

DETERMINATION OF Al, Si AND P IN CERTIFIED REFERENCE MATERIALS BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

Neutron analysis activation is not commonly used for aluminum, phosphorus and silicon determination, due to the difficulty to obtain reliable results. In this study, Al was determined by measuring ^{28}Al and the contribution of P and Si due to ^{28}Al formed in $^{31}\text{P}(n,\alpha)^{28}\text{Al}$ and $^{28}\text{Si}(n,p)^{28}\text{Al}$ reactions were corrected using correction factors determined experimentally. Phosphorus was determined by measuring ^{32}P (pure beta emitter) formed in reaction $^{31}\text{P}(n,\gamma)^{32}\text{P}$. Silicon was determined by epithermal neutron analysis activation (ENAA) and measuring ^{29}Al radionuclide formed in $^{29}\text{Si}(n,p)^{29}\text{Al}$ reaction. Aliquots of certified reference materials (CRMs) and synthetic standards of the elements were irradiated together, using the pneumatic transfer station of IEA-R1 nuclear research reactor. Results obtained for biological and geological CRMs showed good precision and accuracy with $|Z\text{-score}| < 2$ for Al, P and Si determinations. The detection limits for Al, P and Si determinations CRMs were also evaluated. Results obtained in this study demonstrated the viability of applying INAA procedures in the determination of Al, P and Si.

1. INTRODUCTION

Certified reference materials (CRMs) are frequently analyzed to validate analytical procedures, to ensure the quality of the results and to have documentation with the values of uncertainties. So the use of CRMs for quality control is recommended and required to demonstrate the reliability of the results. In this study Al, P and Si were analyzed in CRMs for quality control of their results by applying the method of instrumental neutron activation analysis (INAA).

Instrumental neutron analysis activation (INAA) is a method with several advantages such as accuracy of results, multielementar analysis and high sensitivity. However, the elements aluminum, phosphorus and silicon are not commonly determined by this method, due to the difficulty to obtain reliable results mainly because of problem of nuclear reaction interferences.

Aluminum is a ubiquitous element and due to its abundance in the environment, a serious contamination problem may occur in sampling and chemical treatment process. Several analytical methods can be used for Al determination such as atomic absorption spectrometry [1], X-ray fluorescence spectrometry [2], spectrofluorimetric method [3] and in some cases these methods require sample dissolution that can increase the probability of contamination. In case of INAA, Al determination presents the problems of P and Si nuclear reaction interferences. Aluminum is determined by measuring ^{28}Al formed in $^{27}\text{Al}(n,\gamma)^{28}\text{Al}$ reaction,

the same radioisotope formed in $^{31}\text{P}(n,\alpha)^{28}\text{Al}$ and $^{28}\text{Si}(n,p)^{28}\text{Al}$ reactions. In Table 1 are presented the radionuclides of interest of this study.

The determination of P is of great interest in several kinds of matrices since it is an essential element for life. This element, combined with nitrogen and potassium, is an important nutrient for plants, mainly in the development. In INAA, P is not determined by gamma spectrometry. An alternative method of determination of P by INAA is carried out bremsstrahlung measurement or beta counting.

Silicon is the second most abundant crustal element and its determinations are of great importance for environmental and geological researches [4]. For Si determination by INAA there are three stable isotopes ^{28}Si , ^{29}Si and ^{30}Si that can be activated by neutrons. In the case of Si determination by measuring ^{28}Al formed in the reaction $^{28}\text{Si}(n,p)^{28}\text{Al}$ there is interference of Al that also forms ^{28}Al . The determination of Si by measuring ^{31}Si depends on the concentration of this element in the sample, due to its low isotopic abundance of 3.18 %. Silicon can be also determined by epithermal neutron activation analysis (ENAA) by measurement of ^{29}Al formed in the reaction $^{29}\text{Si}(n,p)^{29}\text{Al}$.

Within this context the objective of this study was to determine Al, P and Si in certified reference materials by INAA in order to evaluate the accuracy and precision of their results.

