INAA OF RM IAEA–155 WHEY POWDER

Peng Lixin (彭立新) and Tian Weizhi (田伟之)
(China Institute of Atomic Energy, Beijing 102413, China)

(Received September 1992)

ABSTRACT

An IAEA biological RM IAEA–155 whey powder was analysed for phosphorus, as well as other 24 elements by INAA. The bremsstrahlung photons produced by ^{32}P is measured by a HpGe spectrometer. The interferences involved in P determination were comprehensively studied and this method was also applied to the determinations of P in several established biological NBS SRMs and proved to be reliable for a wide range of P contents in biological samples.

Keywords: Bremsstrahlung measurement Phosphorus determination NAA Biological samples Standard reference materials

1 INTRODUCTION

The determinations of P in biological samples were carried out with neutron activation analysis (NAA) through $^{31}P(n,\gamma)^{32}P$ reaction followed by radiochemical separation and counting for β activity produced by ^{32}P during the early 60's. Since chemical separation is quite tedious, time–consuming and destructive, attention has recently been focused on instrumental NAA (INAA) method. In a recent study, Bajo *et al*[1] suggested measurement of bremsstrahlung from ^{32}P by using a well–type NaI(Tl) detector. However, it is our feeling that more accurate results may be obtained by using Ge detector and comprehensive analysis of the spectral interferences. In present work phosphorus in RM IAEA–155 whey powder was for the first time determined by measurement of bremsstrahlung produced by ^{32}P using Ge γ–ray spectroscopy. Phosphorus contents in some established standard reference materials (SRMs) were also determined to confirm the reliability of the technique.

2 EXPERIMENTAL

2.1 Standards and quality assurance samples

The high purity reagent $Na_3PO_4 \cdot 12H_2O$ was used for preparing chemical standard. The following SRMs were chosen as multielemental standards and/or quality assurance samples: NBS SRM1572, NBS SRM1577, NBS SRM1632a, NBS SRM1633a and SRM GSD-12.

The interference standards such as Sc, Fe, Co, Zn, Rb, S[$(NH_4)_2SO_4$], Cl(NaCl) and Ca($CaCO_3$) were irradiated together with samples as for correcting the potential interferences for phosphorus determinations in whey powder IAEA-155 and other SRMs.

2.2 Irradiation and counting

The irradiations were performed on the HWRR in CIAE. Thermal neutron fluxes are 3×10^{13} $ncm^{-2}s^{-1}$ for long irradiation and 1×10^{13} $ncm^{-2}s^{-1}$ for short one.

The countings were carried out with a HpGe detector (1.9 keV, 2.6 %), a Canberra S-40 MCA and a PDP-11/34A computer.

2.3 Supplementary measurements for interference corrections in phosphorus determinations

A count in an integral energy range, Bc(100—150 keV in this work), was used as a measure of ^{32}P bremsstrahlung, based on optimal ratio of ^{32}P/interference contributions. Bc for all the interference standards for phosphorus determinations, as well as for whey powder samples and phosphorus standards were recorded for interference corrections.

3 RESULTS AND DISCUSSION

3.1 Results

Analytical results for whey powder IAEA-155, along with the evaluation of IAEA[2,3] are given in Table 1.

Table 1

Analytical results of Whey Powder IAEA—155

Element	Unit	This work*	IAEA evaluation	Element	Unit	This work*	IAEA evaluation
Al	μg/g	42.9±7.4 (5)	* 36.4±19.6	Na	mg/g	15.9±0.1 (6)	15.8±0.6
Br	μg/g	42.6±0.6 (6)	39.1±3.0	P	mg/g	16.3±0.6 (6)	16.2±0.8
Ca	mg/g	39.7±0.8 (6)	* 35.5±5.8	Rb	μg/g	45.8±1.2 (6)	39.2±2.8
Cl	mg/g	66.2±1.8 (6)	69.2±3.3	S* *	mg/g	5.0±0.6 (1)	
Co	ng/g	59.7±4.4 (6)	42.7±13.4	Sb	ng/g	6.00±0.28 (6)	
Cr	ng/g	590±68 (6)	590.0±80.0	Sc	ng/g	26.1±0.4 (6)	28.0±7.0
Cs	ng/g	88.0±3.0 (6)	86.0±16.0	Se	ng/g	61.9±1.7 (6)	64.0±13.0
Eu	ng/g	7.38±0.78 (6)		Sm	ng/g	30.4±2.4 (4)	
Fe	μg/g	69.5±2.2 (6)	* 61.7±13.2	Sr	μg/g	12.7±0.4 (4)	* 10.1±5.0
K	mg/g	47.2±1.0 (6)	* 40.9±7.4	Ta	ng/g	1.89±0.28 (6)	
La	ng/g	246.0±16.0 (6)		Tb	ng/g	6.44±0.70 (6)	
Mg	mg/g	3.12±0.52 (6)	3.19±0.13	Th	ng/g	3.58±0.24 (3)	
Mn	μg/g	9.62±0.74 (6)	9.30±0.52	Zn	μg/g	35.4±0.4 (6)	34.3±1.5

