STUDY ON INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF ALUMINIUM IN GEOLOGICAL AND BIOLOGICAL REFERENCE MATERIALS

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SUMMARY

The determinations of Al are of great interest in the environmental and biomedical studies as well as in the evaluation of the economic potential in ore prospecting programs. Reliable determinations of this element by instrumental neutron activation analysis (INAA) have been a challenge for several researchers. The major difficulties are the interferences of P and Si that form ^{28}Al, the same radioisotope used in the analysis of Al. The elements Na and Cl can also interfere with the detection of Al, when they are present in large quantities. The detection of Al is often masked by high radio-activities of ^{24}Na and ^{38}Cl. In this work Al was determined in several kinds of biological and geological reference materials and their results indicated a good agreement with the certified values. In some samples, the contribution of P and Si interferences were considered in the Al determination by using correction factors determined experimentally. The detection limits in Al determinations were evaluated. The method is rapid, free of contamination from reagents, precise and can be adopted for routine determinations of this element in biological and geological matrices.

Key words: Neutron activation analysis, Aluminium, Reference materials

INTRODUCTION

Aluminium is ubiquitous in the environment, comprising 8 % of the Earth´s crust. Its position in the periodic table had led suggestions that it is an essential element in the human nutrition but nowadays, there is no conclusive evidence if Al has an essential role in metabolism in organisms of humans and animals.

Therefore, during the last decades, there has been an increased interest in the study of Al biological effects because of the evidence of its systemic toxicity especially in long-term haemodialysis patients causing encephalopathy (dementia), ostelomalacia and anaemia. The effects of Al in Alzheimer's disease as well as on acid rain in environment have also received much attention.

On the other hand Al is an element with important applications in the industry and in the manufacture of several artefacts, electrical equipments, cooking utensils, packaging containers, cosmetics and pharmaceuticals.

Consequently, Al determinations have been carried out in of several kinds of important matrices of the areas of health, environment, industry, nutrition and geology .

Reliable determinations of Al have been a challenge for the analytical chemists since this element present at very low concentrations mainly in biological samples. Because of this environmental abundance of Al, spurious contamination of the samples poses a serious problem in the of Al biological samples, requiring strict attention during the collection or handling of the samples for the determination of this element

Analytical methods that have the requisite sensitivity have been applied to the determinations of Al mainly in biological samples. Atomic emission and atomic absorption spectrometry using a graphite furnace atomiser have been most widely applied to aluminium analysis in biological specimens. Nevertheless, several investigators have applied instrumental neutron activation analysis to determine aluminium since this technique requires minimum manipulation because no chemical separations are performed, hence there may be no or little contamination from reagents.

Although the sensitivity for Al is excellent using the instrumental neutron activation analysis, two interfering reactions must be considered. The radioisotope ^{28}Al with half life of 2.24 min that is produced by the $^{27}Al(n,\gamma)^{28}Al$ reaction when the aluminium is bombarded with thermal neutrons it is also produced by $^{31}P(n, \alpha)^{28}Al$ and $^{28}Si(n, p)^{28}Al$ reactions with fast neutrons. Phosphorus is present in large enough quantities in biological materials that its contribution of ^{28}Al must be corrected. Also prior to irradiation, the Al can be separated chemically from P but the non-destructive advantage of instrumental neutron activation is lost. The interference caused by silicon in most biological materials requires only a small corrections or it can be even be considered negligible, but for geological samples it could be very serious.

Several papers have been presented for the correcting this interference. The techniques to correct these interferences include the separation of aluminium before

irradiation[1-3] and the correction to the apparent ^{28}Al activity from P or Si contribution by using thermal and epithermal neutron activation analysis[4-7].

In the present study these interference contributions of P or Si interference were considered for the determinatios of Al in biological and geological reference materials using interference factors which were experimentally determined. It was also examined the detection of ^{28}Al in the presence of high activities of ^{38}Cl and ^{24}Na with half lives of 37.24 min and 14.96 h, respectively.

