Journal of Radioanalytical Chemistry, Vol. 12 (1972) 209—219

QUANTITATIVE ANALYSIS OF PHOSPHORUS BY (p, γ) REACTIONS

G. DEMORTIER, F. BODART

Facultés Universitaires de Namur, L.A.R.N., Namur (Belgium)

Measured values of the intensities of characteristic γ-rays emitted under the bombardment of protons on a thick target of phosphorus are tabulated. The intensity of each characteristic γ-ray is measured and used for quantitative analysis of phosphorus in any sample with a sensitivity of 50 to 1 000 ppm.

Introduction

The aim of the present work is to apply to the quantitative analysis of phosphorus the known dependence of the intensity of γ-rays produced during the bombardment of phosphorus with protons.

To determine the best approach to this analysis, we intend to

- study the γ-ray reactions induced by the bombardment of a thick target of pure phosphorus with protons,
- select the useful reactions and tabulate the measured values,
- establish the measuring procedure,
- give some preliminary applications.

Physical aspects of the problem of analysis
Production and selection of the γ-rays

Production of the γ-rays by the bombardment of P with protons

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

The spectra of the γ-rays emitted by the pure P target bombarded by protons of energy varying between 500 and 2 500 keV are recorded by the experimental apparatus described elsewhere.[1]

Pure phosphorus powder is compressed in the door of a cylindrical drum revolving around its axis (Fig. 1). The impact of the beam is then distributed over a

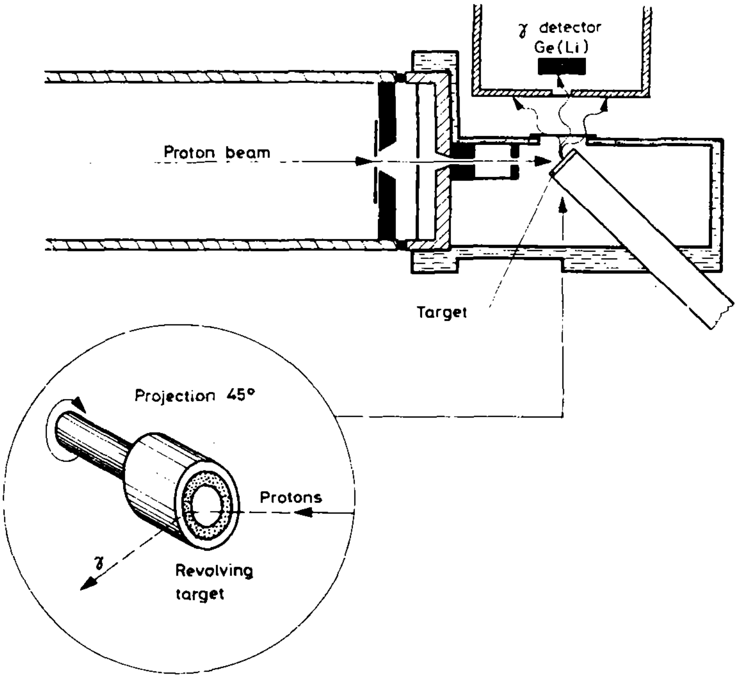

Fig. 1. Sketch of the experimental set-up at the target site

large surface and the heat released locally is considerably reduced. It is therefore possible to maintain a proton beam of 1 to 2.5 MeV reaching intensities of 10^{-8} A during several hours without causing observable destruction or evaporation. The front face of the target is covered by a thin gold layer, produced by evaporation, to ensure a good collection of the incoming proton charges.

In Fig. 2 are shown the spectra generated by protons of 1, 1.5, 2 and 2.5 MeV, for the same number of μC incident on the target (note the difference in the scales along the ordinate).

