PHOSPHORUS ANALYSIS IN MILK BY ACTIVATION WITH FAST NEUTRONS USING VAN DE GRAAFF ACCELERATOR.

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ABSTRACT

Determination of phosphorus in milk by activation using 14 MeV neutrons generated by a Van de Graaff accelerator is related. Cyclic and conventional irradiations were performed. In both cases, the variation of the neutron flux was followed by a BF_3 detector, and mathematical equations were applied to the normalization of the counting rates. Results for phosphorus analysis in IAEA (International Atomic Energy Agency) reference material A-11 are $(0.9 \pm 0.1)\%$ by conventional irradiation and $(1.0 \pm 0.1)\%$ by cyclic irradiation and the detection limits were of 0.12 mg and 0.04 mg, respectively, in 100 mg of sample.

Key words; phosphorus, milk, fast neutrons, Van de Graaff accelerator.

INTRODUCTION

The phosphorus analysis in biological samples is of special concern due to its vital role in biological process, specially in milk, that is ingered by people in the feed diet. Milk is one of major sources of phosphorus.

Neutron activation analysis is an atractive method to determine the concentration of phosphorus in biological samples[1].

The aim of the present work was to establish an instrumental method for phosphorus analysis in milk by activation using fast neutrons produced in a Van de Graaff accelerator. Phosphorus was determined via $^{31}P(n,\alpha)^{28}Al$ reaction, which emitts a gamma ray of 1778.9 keV.

Considering that variations in the neutron flux occur frequently during the sample irradiation with fast neutrons[2], efforts were carried out in order to minimize errors in the counting rates. Therefore, a BF_3 detector was employed to follow the variations of neutron flux and all the counting rates were normalized. Besides, a cyclic irradiation procedure is also proposed, since a cumulative counting of the induced activity increases the sensibility and improves the detection limits.

EXPERIMENTAL

Ge Detector Calibration. A detector efficiency calibration at a short source to detector was performed using several nuclides emitting single gamma ray, according to KAWADE et al[3].

BF_3 Detector Calibration. The neutron flux was determined by irradiation of 99.999% pure aluminium foil (44.3 mg, 7 mm diameter and 1mm thickness) wrapped in cadmium for 10 minutes and measuring the activity of ^{24}Na produced via $^{27}Al(n,\alpha)^{24}Na$.

By means of the neutron activation equation and its parameters, such as content of aluminium, nuclear parameters of the reaction above mentioned and the counting rate obtained for ^{24}Na, the neutron flux produced during the irradiation was calculated. This value (ϕ_m) was related to the medium counting of neutrons C_m registered in the BF_3 detector, being obtained the value of $\phi_m/C_m=3.34 \times 10^4$ n cm^{-2} per counting of the BF_3 detector, with a error of 3.2%[4].

Reference material. Milk (A-11) from the International Atomic Energy Agency.

Phosphorus Analysis Procedure.

Part I - Conventional Irradiation. Commercial milk and reference material were pressed into pellets (7 mm diameter), weighed (mass varied from 30 to 180 mg) and transferred to polyethylene plastic envelops. These vials with cadmium shielding were irradiated for 5 minutes under a flux of 3×10^7 n cm^{-2} s^{-1}. After a decay time of about 60 seconds, samples were counted in a Ge detector for 5 minutes, and the photopeak count rate of the 1778.8 keV line of the ^{28}Al was evaluated by the Maestro II (ORTEC) software.

The neutron counting spectrum of the BF_3 detector obtained during the irradiation period was divided in small time intervals (10 seconds). By using the counting registered in each one of these intervals (C_ℓ), and the value ϕ_m/C_m obtained in the BF_3 calibration, it was possible to calculate the neutron flux of each interval (ϕ_ℓ), by the equation (1).

$$\phi_\ell = \frac{C_\ell}{C_m}\phi_m \qquad (1)$$

where:

ϕ_ℓ = neutron flux at the l interval.

C_ℓ = medium counting at the ℓ interval.

$\frac{\phi_m}{C_m}$ = 3.34×10^4 n cm^{-2} per counting of the BF_3 detector.

The concentration of phosphorus (F) was determined using the following relation:

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$$F = \frac{C_{obs}\,\lambda M}{N\,m\,\sigma\,f\,\varepsilon\,f_\gamma\left(1-e^{-\lambda t_i}\right)\left(1-e^{-\lambda t_c}\right)\sum_{\ell=1}^{n}\phi_\ell e^{-\lambda t_{e\ell}}} \qquad (2)$$

where:

C_{obs} = Total number of counts under the photopeak;

λ = decay constant;

M = atomic weight;

N = Avogadro's number;

m = mass of the irradiated element;

σ = cross section of the reaction;

f = isotopic abundance;

ε = detector efficiency;

f_γ = absolute transition probability by gamma decay;

t_i = irradiation time;

t_c = counting time, and

$t_{e\ell}$ = waiting time between the end of irradiation of the interval ℓ and begining of the counting at the gamma system.