EXPERIMENTAL

Standards of elements

Standard of aluminium. Standards of Al to be irradiated with the sample were prepared using two standard solutions of this element. One of standard solution was prepared dissolving 99.0 % purity Al foil from Goodfellow with HNO_3 p.a Merck and then diluting with distilled water. The second Al standard solution utilised was provided from Spex CertiPrep. The synthetic standards of Al (50.150 μg and 800.0 μg) were prepared by pipetting 50 μL of standard solutions onto sheets of Whatman No. 41 filter paper. After drying these sheets at room temperature they were placed into a clean polyethylene bags and irradiated together with the samples.

Standards of phosphorus and silicon. In the case of P, about 30 mg of AlfaAesar 99.998 % purity ammonium dihydrogen phosphate, Puratronic, were weighed directly in polyethylene bags to be used as standard. For Si standard, also about 30 mg of silicon dioxide from Johnson Mathey Chemical Limited was used.

Reference materials analysed.

In order to evaluate the precision and the accuracy of the results the following biological and geological reference materials were analysed: 1515 Apples Leaves, 1572 Citrus Leaves, 1566a Oyster Tissue, 1547 Peach Leaves, 1575 Pine Needles, 1570a Spinach Leaves and 1573a Tomato Leaves from National Institute of Standards and Technology (NIST), USA; CRM 07 Tea Leaves from National Institute for Environmental Studies (NIES), Japan; NBS 120C Florida Phosphate Rock from NIST and the standard rocks W-1, BCR-1 and DST-1 from United States Geological Survey (USGS)

The moisture content in the biological reference materials was ascertained by drying in an oven at 85 °C for about 6 hours. The following values (in %) of weight loss were used for correcting the final results: 6.94 for Apples Leaves, 5.51 for Citrus Leaves, 10.53 for Oyster Tissue, 8.61 for Peach Leaves, 7.73 for Pine Needles, 5.19 for

Spinach Leaves, 7.60 for Tomato Leaves and 5.72 for Tea Leaves. The weight loss by drying was negligible for geological reference materials.

Procedure for INAA

Samples (about 30 mg in the case of geological materials and 150 mg of biological materials) and synthetic standards were heat sealed in polyethylene bags and irradiated at the IEA-R1 research nuclear reactor of the IPEN-CNEN/SP. These irradiations were carried out using pneumatic transfer system facility under thermal neutron flux of 4.6 10^{11} n cm^{-2} s^{-1} and epithermal neutron flux of 1.4 10^{11}n cm^{-2} s^{-1}. The irradiation periods varied from 0.5 to 5 minutes depending on the composition of the reference material. After about 4 minutes, the gamma ray measurements were performed using an EG&G Model GMX20190 hyperpure Ge detector coupled to an EG&G Ortec ACE8K card connected to a personal computer. The resolution (FWHM) of the system was 1.90 keV for the 1332 keV gamma ray of ^{60}Co and 0.87 keV for the 122 keV gamma ray of ^{57}Co. Counting time of 200 seconds was used and the peak of 1778 keV of ^{28}Al was measured. Analyses of gamma spectra were carried out using VISPECT2[8] computer program developed at the Radiochemistry Division and the elemental concentrations were calculated by comparative method.

The interference contribution of P and Si in the determination of Al was experimentally determined. To obtain actual concentration of Al, the interference contributions were obtained by multiplying the amount of P or Si with this interference factor. The interference contribution was then subtracted from the apparent concentration of Al measured.

The interference factors IF were obtained using high purity reagents of P and Si in the simultaneous irradiation used for the corrections. The magnitude of the interference was defined as the ratio of the radioactivity from interesting element to that interfering element.

These IF values were evaluated irradiating the standards of interfering elements P or Si and Al standard with thermal and ephithermal neutrons. A cadmium capsule with 1 mm thickness was used in the case of irradiation with epithermal neutrons.