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

The important contribution of (p, γ) reactions on Na is not abnormal. The measured intensity of γ-rays of 439 keV induced by the reaction ^{23}Na(p, p'γ)^{23}Na is more than 150 times greater than that of the reaction ^{31}P(p, p'γ)^{31}P for 2.5 MeV protons.[2]

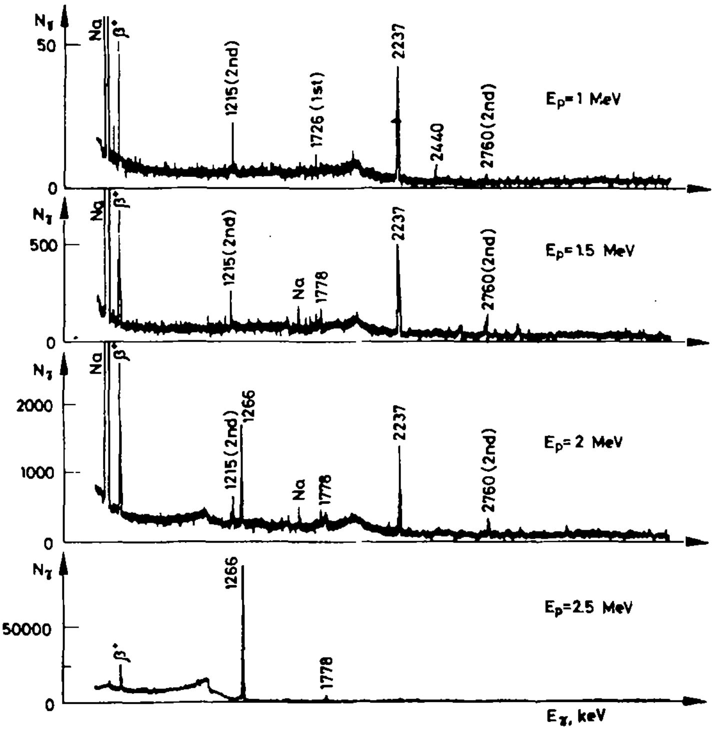

Fig. 2. Typical spectra of γ-rays emitted under the bombardment of 1, 1.5, 2 and 2.5 MeV protons on a thick target of pure phosphorus

Table 1

Characteristic γ-rays emitted by the reaction of protons on phosphorus

E_γ detected, keV	E_γ actual, keV	Reaction	Intensity			
			E_p = 1 000	1 500	2 000	2 500
1 215 (2. es)	2 237	^{31}P(p, γ)^{32}S	16	180	360	700
1 266	1 266	^{31}P(p, p'γ)^{31}P	—	—	1 700	124 000
1 726 (1. es)	2 237	^{31}P(p, γ)^{32}S	5	55	110	200
1 778	1 778	^{31}P(p, $\alpha\gamma$)^{27}Al	—	—	210	4 100
2 237	2 237	^{31}P(p, γ)^{32}S	65	700	1 400	2 650
2 440	2 440	^{31}P(p, γ)^{32}S 4 700 → 2 237	6	(n)	(n)	(n)
2 760 (2. es)	3 780	^{31}P(p, γ)^{32}S	4	40	70	(n)
3 270 (1. es)	3 780	^{31}P(p, γ)^{32}S	(n)	(n)	(n)	(n)
3 780	3 780	^{31}P(p, γ)^{32}S	(n)	(n)	(n)	(n)

N.B.: 435 and 1 630 keV are due to traces of Na in the sample used.

