mg$	$^{25}Mg(p, p'\gamma)^{25}Mg$	$^{25}Mg(p, p'\gamma)^{25}Mg$
Si	E_γ, keV	1 273		
	$N_\gamma/\mu C \cdot st$	538 ± 25		
	Reaction	$^{29}Si(p, p'\gamma)^{29}Si$		
P	E_γ, keV	1 266	2 237	
	$N_\gamma/\mu C \cdot st$	4 200 ± 200	2 200 ± 200	
	Reaction	$^{31}P(p, p'\gamma)^{31}P$	$^{31}P(p, \gamma)^{32}S$	

Practical method of analysis

The choice of the acceleration energy for the protons and of the γ-radiation to be detected

The speed of analysis of the aluminium concentration in the surface layer of a sample is a function of the intensity of the emitted γ-rays, of the correspondence between z (the number of γ-rays counted in the peak) and f (the number appearing in the continuous background at the peak site), and of the specific physical factors concerning each individual sample. Among these last-named are the characteristic interferences from γ-rays of the element under analysis and those from other compounds in the sample, and the possible destruction of the sample under extensive bombardment (the effect of this complication can be reduced by using a revolving target).

Disregarding these physical factors, the optimal acceleration energy of the protons can be predicted.

When the sample consists mainly of light elements which usually emit few γ-rays under proton bombardment, it will be advantageous to work at a fairly high energy.

For an acceleration energy of the order of 2 000 keV, γ-radiations of 843 or 1 013 keV are of comparable intensities. If interference by Mg is suspected, a proton energy of the order of 1 500 keV will be used and the γ-radiation of 1 778 keV detected.

When the sample consists mainly of heavy elements, a lower proton energy will be used. For the measurement of concentrations in the per cent range, a choice of proton energy slightly higher than the resonance energy at $E_p = 632$ keV and the detection of the γ-rays of 1 778 keV are recommended. For lower concentrations it is sometimes advantageous to select an energy E_p of 1 MeV (i.e. slightly higher than the intense and isolated resonance energy at 991.88 keV), where the γ-rays are more intense than at 632 keV.

This choice of energy is merely a recommendation. It will often prove interesting to generate the spectrum of the emitted γ-rays at several energies E_p and select that one which produces the fastest results.

Rapid identification of Al in a sample

The analysis of a spectrum of γ-radiations emitted by a sample subjected to proton bombardment permits the identification of Al in a few minutes (for a beam intensity of the order of 1 μA). The sample contains Al if γ-rays of 843 and 1 013 keV of comparable intensities are observed under the bombardment with 2 MeV protons and if these two radiations disappear from the spectrum when the proton acceleration energy is diminished below 1 500 keV.

This last procedure makes sure that the γ-rays are not generated by a reaction with Mg.

If an accelerator of sufficient energy is not available for this method of analysis, the detection of the 1 778 keV γ-rays produced by bombardment with protons of lower energy may be possible. This second procedure can prove more interesting than the first in the case where the sample consists mainly of heavy elements.

If these two tests for Al give a negative result, the sample does not contain more than 0.1% Al.

Smaller quantities may be detected by longer exposures.

Measurement of the average concentration

The stopping power (S) of the sample is calculable. The prodecure to be followed consists of the steps below:

– bombard with protons of selected energy (see previous section) a sample containing a known quantity of Al and arranged in the manner shown in Fig. 1;

– count the number (Z) of γ-rays emitted for a fixed number of μC;

– replace this standard by the sample to be analysed and take care that all other conditions remain the same;

– count the number (z) of γ-rays emitted for the same number of μC. Repeat this measurement if the statistical error of computation is big and calculate the average value ($\bar{z}$);

– apply the relation:[1]

$$\frac{y_{ech}}{y_{st}} = \frac{\bar{z}}{Z}\,\frac{S_{ech}(\bar{E})}{S_{st}(\bar{E})} \tag{1}$$

where y_{ech} – proportion of atoms being analysed in the sample,

y_{st} – proportion of atoms in the standard,

z (or $\bar{z}$) – number of γ-rays detected during the bombardment of the sample,

Z – number of γ-rays detected during the bombardment of the standard,

S – stopping power (this may be found in Ref.[8]).