Numbers in parentheses refer to the number of individual values represented in the mean * IAEA preliminary evaluation * * Measurement by X-ray fluorescence

The results for phosphorus and other 24 elements in Table 1 show in good agreement with values recommended by IAEA within error limits at a 95 % level of confidence except for Rb.

3.2 Interferences

The measurement of Al through $^{27}Al(n,\gamma)^{28}Al$ suffered an interference from the fast neutron reaction $^{31}P(n,\alpha)^{28}Al$. This was corrected from the phosphorus content in this material, 16.3 mg/g and an interference factor of 3.4×10^{-4} based on the calculation[3]. The apparent and actual Al concentrations are 48.4 ± 3.7 μg/g and 42.9 ± 3.7 μg/g, respectively.

The determination of phosphorus is carried out through $^{31}P(n,\gamma)^{32}P$ reaction, which only has a pure β nuclide (^{32}P) as an indicator. Interferences involved in phosphorus determination by INAA based on Ge γ-spectroscopy can be divided into four categories.

a. Natural background Bc(bg)–subtracted directly.

b. β^-–γ emitters coexisted in samples when the spectra for phosphorus determination were taken. When phosphorus was measured after 28 d decay, the major γ emitters existed in IAEA–155 samples were ^{46}Sc, ^{59}Fe, ^{60}Co, ^{65}Zn, ^{86}Rb, ^{134}Cs and ^{47}Sc (from ^{47}Ca). Bremsstrahlung photons from β^- and/or Compton continuum from γ-ray of these nuclides will contribute to Bc. Factor F_i ($=Bc^s(i)/Ap^s(i)$) for each of the above mentioned seven pure nuclides produced by coirradiated interference standards was separately measured with $Bc^s(i)$ being integrated counts in the energy region of 100—150 keV and $Ap^s(i)$ being an analytical γ-peak count for nuclide i. The superscript s stands for the interference standards. Relevant parameters for the seven nuclides are listed in Table 2.

c. Pure β^- emitters other than ^{32}P: All the pure β^- emitters produced by reactor neutrons are listed in Table 3. An analysis shows that significant interferences can be given only by S($^{33}S(n,p)^{33}P$ and $^{34}S(n,\gamma)^{35}S$, Cl($^{35}Cl(n,p)^{35}S$, and Ca($^{44}Ca(n,\gamma)^{45}Ca$).

Table 2

Relevant nuclear parameters for interfering emitters[4]

Isotope	$T_{1/2}$	E_β max / MeV	$E\gamma$ / MeV	Isotope	$T_{1/2}$	E_β max / MeV	$E\gamma$ / MeV
$^{47}Ca(^{47}Sc)$	4.7 d (3.43 d)	2.06	1.297 (0.159)	^{65}Zn	245 d	–	1.115
^{46}Sc	84 d	0.36	0.889, 1.120	^{86}Rb	18.66 d	1.82	1.076
^{59}Fe	45.1 d	0.46	1.099, 1.297	^{134}Cs	2.07 y	–	0.604, 0.795
^{60}Co	5.24 y	0.31	1.173, 1.332				

Specific counting rates $Bc^s(S)$ and $Bc^s(Cl)$ were obtained by measuring interference standards S and Cl. Interference factors F_j can be calcualted by $F_j=Bc^s(j)/Bc^s(P)$ with *j* being S or Cl and $Bc^s(P)$ being specific Bc^s of phosphorus, Interference from Ca has already been calculated in b.