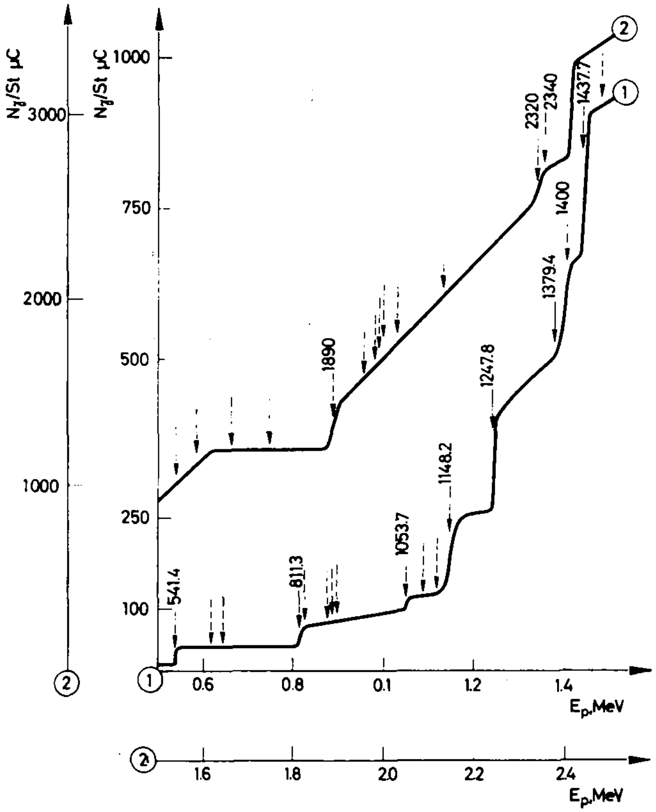

Fig. 3. Absolute intensity of the 2 237 keV γ-rays from the reaction $^{31}P(p, \gamma)^{32}S$. The γ-rays are detected at 90° with respect to the direction of the incident proton beam

The intensities of the following γ-rays are measured and tabulated:

- 2 237 keV γ-ray from the reaction $^{31}P(p, \gamma)^{32}S$
- 1 266 keV γ-ray from the reaction $^{31}P(p, p'\gamma)^{31}P$
- 1 778 keV γ-ray from the reaction $^{31}P(p, \alpha\gamma)^{27}Al$.

In the following sections we shall make a critical analysis of the results, choosing the best proton acceleration energy and the energy of the γ-ray to be detected.

The reaction $^{31}P(p, \gamma)^{32}S$ ($E_\gamma = 2\,237$ *keV*)

The intensity of the γ-rays is measured between 500 and 1 600 keV in steps of 3 keV, and between 1 600 and 2 500 keV in steps of 20 keV. The emitted γ-rays pass through a thin mylar window (2.5 mg/cm^2) before reaching the detector, located at 90° with respect to the direction of the proton beam.

The intensity $N_\gamma(E_p)$ of the emitted γ-rays as a function of the proton energy shows an increase by a factor of 10^3 between 500 and 2 500 keV (Fig. 3). The intensity increases at lower energy in a well-defined stepwise manner. A jump in the intensity corresponds to the appearance of a resonance in the reaction $^{31}P(p, \gamma)^{32}S$. The presence of horizontal stretches indicates that γ-rays are only emitted for discrete resonance energies.

The most outstanding and useful regions for the analysis of P in the surface of the sample are situated just above the resonance energies of 541.4, 1 148.2, and 1 247.8 keV. These resonances are characterized by a large increase in the intensity of the emitted γ-rays (intense resonance) and especially for the first one by a long plateau on both sides of the resonance (isolated resonance).

Table 2

Intensities of the 2 237 keV γ-rays emitted under bombardment by protons from a thick target of pure P. The errors in the absolute values are less than 15%, and the errors in the relative intensities are less than 5%