The value $\bar{E}$ is the value of E_p where $N_\gamma(E_p)$ is halfway along the ordinate, i.e. $N_\gamma(\bar{E}) = 1/2 N_\gamma(E_p)$.

This empirical rule gives results correct to approximately 1%.

To begin with, it is assumed that S_{ech} is dependent only on the known constituents. If y_{ech} is of the order of 1% or less, the assumption is valid. If y_{ech} is bigger, an iteration calculation must be made by substituting into S_{ech} the newly calculated value of y_{ech}.

The stopping power (S) cannot be calculated. The same procedure is followed as in the first case and eventually one of the methods described in Ref.[1] is applied.

If the composition is unknown, a comparative analysis of another constituent can be executed. In the report LARN-705 an example of a comparative analysis of Al–Na is described.[6]

Remark: If the absence of interferences is definite, the detection and simultaneous counting of several characteristic γ-rays of the element under analysis allow a faster measurement. Eq. (1) is then written:

$$\frac{y_{ech}}{y_{st}} = \frac{\Sigma \bar{z}\, S_{ech}(\bar{E})}{\Sigma Z\, S_{st}(\bar{E})}\,.$$

Sensitivity of the method

According to convention, the limit of sensitivity σ_m is considered to be reached when the peak height of the characteristic γ-rays is equal to half of that of the average background noise recorded in the neighbourhood of the peak. By visualizing this peak as a triangle, the peak count will then equal 1/4 of the background count at the peak site.

For the measurement of low concentration, it is important to decide with the greatest care on the acceleration energy of the protons and therefore also the characteristic γ-radiation to be detected, basing the decision either on trials at various energies, or on the method described above for the rapid identification of Al. An accelerator of variable energy between 500 and 2 500 keV is indispensable for a complete critical analysis of the best energy of acceleration.

Of course, the sensitivity improves with increasing bombardment time, but the bombardment of a sample with a beam of the order of 1 μA for several hours is accompanied by the risk of deterioration. This deterioration is manifested in the form of craters of depth equal to $R(E_p)$, i.e. a few dozen microns. This mode of destruction is typical in a crystalline substance. It was observed during prolonged bombardment of silicon.[7]

Preliminary applications

The following applications were chosen for their specific characteristics, i.e. for the peculiar difficulties they present.

Analysis of Al in stainless steel

Different samples of stainless steel were bombarded and different concentrations of Al were obtained, depending on the origin of the sample.

The sensitivity limits (y_{min}) are a function of the detected γ-rays and of the energy of the protons employed for the bombardment. They were estimated for different practical conditions of analysis (Table 7).

The analysis at $E_p = 2\,000$ keV is therefore especially interesting where speed is essential.

The analysis of Al in stainless steel by the detection of γ-rays of 843 keV is impossible because of their proximity to the 847 keV γ-rays resulting from the reaction $^{56}Fe(p, p'\gamma)^{56}Fe$.[9]

Table 7

Bombardment INOX

E_p, keV	E_γ, keV	Time, min	Beam intensity, μA	y_{min}, ppm
650	1 778	30	2	750
1 000	1 778	30	2	2 000
2 200	1 013	3	0.2	1 200

The accuracy of the determination is reduced by the limited knowledge of the S values and by computation statistics. For a particular analysis (stainless H. V. E.) it has been found that

$$y_{ech} = 3\,110 \pm 120 \text{ ppm}.$$

The precision is of the order of 5%.

Analysis of Al in uranyl nitrate

A sample of uranyl nitrate was bombarded by protons of 995 keV for 1 hr using a beam of 1.4 μA, and the count of emitted γ-rays was compared with that of a standard of pure Al.