Table 3

Pure β^- emitters produced by reactor neutron reactions[4,5]

Reaction	θ* / %	$T_{1/2}$	σ_0	I	E_{β}max / MeV
$^{2}H(n,\gamma)^{3}H$	0.015	12.35 y	0.53 mb	0.23 mb	0.0186
$^{6}Li(n,\alpha)^{3}H$	7.5	12.35 y	940 b	425 b	0.0186
$^{9}Be(n,\gamma)^{10}Be$	100	1.6×10^{6} y	9.2 mb	4 mb	0.555
$^{10}B(n,p)^{10}Be$	19.8	1.6×10^{6} y	0.18 b	—	0.555
$^{13}C(n,\gamma)^{14}C$	1.11	5736 y	0.9 mb	1.3 mb	0.156
$^{14}N(n,p)^{14}C$	99.64	5736 y	1.81 b	870 mb	0.156
$^{17}O(n,\alpha)^{14}C$	0.039	5736 y	235 mb	105 mb	0.156
$^{31}P(n,\gamma)^{32}P$	100	14.28 d	180 mb	80 mb	1.71
$^{32}S(n,p)^{32}P$	95	14.28 d	69 mb	—	1.71
$^{35}Cl(n,\alpha)^{32}P$	75.77	14.28 d	80 μb**	—	1.71
$^{35}Cl(n,\alpha)^{32}P$	75.77	14.28 d	8.8 μb	—	1.71
$^{33}S(n,p)^{33}P$	0.75	75.3 d	2 mb**	—	0.250
$^{33}S(n,p)^{33}P$	0.75	75.3 d	58 mb	—	0.250
$^{34}S(n,\gamma)^{35}S$	4.2	87.2 d	240 mb	—	0.167
$^{35}Cl(n,p)^{35}S$	75.77	87.2 d	52 mb**	—	0.167
$^{35}Cl(n,p)^{35}S$	75.77	87.2 d	490 mb	369 mb	0.167
$^{35}Cl(n,\gamma)^{36}Cl$	75.77	3.0×10^{5} y	43 b	17 b	0.71
$^{38}Ar(n,\gamma)^{39}Ar$	0.063	34.8 d	0.8 b	0.4 b	0.565
$^{44}Ca(n,\gamma)^{45}Ca$	2.08	163 d	1.0 b	560 mb	0.258
$^{45}Sc(n,p)^{45}Ca$	100	163 d	22 mb	—	0.258
$^{43}Ti(n,\alpha)^{45}Ca$	73.7	163 d	34 mb	—	0.258
$^{56}Fe(n,2n)^{55}Fe$	91.7	2.7 y	68 μb		
$^{62}Ni(n,\gamma)^{63}Ni$	3.66	100 y	14.2 b	6.8 b	0.066
$^{64}Ni(n,2n)^{63}Ni$	1.08	100 y	360 μb	—	0.066
$^{63}Cu(n,p)^{63}Ni$	69.1	100 y	6.3 mb	—	0.066
$^{66}Zn(n,\alpha)^{63}Ni$	27.8	100 y	860 μb	—	0.066
$^{78}Se(n,\gamma)^{79}Se$	23.5	6.5×10^{4} y	430 mb	4.7 b	0.160
$^{92}Zr(n,\gamma)^{93}Zr$	17.11	1.5×10^{6} y	260 mb	540 mb	0.060
$^{106}Pd(n,\gamma)^{107}Pd$	27.33	6.5×10^{6} y	300 mb	5.73 b	0.040
$^{120}Sn(n,\gamma)^{121}Sn$	32.85	26.8h	140 mb	—	0.383
$^{142}Ce(n,\gamma)^{143}Ce^{\#}$	11.07	33.0 h	950 mb	—	0.932
$^{143}Nd(n,p)^{143}Pr$	12.17	13.58 d	17 μb	—	0.932
$^{146}Nd(n,\alpha)^{143}Ce^{\#}$	17.22	33.0 h	6 μb	—	0.932
$^{205}Tl(n,\gamma)^{206}Ti$	70.5	4.2 min	100 mb	700 mb	1.53
$^{208}Pb(n,\gamma)^{209}Pb$	52.4	3.31h	487 μb	10 mb	0.645
$^{209}Bi(n,\gamma)^{210}Bi$	100	5.01 d	33 mb	—	1.16

* Abundance of target isotope ** Reaction induced by thermal neutrons # ^{143}Ce—^{143}Pr (13.58 d)

d. ^{32}P produced by elements other than P via either reactor fast or thermal neutrons.

As shown in Table 3, reactions of this category are $^{32}S(n,p)$ and $^{35}Cl(n,\alpha)$. Contributions from these two reactions have already been included in considerations in c.