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	3	1 020	89	1 440	850	1 980	1 730
520	3	1 040	92	1 450	905	2 000	1 780
540	3	1 045	93	1 460	910	2 020	1 820
541.5	19	1 053	115	1 480	915	2 040	1 860
543	36	1 060	131	1 500	930	2 060	1 910
560	36	1 080	140	1 520	960	2 080	1 960
580	36	1 100	145	1 540	995	2 100	2 000
600	36	1 120	155	1 560	1 040	2 120	2 045
620	36	1 140	160	1 580	1 100	2 140	2 090
640	36	1 148	196	1 600	1 150	2 160	2 135
660	36	1 160	230	1 620	1 210	2 180	2 180
680	36	1 180	250	1 640	1 210	2 200	2 220
700	36	1 200	250	1 660	1 210	2 220	2 260
720	36	1 220	250	1 680	1 210	2 240	2 300
740	36	1 230	250	1 700	1 210	2 260	2 340
760	36	1 235	262	1 720	1 210	2 280	2 380
780	36	1 240	275	1 740	1 210	2 300	2 430
800	36	1 247	340	1 760	1 210	2 320	2 530
810	36	1 251	415	1 780	1 210	2 330	2 610
811.5	52	1 260	430	1 800	1 210	2 340	2 640
813	65	1 280	445	1 820	1 210	2 360	2 700
815	65	1 300	460	1 840	1 210	2 370	2 715
820	65	1 320	475	1 860	1 210	2 380	2 730
840	67	1 340	487	1 870	1 250	2 400	2 760
880	70	1 360	500	1 880	1 270	2 410	3 070
900	73	1 380	510	1 890	1 370	2 415	3 270
920	75	1 400	650	1 900	1 450	2 420	3 300
940	77	1 405	660	1 910	1 500	2 440	3 320
960	79	1 410	665	1 920	1 550	2 460	3 340
980	81	1 420	670	1 940	1 590	2 480	3 360
1 000	86	1 430	675	1 960	1 690	2 500	3 380

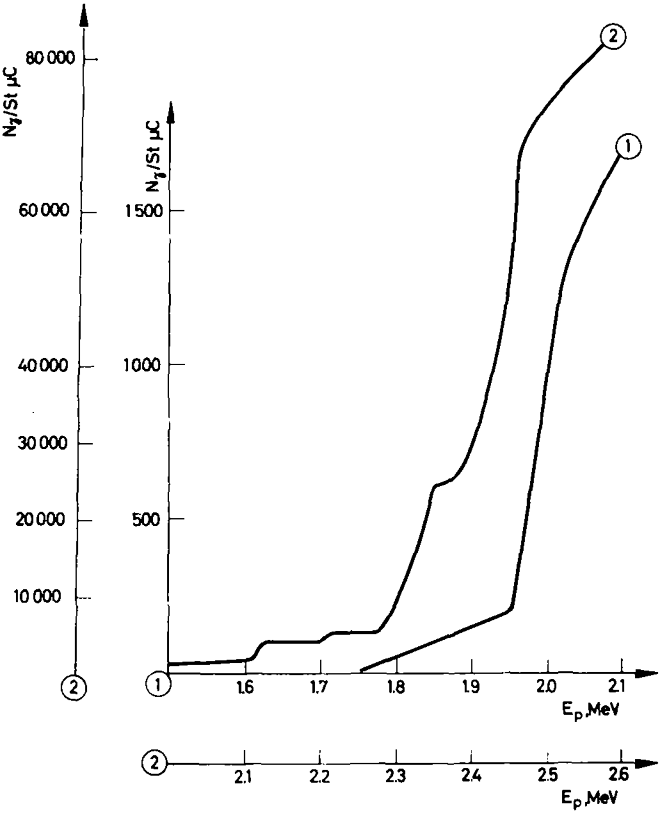

Fig. 4. Absolute intensity of the 1 266 keV γ-rays from the reaction $^{31}P(p, p'\gamma)^{31}P$. The γ-rays are detected at 90° with respect to the direction of the incident proton beam

The values of the measured intensities of these γ-rays are given in Table 2. The number $N_\gamma/\mu C \cdot st$ is the absolute number of emitted γ-rays per steradian and μC of proton beam incident on a thick target of pure P. The precision of all the measured values is better than 10%. The efficiency of the detector is taken into account.[3]

The reaction $^{31}P(p, p'\gamma)^{31}P$ $(E_\gamma = 1\ 266\ keV)$

The intensity of this reaction is measured from $E_p = 1\ 750$ keV to 2 500 keV. Fig. 4 shows the results. Numerical values are given in Table 3.