Table 1: Characteristics of Al, P and Si radionuclides [5]

Element	Reaction	Isotopic abundance (%)	Cross section (mb)	γ -ray energy (keV)	Half-life
Al	$^{27}\text{Al}(n,\gamma)^{28}\text{Al}$	100	226	1,778.99	2.24 min
P	$^{31}\text{P}(n,\gamma)^{32}\text{P}$	100	180	β^- , 1710	14.28 d
P	$^{31}\text{P}(n,p)^{31}\text{Si}$	100	-	1,266.20	2.62 h
P	$^{31}\text{P}(n,\alpha)^{28}\text{Al}$	100	1.9	1,778.99	2.24 min
Si	$^{28}\text{Si}(n,p)^{28}\text{Al}$	92.23	6,4	1,778.99	2.24 min
Si	$^{30}\text{Si}(n,\gamma)^{31}\text{Si}$	3.18	108	1,266.20	2.62 h
Si	$^{29}\text{Si}(n,p)^{29}\text{Al}$	4.67	3.01	1,273.36	6.56 min

2. MATERIALS AND METHODS

2.1. Certified Reference Materials

In this study, the certified reference materials (CRMs) NIST 1515 Apple leaves, NIST 1633b Constituent elements in coal fly ash, NIST 1646a Estuarine sediment, NIST 1566b Oyster tissue, NIST 1573a Tomato leaves and NIST 1570a Trace elements in spinach leaves provided by National Institute of Standards and Technology and CTA-FFA-1 Fine fly ash, INCT-MPH-2 Mixed Polish herbs, INCT-TL-1 Tea leaves, INCT-OBTL-5 Oriental Basma tobacco leaves from Institute of Nuclear Chemistry and Technology were analyzed. The percentage of moisture of these CRMs were determined in order to calculate the element

concentrations on dry basis. For these determinations, an aliquot of each material was dried according to their respective certificates.

2.2. Standards of elements

Certified standard solutions of Al, P and Si from Spex CertiPrep, USA were used to prepare synthetic standards of elements. Aliquots of each solution were pipetted on sheets of Whatman n° 40 and then were dried in a desiccator at room temperature. These sheets were placed in polyethylene bags that were heat-sealed. The reagents ammonium dihydrogen phosphate, Puratronic of 99.998 % purity from Alfa Aesar and metallic silicon of 99.999 % purity from Alfa Aesar were also used as standard for P and Si respectively.

2.3. Neutron Analysis Activation Procedures

2.3.1 Procedure for aluminum determination

The INAA procedure for Al determination consisted on irradiating about 180 mg of each certified reference material weighed in polyethylene bag along with synthetic standard of Al at the IEA-R1 nuclear research reactor. The thermal neutron flux of $1.9 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$, epithermal neutron flux of $5.43 \times 10^{10} \text{ n cm}^{-2} \text{ s}^{-1}$ and fast neutron flux of $3.7 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$ were utilized in the irradiations. The irradiation times varied from 5 to 30 s, depending on the sample. The induced gamma activities of the irradiated sample and standard were measured after about 3 min of decay time for 200 s in a hyperpure Ge detector (Model GC3019) coupled to a Digital Spectrum Processor DSA 1000, both from Canberra. The resolution (FWHM) of the used system was 1.90 keV for the 1332 keV γ -ray of ^{60}Co and, 0.90 keV for the 122 keV γ -ray of ^{57}Co . Spectra were collected and processed using Canberra Genie 2000 Version 3.1 software. Aluminum was identified by gamma ray energy of 1,778.99 keV of ^{28}Al with half-life 2.24 min. The concentration of Al was calculated by comparative method [6].

The radioisotope ^{28}Al is also formed when P and Si are present in the sample, due to interference nuclear reactions $^{31}\text{P} (n,\alpha) ^{28}\text{Al}$ and $^{28}\text{Si} (n,p) ^{28}\text{Al}$. So in order to eliminate the contribution of these interferences, the synthetic standards of P and Si were also irradiated to obtain the interference correction factors.

2.3.2 Determination of interference correction factors of P and Si in the Al determination

The correction factors of interference for P and Si were determined experimentally irradiating the standards of Al and P or Si. The correction factor was calculated using the relation [7]:

$$F = [A_{\text{sp,(n,\gamma)}}]/[A_{\text{sp}}] \quad (1)$$

where F is the correction factor, $A_{\text{sp,(n,\gamma)}}$ is the specific activity of ^{28}Al formed by Al standard, A_{sp} is the specific activity formed by the interfering element, both for the same decay time.

The non-corrected concentration of Al was calculated by comparative method [6] and the corrected concentration of Al was calculated using equation 2.

$$C_{\text{corrected}} = C_{\text{non-corrected}} - [(F_{\text{P}} \times C_{\text{P}}) + (F_{\text{Si}} \times C_{\text{Si}})] \quad (2)$$

where $C_{\text{corrected}}$ is the true concentration of Al, $C_{\text{non-corrected}}$ is the apparent or uncorrected concentration of Al, F_P and F_{Si} are the correction factors for P and Si respectively and C_P and C_{Si} are the concentrations of P and Si respectively in the sample. For the P and Si concentrations the certified values or those determined in this study were used.