The experimental results are given below; the molecular weight of the sample [$UO_2(NO_3)_2 \cdot 6\,H_2O$] equals 502.

Under prolonged bombardment (1 hr) a progressive evaporation of water is possible. By assuming that the water evaporates rapidly, a molecular weight of 394 is computed and a new calculation of S_{ech} has to be made.

This complication can be surmounted either by cooling the sample to the temperature of liquid nitrogen, or by getting rid of the water beforehand.

The uranyl nitrate sample contained

$$y_{ech} = 387 \pm 118 \text{ ppm Al}.$$

The lower limit of the amount of Al detectable is

$$y_{ech,min} = 75 \text{ ppm}.$$

For a sample containing less than 100 ppm the analysis is only qualitative.

Analyses of rock samples containing Al and Na

Samples of mairupt and muscovite were bombarded with protons of 1.4 MeV, and the γ-radiation of 1 778 keV was detected. The following compositions served as the basis for the calculation of S:

Mairupt: $NaAlSi_3O_8$; Muscovite: $KAlSi_3O_{10}(OH)_2$.

Table 8

Comparison of the calculated and measured data

Sample	Al, % theoretical	Al, % found
Mairupt	10.4	13 $\pm$1
Muscovite	7.8	5.96$\pm$0.4

In Table 8 the measured percentages are compared with the percentages calculated for the theoretical compositions.

The differences imply compositions different from those presumed.

A comparative analysis of the Al and Na concentrations in these substances (see report LARN-705) gives the results shown in Table 9.

Table 9

The ratio of Al to Na concentrations

Sample	Na/Al (calculated), atoms	Na/Al (found), atoms
Mairupt	1	0.35
Muscovite	0	0.04

Analysis of Al in a heavy substance

A finely powdered mixture of W and Al_2O_3 in the proportion of $10^4/1$ was bombarded by protons of 1 and 2.2 MeV. The γ-rays of 1 778 and 1 013 keV were recorded. The results are given in Table 10. During the bombardment at 1 MeV and the detection of the 1 778 keV γ-rays, the limit defined above as the sensitivity of the method was attained.

The method can be made more sensitive, detecting 10 ppm, by using protons of 2.2 MeV and by detecting the 1 013 keV γ-radiation.

It is not surprising that the results recorded at different energies of E_p should be different. It is rather difficult in fact to obtain a completely homogeneous mixture of substances in which the concentrations differ so much ($10^4/1$). Since the layers penetrated by the protons of 1.0 and 2.2 MeV are not the same, a difference in the measurements made on the same sample points to an inhomogeneous mixture $W-Al_2O_3$.

Table 10

Results recorded at different proton energies

E_p, keV	E, keV	y_{ech}, ppm	$y_{ech,min}$, ppm	Time, min	Beam intensity, μA
1 000	1778	120 ± 5	80	200	2
2 200	1013	150 ± 5	10	20	0.5

Contrary to the rule, it is seen that maximum sensitivity is attained for the higher proton energies. Actually, each analysis depends on the specific sample. A critical analysis of γ-ray intensities at different proton energies is always to be preferred.

Conclusions

(1) When a thick target of pure Al is bombarded by protons, γ-radiations of 843, 1 013, 1 368 and 1 778 keV are produced, as well as some others of lower intensities (see Table 1). The intensities of these four γ-rays as a function of the proton energy have been measured for incident energies between 500 and 2 500 keV.

(2) The analysis of Al in the surface of materials is possible to a depth of the order of 20 μm.

(3) The possible interferences by Na, Mg, Si and P can be easily identified.

(4) The sensitivity of the method is of the order of 10 to 1 000 ppm and depends on the sample. The limits given here were obtained at LARN in practical trials on several samples and for measurements not exceeding 60 min. Concentrations of 1 000 ppm can be easily detected in samples consisting of solid organic matter.

*

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