RESULTS AND DISCUSSION

Table 1 shows the results of interference factors for P and Si corrections obtained in the irradiation with thermal and epithermal neutrons. The magnitude of the se interferences caused by (n,p) and (n,α) reactions depends on the relationship between thermal and epithermal neutron fluxes and also of the relation between the Al and Si and of P.

Table 1. Interference factors of P and Si in the determination of Al

	P		Si
Irradiation	n	IF(μg Al/mg P)	n	IF(μg Al/mg Si)
Thermal	22	2.55 ± 0.13	24	7.21 ± 0.50
Epithermal	7	183.1 ± 14.5	5	253.3 ± 24.5

The interference of Na and Cl with the detection of Al was also examined experimentally by irradiating different masses of interfering elements with Al. When the relations of Na and Al concentrations or of Cl and Al concentrations are higher than 500 it was impossible to analyse Al. The detection of ^{28}Al was masked by high radioactivity of ^{24}Na ($T_{1/2}$ = 14.96 h) and of ^{38}Cl ($T_{1/2}$ = 37.24 min)

Results obtained in the analyses of geological reference materials are presented in Table 2 together with the certified values. The contributions of Si and P were considered for the reference materials DST-1 and NBS-120C, respectively. The magnitude of the interference caused by (n,p) and (n,α) reactions are influenced by the composition of the samples. The standardised differences or z-values[9] obtained for different geological reference materials are in Fig.1. The |Z| values obtained were lower than 3 indicating that the results obtained are within the range of values presented in the certificates at a the significance level of 1 %. These results presents a good precision and agreement between our results and those certified values presented.

Table 3 shows the results obtained in the analyses of biological reference materials and the z-values for Al analysed in biological reference materials are presented in Fig. 2. The contribution of P interference was discounted only in the case of Oyster Tissue material. For other materials this interference was negligible. As it can be seen, these results exhibited a good agreement with the certified values also a good precision. The relative errors were lower than 6.4 % and with relative standard deviations varied from 3.8 to 9.3 %.

The detection limits of Al in the analyses of reference materials were evaluated according to Currie[17] and presented in Table 4. These results indicate the high sensitivity of INAA method in the analyses of Al and the detection limit values are dependent upon the sample composition.

Table 2. Concentrations of Al in geological reference materials obtained by thermal neutron activation analysis.

Results in percentage

This work	Geological reference material				
	W-1	BCR-1	DST-1	NBS-120C	IPT 48
$X \pm s$	7.90 ± 0.55	7.07 ± 0.29	0.19 ± 0.02*	0.71 ± 0.05**	0.0836 ± 0.053
N	6	6	6	6	15
s_r, %	7.0	4.1	10.5	7.0	6.3
E_r, %	0.36	1.82	11.2	3.8	7.0
Certified value (10-12)	7.93 ± 0.14	7.21 ± 0.13	0.17 ± 0.09	0.688 ± 0.021	0.0899± 0.0105
[P] / [Al]	0.0076	0.029	0.0053	21.28	0.107
[Si] / [Al]	2.763	3.838	7.47	3.7	2.33

$X \pm s$ = Mean and standard; s_r = relative standard deviation; E_r = relative error

* - Contribution of Si interference was considered

** - Contribution of P interference was considered

Table 3. Aluminium analyses in biological reference materials. Results are given in $\mu g\ g^{-1}$

Biological reference materials	This work			Ref (13-15)	
	X ± s	s_r %	E_r %	Certified values for [Al]	[P] / [Al]
Apple Leaves	293 ± 19	6.4	0.9	286 ± 9	5.6
Citrus Leaves	92 ± 7	7.2	0.3	92 ± 15	14.1
Oyster Tissue	215 ± 13*	5.9	6.4	202.5 ± 12.5	30.8
Peach Leaves	263 ± 24	9.3	5.7	249 ± 8	5.5
Pine Needles	584 ± 21	3.8	0.5	545 ± 30	2.2
Spinach Leaves	294 ± 27	9.3	5.7	310 ± 11	16.7
Tea Leaves	734 ± 68	9.3	5.0	775 ± 20	-
Tomato Leaves	604 ± 49	8.0	5.0	598 ± 12	3.6