2.3.3 Procedure for phosphorus determination

For P determination, aliquots (180 mg) of each CRM and P standard were simultaneously irradiated from 4 min to 1 hour with thermal neutrons flux of $4.4 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. The beta activity measurements were performed after a decay time of 10 days using a Geiger-Müller counter. Phosphorus was determined by measuring ^{32}P radionuclide, pure beta emitter ($E_\beta = 1,710 \text{ keV}$) formed by $^{31}\text{P} (n,\gamma) ^{32}\text{P}$ reaction and this radionuclide was identified determining its half-life of 14.28 d. Samples were also measured by gamma ray spectrometry to check the presence of short-lived gamma ray emitter radionuclides.

2.3.4 Procedure for silicon determination

Silicon was determined in CRMs by epithermal neutron activation analysis by measurement of ^{29}Al formed in $^{29}\text{Si}(n,p)^{29}\text{Al}$ reaction. Synthetic standard of Si and an aliquot of each CRM weighed in polyethylene bag were irradiated inside a cadmium capsule with 1 mm thickness. The irradiation times used were 20 or 60 seconds depending on the sample, at the IEA-R1 nuclear research reactor with epithermal neutron flux $5.43 \times 10^{10} \text{ n cm}^{-2} \text{ s}^{-1}$. The measurements were performed using a gamma ray spectrometer and ^{29}Al were identified by half-life of 6.56 min and gamma ray energy of 1,273.36 keV.

2.4 Treatment of Data

The standardized difference or Z-score value was used to evaluate the precision and accuracy of Al, P and Si results in certified reference materials and it was calculated by using the relation presented by Konieczka and Namiesnik [8]. The detection limit is the lowest concentration of an element that can be detected by a method and this parameter was calculated according to Currie [9].

2.4.1 Contribution rate of interference

The contribution rate (CR) was obtained to evaluate the degree of interferences from P and Si in Al determinations and it was calculated using the following relation:

$$CR = \frac{(C_{\text{Al non-corrected}}) - (C_{\text{Al corrected}})}{C_{\text{Al corrected}}} \times 100 \quad (3)$$

where $C_{\text{Al non-corrected}}$ is the non-corrected Al concentration ; $C_{\text{Al corrected}}$ is the corrected concentration of Al.

3. RESULTS AND DISCUSSION

3.1. Results of Preliminary Experiments

In the preliminary experiments, we verified if the impurities of Al, P and Si in polyethylene bags and filter paper sheets might interfere in determinations of these elements. Polyethylene bags were used for irradiation the samples and standards and the filter paper sheets were used as support for preparing synthetic element standards. Phosphorus and silicon were not detected in these materials. The mean mass of Al in these materials were very low, $(0.14 \pm 0.03) \mu\text{g}$ in each polyethylene bag and $(0.12 \pm 0.02) \mu\text{g}$ in a paper filter sheet, and the quantities of Al in these materials were considered negligible.

3.2. Results of Correction Factors

The mean correction factors obtained for Al determination were of $(2.38 \pm 0.03) \mu\text{g mg}^{-1}$ for P and $(5.29 \pm 0.03) \mu\text{g mg}^{-1}$ for Si, whose results were obtained in 16 irradiations. These values were obtained in different days and periods of day. The interference correction factors depend on the relation between thermal, epithermal and fast neutron flux [10, 11]. So to use accurate correction factor, they were determined for each Al determinations.

3.3. Results of Element Concentrations Obtained in Certified Reference Materials

Results obtained for P and Si are presented in Table 2 and those for Al in Table 3. The results of P and Si (Table 2) were used to calculate the interference contribution of these elements in Al determination.

Table 2: Concentrations of P and Si in certified reference materials

Certified reference materials	M \pm SD (RSD) ^a	Certified values	Z _{score}	Detection limit
Phosphorus concentration ($\mu\text{g g}^{-1}$)				
1566b Oyster tissue	6039 \pm 789 (13.1)	- ^b	-	45
1573a Tomato leaves	2617 \pm 327 (12.4)	2160 \pm 40	1.41	31
1570a Spinach leaves	5443 \pm 319(5.9)	5180 \pm 110	0.81	35
Silicon concentration (%)				
1633b Coal fly ash	22.17 \pm 0.82 (3.7)	23.02 \pm 0.08	-1.04	1.2
FFA-1 Fine fly ash	22.53 \pm 0.22 (1.0)	22.48 \pm 0.92	0.09	1.3
MPH-2 Mixed Polish herbs	2.86 \pm 0.21 (7.3)	- ^b	-	0.3

a. arithmetic mean, standard deviation and relative standard deviation from four determinations; b⁻value not presented in the certificate

In Table 2, P and Si results in CRMs showed good accuracy with $|Z\text{-score}| \leq 1.41$. The relative standard deviations for P results varied from 5.9 to 13.1 % and for Si from 1.0 to 7.3 %, indicating also good precision. The detection limit values presented in this Table are

lower than element concentrations in these materials, indicating that the method is adequate for the analysis this matrices. Concentrations of P showed somewhat higher than the certified values, probably due to contribution of gamma ray and beta activities of radionuclides with long half-lives in the measurements of ^{32}P .