Net phosphorus contributions to Bc can thus be calculated as

$$Bc = Bc(app) - \Sigma^{n}_{i=1} F_i \times Ap(i) - \Sigma^{n}_{j=1} Bc^{s}(j) \times W(j)$$

Where Bc(app) is gross counts of 100—150 keV energy region in γ-ray spectra of IAEA-155 after subtracting Bc(bg), Ap(i) is γ-peak count for each of ^{46}Sc, ^{59}Fe, ^{60}Co, ^{65}Zn, ^{86}Rb, ^{134}Cs and ^{47}Sc in IAEA-155 γ-ray spectrum, $W(j)$ is weights of elements S or Cl in IAEA-155 sample.

Interferences from all kinds of contributions are summarized in Table 4.

$$C_P(app) = Bc(app)/(Bc(P)W) = 17.1 \pm 0.6 \text{ mg/g}$$

the corrected P concentration

$$C_P = C_P(app) - 4.5\% \, C_P(app) = 16.3 \pm 0.6 \text{ mg/g}$$

Table 4

Summary of interference contributions to P determination

Interfering elements	Ca	Sc	Fe	Co	Zn	Rb	Cs	S	Cl	Total
E_γ / keV	159	889	1099	1173	1115	1076	604			
F_i	0.555	0.634	0.768	0.751	0.573	1.55	0.784			
F_j								0.012	0.0055	
[Bc (interfer.)/ Bc (app)] / %	0.56	0.16	0.03	0.02	0.29	0.88	0.06	0.35	2.15	4.5

3.3 Confirmation for P determination

The activated IAEA-155 samples together with standard $Na_3PO_4 \cdot 12H_2O$ were measured at the same geometry for 12 times over a period of 85 days. The equations for interference-corrected counts Bc(whey) and Bc^s as functions of time have been established as:

Whey powder $\ln Bc(t) = -0.04814t + 7.81773$

$Na_3PO_4 \cdot 12H_2O$ $\ln Bc(t) = -0.04859t + 7.75096$

where, t is the decay time of the nuclide ^{32}P in day and then $T_{1/2}$(whey powder) = 14.39 d, $T_{1/2}(Na_3PO_4 \cdot 12H_2O) = 14.26$ d

The half-lives were obtained by least square fitting technique for IAEA-155 sample and phosphorus standard to be 14.39 d and 14.26 d, respectively. The excellent agreement between the two and the literature value 14.28 d verifies the reliability of the whole procedure.

The quality of the method for phosphorus determination is further assured by determining phosphorus in several established SRMs as shown in Table 5.

3.4 Conclusion

a. Ge γ- ray spectrometry is a sensitive, accurate and non- destructive method for INAA of phosphorus, which only has a pure β emitter ^{32}P as an indicator.

Table 5

Phosphorus concentrations in NBS SRMs

Sample	Unit	This work	NBS certification[6]
1577	μg / g	10500 ± 300	10500 ± 1600
1570	μg / g	5470 ± 200	5500 ± 200
1571	μg / g	2060 ± 90	2100 ± 100
1572	μg / g	1390 ± 70	1300 ± 195

b. When bremsstrahlung counts are used as a measure of phosphorus content, comprehensive considerations should be taken on interferences of Compton contributions from all the coexisting γ- rays, bremsstrahlung photon contributions from all the coexisting β- γ and pure β^- emitters other than ^{32}P, and ^{32}P produced by elements other than phosphorus.

c. While the interference factors for individual interference are dependent of irradiation and/or counting conditions, they are reasonably constant for a certain lab (usually use irradiation channels with similar Φ_f/Φ_{th} ratios and the same counting instruments with the same energy response). Therefore, for a given lab, these factors can be used (directly or after a calculation) once for all, especially when interference contributions are minor.

d. As shown in Table 5, the present method can be used for accurate determination of phosphorus with concentration greater than 1500 μg/g for biological samples.

REFERENCES

1 Bajo S, Wyttenbach A. Talanta, 1988; 35:747
2 IAEA, AQCS, 1991, p.24
3 Tian Weizhi, Zhang Shuxin. J Nucl Radiochem (in Chinese), 1989; 11:84
4 Erdtmann G. Neutron activation tables. Weinheim:Verlay chemie, 1976; 1—146
5 Reus U. Westmeier. Atomic Data and Nucl Data Tables, 1983; 29:1—406
6 Gladney E S. Analytica Chimica Acta, 1980; 118:385