The intensity approaches zero for proton energies less than 1 700 keV. No characteristics of isolated resonances are observed in this reaction. The intensity of the 1 266 keV γ-rays is the biggest one of all the γ-rays emitted by the bombardment of P with protons for incident energies greater than 2.15 MeV. At 2.5 MeV,

Table 3

Intensities of the 1 266 keV γ-rays emitted under bombardment by protons from a thick target of pure P. The errors in the absolute values are less than 15%, and the errors in the relative intensities are less than 5%

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	$\frac{N_\gamma}{\mu C \cdot st}$
1 750	20	1 990	850	2 140	4 035	2 340	20 250
1 780	25	2 000	1 000	2 160	4 035	2 360	23 800
1 800	35	2 010	1 200	2 180	4 130	2 370	24 500
1 820	50	2 020	1 280	2 200	4 220	2 380	25 560
1 840	70	2 030	1 370	2 210	4 900	2 400	32 000
1 860	85	2 040	1 450	2 220	5 540	2 420	37 300
1 880	105	2 050	1 500	2 230	5 540	2 430	40 000
1 900	120	2 060	1 550	2 240	5 540	2 440	49 000
1 920	140	2 080	1 620	2 250	5 540	2 460	68 000
1 940	160	2 100	1 700	2 260	5 540	2 480	71 500
1 950	200	2 110	1 800	2 270	5 540	2 500	73 700
1 960	360	2 120	3 200	2 280	6 440	2 520	76 250
1 970	520	2 125	4 030	2 300	9.500	2 540	78 000
1 980	700	2 130	4 035	2 320	13 850	2 560	81 300

Table 4

Intensities of the 1 778 keV γ-rays emitted under bombardment by protons from a thick target of pure P. The errors in the absolute values are less than 15%, and the errors in the relative intensities are less than 5%

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	$\frac{N_\gamma}{\mu C \cdot st}$
1 750	35	2 000	173	2 210	1 040	2 420	1 635
1 780	52	2 020	185	2 218	1 445	2 430	2 000
1 800	65	2 040	195	2 240	1 465	2 440	2 220
1 820	80	2 060	205	2 260	1 490	2 460	2 790
1 840	90	2 080	230	2 280	1 510	2 470	3 110
1 860	100	2 100	280	2 300	1 530	2 480	3 180
1 880	110	2 120	330	2 320	1 550	2 500	3 300
1 900	118	2 130	400	2 340	1 570	2 520	3 440
1 920	130	2 140	400	2 360	1 585	2 530	4 080
1 940	140	2 160	400	2 380	1 595	2 540	4 930
1 960	151	2 180	400	2 400	1 615	2 550	5 200
1 980	161	2 200	400	2 410	1 625	2 560	5 440

the intensity of this γ-ray is more than 20 times greater than that of the 2 237 keV γ-ray. This means that in practical cases the height of the peak corresponding to 1 266 keV is more than 40 times greater than that of the 2 237 keV peak, when a Ge(Li) detector of standard size is used.