X ± s = Arithmetic mean and standard deviation of six determinations of Al; s_r = relative standard deviation; E_r = relative error

* - Contribution of P interference was discounted

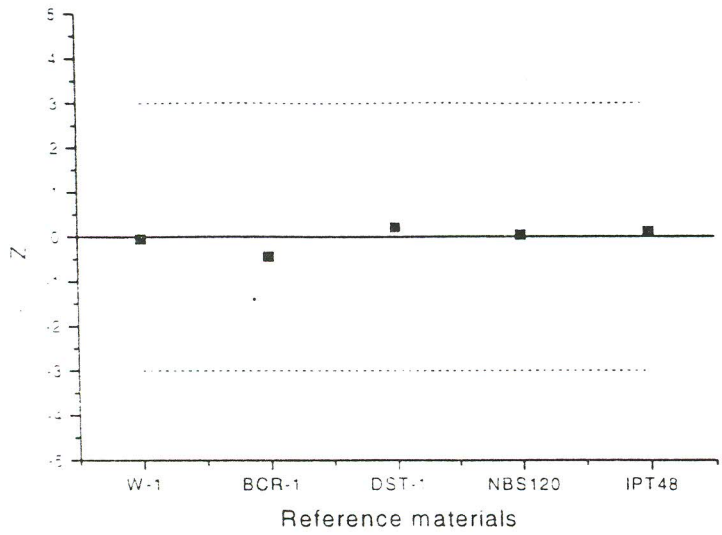

Fig.1. Values of standardised difference (z- values) for Al determinations in geological reference materials

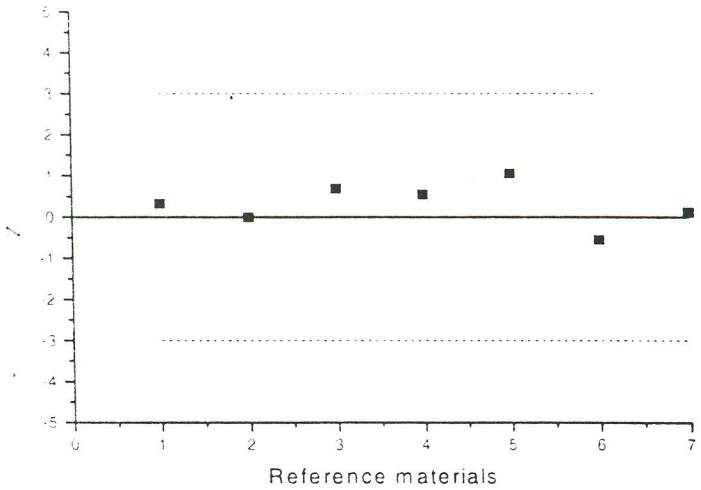

Fig.2. Values of z obtained in Al determinations for biological reference materials: 1- Apples Leaves; 2 – Citrus Leaves; 3 – Oyster Tissue; 4 – Peach Leaves; 5 – Pine Needles; 6 – Spinach Leaves; 7 – Tomato leaves

Table 4. Detection limit values for Al determinations in different reference materials

Reference material	Detection limit, $\mu g\ g^{-1}$	Reference material	Detection limit, $\mu g\ g^{-1}$
W-1	629	Oyster Tissue	19
BCR-1	827	IPT 48	15.4
DST-1	267	Spinach Leaves	7.7
NBS 120C	118	Tea Leaves	6.8
Pine Needles	50.1	Citrus Leaves	2.2
Tomato Leaves	33	Apple Leaves	3.1

CONCLUSIONS

Instrumental neutron activation analysis is one of the most powerful techniques for determining Al since the determination is rapid, free of contaminants, precise, accurate and it can adopted for routine analyses in biological and geological matrices.

Nuclear interferences of P and Si in the determination of Al depend on the relation between the concentrations of the interfering element and Al and if this interference is taken into account, the neutron activation analysis becomes very efficient method for aluminium determination.

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