Blank Analysis. Samples of blank consisted of polyethylene plastics were irradiated and counted at the same conditions for phosphorus analysis. The value of phosphorus found by means of equation 2 was discounted from the level of phosphorus determined at the different irradiated samples.

Part II - Cyclic Irradiation. The sample preparation and the procedure adopted for the irradiation were the same described in the part I.

The cycle irradiation was defined as:

t_i - irradiation time, 5 minutes;

t_e - waiting time, 2 minutes;

t_c - counting time, 5 minutes;

t_r - return time of the sample to the irradiation for the next cycle, 2 minutes.

T = the total time of the cycle irradiation, where;

$T = t_i + t_e + t_c + t_r$.

By the Equation (2), the counting obtained at the end of the first irradiation cycle is:

$$C_{obs_1} = k\sum_{\ell=1}^{n}(\phi_1)_\ell\, e^{-\lambda t_{e\ell}} \qquad (3)$$

where:

$$k = \frac{N\,m\,\sigma\,f\,F\,\varepsilon\,f_\gamma\left(1-e^{-\lambda t_i}\right)\left(1-e^{-\lambda t_c}\right)}{\lambda M} \qquad (4)$$

For the second irradiation cycle;

$$C_{obs_2} = k\left[\sum_{\ell=1}^{n}(\phi_2)_\ell\, e^{-\lambda t_{e\ell}} + \left(\sum_{\ell=1}^{n}(\phi_1)_\ell\, e^{-\lambda t_{e\ell}}\right)e^{-\lambda T}\right] \qquad (5)$$

For the third irradiation cycle;

$$C_{obs_3} = k\left[\sum_{\ell=1}^{n}(\phi_3)_\ell e^{-\lambda t_{e\ell}} + \left(\sum_{\ell=1}^{n}(\phi_2)_\ell e^{-\lambda t_{e\ell}}\right)e^{-\lambda T} + \left(\sum_{\ell=1}^{n}(\phi_1)_\ell e^{-\lambda t_{e\ell}}\right)e^{-\lambda 2T}\right] \qquad (6)$$

For the mth irradiation cycle, the sum of the countings at every cycle, C_{obs_t} is:

$$C_{obs_t} = k\Bigg\{\sum_{\ell=1}^{n}(\phi_1)_\ell\, e^{-\lambda t_{e\ell}} + \left[\sum_{\ell=1}^{n}(\phi_2)_\ell\, e^{-\lambda t_{e\ell}} + \left(\sum_{\ell=1}^{n}(\phi_1)_\ell\, e^{-\lambda t_{e\ell}}\right)e^{-\lambda T}\right] + \\ + \left[\sum_{\ell=1}^{n}(\phi_3)_\ell e^{-\lambda t_{e\ell}} + \left(\sum_{\ell=1}^{n}(\phi_2)_\ell e^{-\lambda t_{e\ell}}\right)e^{-\lambda T} + \left(\sum_{\ell=1}^{n}(\phi_1)_\ell e^{-\lambda t_{e\ell}}\right)e^{-\lambda 2T}\right] + \ldots\Bigg\} \qquad (7)$$

From 7,

$$C_{obs_t} = k\,\Phi \qquad (8)$$

where;

$$\Phi=\left\{\sum_{i=1}^{n}(\phi_1)_i\, e^{-\lambda t_{ri}}+\left[\sum_{i=1}^{n}(\phi_2)_i\, e^{-\lambda t_{ri}}+\left(\sum_{i=1}^{n}(\phi_1)_i\, e^{-\lambda t_{ri}}\right)e^{-\lambda T}\right]+\right. \tag{9}$$

Therefore, we obtain the concentration of phosphorus F, evaluating the following relation.

$$F=\frac{\lambda M C_{obs_t}}{N m \sigma f \varepsilon f_\gamma\left(1-e^{-\lambda t_i}\right)\left(1-e^{-\lambda t_c}\right)\Phi} \tag{10}$$

RESULTS

Table 1 shows the results of phosphorus analysis by conventional irradiation.

TABLE 1. Phosphorus Percentage in Milk

Comercial Milk				A-11 Milk	
mass (g)	% P	mass (g)	% P	mass (g)	% P
0.17893	0.7 ± 0.1	0.15788	0.7 ± 0.1	0.12210	0.9 ± 0.1
0.07952	0.7 ± 0.1	0.03441	0.8 ± 0.1	0.12210	0.9 ± 0.1
0.07163	0.8 ± 0.1	0.05686	0.8 ± 0.1	0.12210	1.0 ± 0.2
0.11330	0.7 ± 0.1	0.10378	0.6 ± 0.1	0.12210	0.9 ± 0.1
Mean value	0.7 ± 0.1			Mean value	0.9 ± 0.1
				Certified value	0.910 ± 0.102

By using a cyclic irradiation, the milk sample was irradiated by 5 cycles, being obtained the medium value of (1.0 ± 0.1)% of phosphorus in the milk A-11.