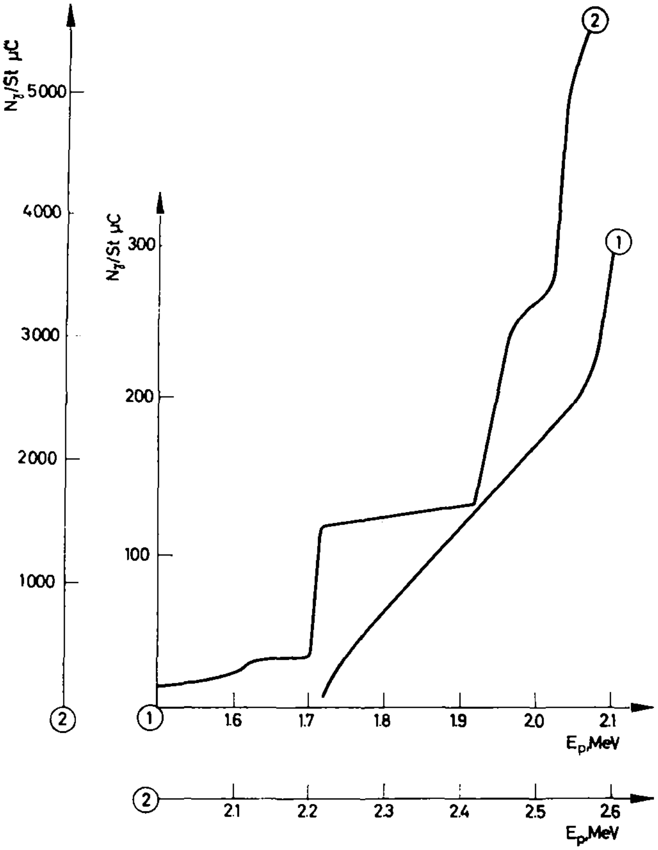

Fig. 5. Absolute intensity of the 1 778 keV γ-rays from the reaction $^{31}P(p, \alpha\gamma)^{27}Al$. The γ-rays are detected at 90° with respect to the direction of the incident proton beam

The reaction $^{31}P(p, \alpha\gamma)^{27}Al$ $(E_\gamma = 1\ 778\ keV)$

The intensity of this reaction is measured between 1 750 and 2 500 keV. Below E_p = 1 700 keV the intensity is not observable. For the highest energies studied at LARN, the intensity reaches a value comparable to that of the reaction $^{31}P(p, \gamma)^{32}S$.

Details are given in Fig. 5 and Table 4.

Interference

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

Table 5

Relative intensities of the γ-rays emitted under the bombardment with 2.5 MeV protons

Bombarded element		Possible interfering γ-rays, keV	
Al	E_γ	1 778	
	I_γ	120 ± 10	
	Reaction	^{27}Al(p, γ)	
Si	E_γ	1 266	1 778
	I_γ	10 ± 10	150 ± 30
	Reaction	^{30}Si(p, p$'\gamma$)	^{28}Si(p, p$'\gamma$)
S	E_γ	1 266	2 237
	I_γ	8 ± 8	10 ± 10
	Reaction	^{34}S(p, $\alpha\gamma$)	^{32}S(p, p$'\gamma$)
Cl	E_γ	2 237	
	I_γ	5 ± 5	
	Reaction	^{35}Cl(p, $\alpha\gamma$)	

Bombarded element		Other emitted γ-rays, keV			
Al	E_γ	843	1 013	1 368	
	I_γ	2 535 ± 50	5 010 ± 100	670 ± 30	
	Reaction	^{27}Al(p, p$'\gamma$)	^{27}Al(p, p$'\gamma$)	^{27}Al(p, $\alpha\gamma$)	
Si	E_γ	1 273			
	I_γ	2 350 ± 100			
	Reaction	^{29}Si(p, p$'\gamma$)			
S	E_γ	806	842	1 220	1 762
	I_γ	120 ± 25	755 ± 25	65 ± 20	60 ± 20
	Reaction	^{32}S(p, γ)	^{33}S(p, p$'\gamma$)	^{34}S(p, γ)	^{34}S(p, γ)
Cl	E_γ	1 220	2 127	2 168	
	I_γ	1 125 ± 50	380 ± 50	900 ± 50	
	Reaction	^{35}Cl(p, p$'\gamma$)	^{37}Cl(p, $\alpha\gamma$)	^{37}Cl(p, γ)	