Table 3: Concentrations of Al in certified reference materials. Results in $\mu\text{g g}^{-1}$, unless indicated

Certified Reference Material	Non-corrected concentration of Al		Corrected concentration of Al		Certified values	$\frac{[\text{P}]}{[\text{Al}]}$ ^c	$\frac{[\text{Si}]}{[\text{Al}]}$ ^d	CR ^e %	Detection limit
	$M \pm \text{SD}^{\text{a}}$	Z_{score}	$M \pm \text{SD}$ (RSD %) ^b	Z_{score}					
1633b Coal Fly Ash	$14.84 \pm 0.73, \%$	-0.28	14.71 ± 0.74 (5.0)	-0.45	$15.05 \pm 0.27, \%$	0.015	1.5	0.9	337
1646a Estuarine Sediment	$2.476 \pm 0.038, \%$	4.58	2.266 ± 0.041 (1.8)	-0.74	$2.297 \pm 0.018, \%$	0.012	17.4	9.3	73
FFA-1 Fine Fly Ash	$14.99 \pm 0.22, \%$	0.41	14.86 ± 0.21 (1.4)	-0.035	$14.87 \pm 0.39, \%$	0.005	1.5	0.9	668
MPH-2 Mixed Polish Herbs	798 ± 53	1.67	624 ± 53 (8.5)	-0.60	670 ± 111	3.7	42.7	27.9	11
1515 Apple Leaves	275 ± 21	-0.51	271 ± 20 (7.4)	-0.73	286 ± 9	5.6	- ^f	1.5	2.4
1577b Oyster Tissue	212 ± 9	1.56	192 ± 9 (4.7)	-0.55	197.2 ± 6.0	30.6	-	10.4	17
TL-1 Tea Leaves	2163 ± 126	-0.67	2158 ± 126 (5.8)	-0.70	2290 ± 280	0.8	-	0.2	12
1573a Tomato Leaves	582 ± 27	-0.58	578 ± 27 (4.7)	-0.72	598 ± 12	3.6	-	0.7	16
1570a Spinach Leaves	296 ± 27	-0.51	281 ± 26 (9.3)	-1.09	310 ± 11	16.7	-	5.3	53

a. arithmetic mean and standard deviation from at least four determinations; b. relative standard deviation from at least four determinations; c. ratio between P and Al concentrations; d. ratio between Si and Al concentrations; e. contribution rate; f. Si concentration lower than detection limit

Table 3 are presented the non-corrected and corrected Al concentrations in CRMs, the ratio between concentrations of the interfering elements and of Al and the contribution rates. The relative standard deviations of the results were lower than 10 %, showing good precision of results. The corrected concentrations of Al showed good accuracy with $|Z_{\text{score}}| \leq 1.1$. The detection limits were lower than the obtained concentrations.

The concentrations of Al in CRMs1646a Estuarine Sediment, FFA-1 Fine Fly Ash, MPH-2 Mixed Polish Herbs, 1577b Oyster Tissue were improved after correction, as showed in the Z_{score} values. However, the corrected concentrations are slightly below the certified value, probably caused by the high activity of ^{38}Cl , ^{24}Na and ^{56}Mn that can difficult the detection of ^{28}Al and due to interference caused by Compton effect [12].

The interference contribution rates obtained for 1646a Estuarine Sediment and the MPH-2 Mixed Polish Herbs were high due to their high Si concentrations in relation to Al. In 1577b Oyster Tissue and 1570a Spinach Leaves the high contribution rate was due to the high P concentration. These results indicate the need to evaluate the contribution of P and Si interferences in Al determination.

4. CONCLUSIONS

The results obtained in this study demonstrated that INAA can be applied in Al, P and Si determinations. The relative standard deviation was lower than 13.1 % and the $Z_{\text{score}} < 1.41$, for Al, P and Si. These results were satisfactory, demonstrating that the applied procedure provided reliable results.

Results obtained in this study showed that NAA in Al determination should be used with caution. Contribution from P and Si interference nuclear reactions should to be evaluated depending on the relation between the concentrations of interfering element and Al.

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