DISCUSSION

Phosphorus analysis in milk (A-11) by conventional and cyclic irradiation presented the medium values of (0.9 ± 0.1)% and (1.0 ± 0.1)%, respectively, these values are in good agreement to the certified value, (0.910 ± 0.102)%. The concentration of phosphorus in commercial milk is lower, P = (0.7 ± 0.1)%.

Results obtained in the cyclic irradiation showed that there is an improvement in the counting statistics as well as in the detection limits. The detection limits calculated by the Currie's criterion[5], were of 0.12 mg and 0.04 mg per 100 mg of sample irradiated, repectively.

The results of the analysis presented errors of about 12%, due to the errors associated to the published values for data nuclear, mainly for cross-sections. In this work, the errors of detector efficiency and counting rates were of 4%.

The phosphorus determination by reactor leads to the formation of other gamma or beta emitter radionuclides. So, the analysis methods require a radiochemical separation of phosphorus, as ammonium phosphomolybdate or a decay time of the interferences, specially.

These interferences can be avoided by activation with 14 MeV neutrons produced by a Van de Graaff accelerator. The very low cross sections for 14 MeV neutrons for the majority of the elements and the neutrons sharp energy spectrum allow us to obtain the gamma spectrum in the milk irradiation, free of interference on the photopeak of ^{28}Al.

The only possible radionuclide interfering could be Si by the $^{28}Si(n,p)^{28}Al$ reaction. But, silicium is present in the milk in a quantity very small (3.4 µg per 100 mg of sample) to cause interference.

Activation analysis of milk by 14 MeV neutrons is a useful technique for the phosphorus determination. The instrumental method is rapid, simple, tedious chemical separation or a decay time are not required.

The normalization method of the neutron flux here employed gives an advantage that fluctuation of the neutron flux during the irradiation does not effect the results. These use of flux monitor in every irradiation is not required. It can be applied to routinely analysis of phosphorus in biological samples.

REFERENCES

[1] Irigaray, J. L.; Capelani, J. C.; Chabard, J. L. **Dosage par neutrons rapides des elementes P, Ca et N dans une biopse osseuse avant une analyse histologique**. In: International Symposium On Nuclear Activation Thecniques In Life Sciences, 22 - 26 May, 1978, Vienna. Proceedings... Vienna: IAEA, p. 433 - 445, 1979.

[2] Hoste, J.; Beek, J. O.; Gijbels, R.; Adams, F.; Winkel, P. V.; Soete, D. **Instrumental and radiochemical activation analysis.**: CRC, London, 1971.

[3] Kawade, K.; Ezuka, M.; Yamamoto, H.; Sugioka, K.; Katoh, T. **Efficiency calibration of Ge(Li) detector at short source-to-detector distance**. Nucl. Instr. Methods, v. 190, p. 101-106, 1981.

[4] Berretta, J. R.; Madi F°, T. **Calibração de um detector BF_3 para monitoração de fluxo de nêutrons de um acelerador tipo Van de Graaff**. In: Congresso Geral De Energia Nuclear, 5., 28 Agosto - 02 Setembro, 1994, Rio de Janeiro. Anais... Rio de Janeiro: ABEN, v. 2, p. 673 - 675, 1994.

[5] Curie, L. A. **Limits for qualitative detection and quantitative determination. Aplication to radiochemistry**. Anal. Chem., v. 4, n. 3, p. 586 - 593, 1968.

RESUMO

Este trabalho teve como objetivo a determinação do teor de fósforo em amostras de leite em pó, usando nêutrons de 14 MeV gerados por um acelerador do tipo Van de Graaff. Foram usadas as técnicas de irradiação cíclica e convencional. Em ambos os casos a variação do fluxo neutronico caracteristica deste tipo de irradiação foi acompanhado por um detector do tipo BF_3. Equações matemáticas foram aplicadas para a normalização das taxas de contagens. Resultados para a análise de fósforo em amostras referência da AIEA (Agência Internacional de Energia Atômica) A-11 foram; $(0{,}9 \pm 0{,}1)\%$ pela técnica de irradiação convencional e de $(1{,}0 \pm 0{,}1)\%$ pela técnica de irradiação cíclica. Os limites de detecção foram de 0,12 mg e 0,04 mg respectivamente em 100 mg de amostra analisada. Amostras de leite comercial também foram analisadas.