The γ-rays of 2 237 keV can be produced by inelastic scattering of protons on sulfur, and by the (p, $\alpha\gamma$) reaction on ^{35}Cl. The minimum energy required for these reactions to be possible is 2 307 and 385 keV, respectively. The γ-rays of 1 266 keV can also be produced by two principal reactions: ^{30}Si(p, γ)^{31}P and ^{34}S(p, $\alpha\gamma$)^{31}P. The first one is possible for all proton energies (no threshold), the second one for proton energies greater than 653 keV. The γ-rays of 1 778 keV can be produced by the reactions ^{27}Al(p, γ)^{28}Si, which has been extensively studied at LARN,[2] and ^{28}Si(p, p$'\gamma$)^{28}Si for proton energies greater than 1 850 keV.

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 Al, Si, S and Cl are bombarded with 2.5 MeV protons, they emit γ-rays of energy different from the characteristic ones of P. We give in Table 5 the relative intensities of the principal γ-rays emitted under the bombardment of these four nuclei. 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 5.

Practical method of analysis

Speed and sensitivity

The speed of analysis of the concentration of phosphorus in the surface layer of a sample is a function of the intensity of the emitted γ-rays, of the ratio of the number of γ-rays counted in the peak to the number appearing in the continuous background at the peak site, and also of the specific physical factors concerning the individual sample. Amongst the latter are the possible interferences with the γ-rays of the element under analysis by those of the other compounds in the sample, and the possible destruction of the sample under extensive bombardment. The latter can be reduced by using a revolving target.

No general procedure can be specified, but the following preliminary experiments must be done:

- searching for the possibility of interference (see Table 5),
- searching for the characteristic γ-rays and the best proton energy. It will often prove interesting to generate the spectrum of emitted γ-rays at several energies E_p and to select the one producing the fastest result.

Nevertheless, it can be said that when the sample consists mainly of light elements which generally produce few γ-rays under the proton bombardment, it will be advantageous to work at a fairly high energy and detect the γ-ray of 1 266 keV which is the most intense. When the sample consists mainly of heavy elements, a lower proton energy will be used.

For low concentrations the choice of an energy slightly higher than the resonance energy at 541.4 keV and the detection of the γ-ray of 2 237 keV is recommended. For higher concentrations it is sometimes advantageous to select an energy slightly higher than the resonance at 1 247 keV which is more intense. This choice of energy is only a recommendation.

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

Of course, the sensitivity improves with the increasing time of bombardment, but the bombardment of a sample with a beam of the order of 1 μA during several hours can produce an important deterioration.

The sensitivity of the determination of the concentration in various samples varies between 50 and 500 ppm, depending on the emission of γ-rays by the rest of the matrix. The principal limitation of the sensitivity occurs when the matrix emits γ-rays of energy slightly different from the characteristic one or when this latter is situated at the Compton edge of some intense γ-ray coming from the rest of the sample. Semiquantitative estimation of the P concentration in the ppm range can be done under fairly favorable circumstances.

Measurement of the average concentration

The average concentration of an element in a sample is given by:[4]

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

where $y_{\mathrm{ech}}, y_{\mathrm{st}}$ – concentrations in the sample and in the standard, respectively,
z, Z – the intensities of the γ-rays emitted by the sample and the standard under the same experimental conditions,
$S_{\mathrm{ech}}, S_{\mathrm{st}}$ – the stopping powers calculated for the useful energy E.

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

References

1. G. DECONNINCK, G. DEMORTIER, Symp. sur l'utilisation des particules en physique, chimie biologie, Lausanne, 1970.
2. G. DEMORTIER, G. DECONNINCK, F. BODART, L. THÔNE, Dosage de Na par réactions (p, γ) (p, p'γ) et (p, αγ), LARN, 705, 1970.
3. G. DEMORTIER, Proc. 5th Symp. on Photon Detectors, Varna, Bulgaria, 1970, in the press.
4. G. DECONNINCK, (in this Proceedings) *J. Radioanal. Chem.*, 12 (1972) 157.