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Full Length Research Paper

The accuracy of the absolute NAA method based on the analysis of standard reference materials (SRMs)

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The aim of this study was to demonstrate and validate the use of the absolute NAA method, inside the Malaysian nuclear agency (MNA) research reactor, by analyzing the IAEA SRMs; soil-1 and soil-7. The analytical results showed that the deviations between experimental and certified values were mostly less than 10% with Z-score ranging from 0 to 2, and only for few element it exceeds 20%. In general, the results for soil-1 and soil-7 obtained from research reactor at irradiation positions 10, 22, 27 and 31 inside the rotary rack agree reasonably well with the certified values.

Key words: Neutron activation analysis (NAA), absolute NAA method, accuracy, standard reference materials (SRMs), Z-score.

INTRODUCTION

The drawbacks of the relative method have prompted an investigation into what information about neutron flux in the irradiation positions, and about nuclear data, concerning the target and product nuclides, that would be required to calculate element masses directly from the gamma-ray spectrum (Kafala and Macmohon, 1993, 2007). The first systematic methodology investigation of the absolute method was reported Girardi et al. (Girardi et al., 1964). It was found that the uncertainties in nuclear data taken from the literature are major source of systematic errors especially on decay schemes and activation cross sections. The absolute method is based on the determination of nucleides masses by means of activation equation. This method which can offer diminution of the experimental work and elimination of errors due to inhomogeneity of the neutron flux within the irradiation capsule (Girardi et al., 1964), offers several advantages over the relative method in terms of speed, cheapness, versatility and ease of automation, and also offers the possibility of muti-element analysis in one single irradiation (Kafala et al., 2007). Besides that, this technique has been used successfully in many cases and it is a very flexible method which can be used in conjunction with many different reactors and counting systems (Bergerioux et al., 1979). Presently, the nuclear parameters are much more reliable due to improvement in the quality of nuclear data and the development of more reliable monitoring systems and efficient computation facilities. These improvements have made the needed corrections to rekindle this method, by providing many research to develop the NAA absolute method (ST-Pierre et al., 1982). During these days, this absolute method is capable of tackling a large variety of analytical problems when it comes to the multi-element determination in many practical samples.The elemental concentration results obtanied by the absolute NAA experiment were compared to the certified values issued by the international atomic energy agency and the results are consistent, which can reflects the exactitude of this method.The accuracies of soil-1 and soil-7 concentrations were statistically evaluated using Z-score method for comparison between experimental results and certified values (liew, 2010).The uncertainty associated in the measurements in the absolute method is mainly linked to the methodology of calibrating the neutron spectrum, the efficiency of the γ-ray detector and nuclear data. The uncertainties in nuclear data were the major source of systematic errors. However, considerable effort has been made to reduce the uncertainties to below 10%. In addition, detector efficiencies can be estimated to an

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Table 1. The criterion for Z-score.

Z-score rang	Criterion
Z ≤ 2	The results is accepted
2 < Z < 3	The result is inspected and possibly accepted
Z ≥ 3	The result is not accepted

accuracy of approximately 3%. (Kafala et al., 2007).

METHOD OF CALCULATION

Determination of the reaction rate (R)

Considerations concerning the relationship between the mass of an element and measured signal (peak area in the gamma-spectrum), are based primarily on the reaction rate (R) of an (n, γ) reaction type measurement taking place in a thermal nuclear reactor. For the quantitative description of the reaction rate several conventions have been recommended, e.g. Westcott, Stoughton and Halperin, Høgdahl (Bereznai, 1980). According to Høgdahl convention the knowledge of neutron reactor parameters including thermal and epithermal neutron fluxes at rotary racks of reactor is requried to calculate reaction rates in the irradiated samples (liew, 2010). The (n, γ) reaction rate per nucleus is discribed (De Corte, 1987) as follows:

$$R = G_{th}\varphi_{th}\sigma_o + G_e\varphi_e I_o \quad (1)$$

Where G_{th} is a correction factor for thermal neutron self-shielding, φ_{th} is sub-cadmium thermal neutron flux, σ_0 is thermal neutron capture cross section at 2200 m/s, G_e is a correction factor for epithermal neutron self-shielding, φ_e is epithermal neutron flux per unit InE and I_0 is the resonance integral for a 1/E spectrum, defined by the expression that follows:

$$I_0 = \int_{E_{cd}}^{\infty} \frac{\sigma(E)dE}{E}$$

with E_{cd} is effective cadmium cut-off energy (= 0.55eV in standard condition).The resonance integral needs to be modified with an α-deviated from ideal spectrum 1/E to non-ideal $1/E^{1+\alpha}$.

$$I_0(\alpha) = \int_{E_{cd}}^{\infty} \frac{\sigma(E)dE}{E^{1+\alpha}}$$

Therefore in real reactor situation the modified reaction rate can be written as:

$$R = G_{th}\varphi_{th}\sigma_o + G_e\varphi_e I_o(\alpha) \quad (2)$$

Equations 1 and 2 are only valid on condition that the cross section varies proportionally with the inverse of the neutron velocity (v) that is σ (v) α1/v up to ~1.5ev (De Corte, 1987).The mass of the irradiated element in the reactor is characterized by the fluxes φ_{th} and φ_e , for an irradiation time t_{irr} , cooling time t_c and counting time t_m , can be expressed as follows:

$$m = \frac{N_p M}{N_a \theta \gamma R \varepsilon(E) S D C} \quad (3)$$

where N_p is the net photo peak count, M is atomic mass, θ is isotopic abundance, ε(E) is the efficiency of detector at gamma energy E, γ is absolute intensity of gamma- line, $S = 1-\exp(-\lambda t_{irr})$ is saturation factor, $D = \exp(-\lambda t_c)$ is decay correction factor and $C = 1-\exp(-\lambda t_m)$ is correction decay during measurement.

Determination of Z- score

The accuracy of the soil-1 and soil-7 in term of concentration were statistically evaluated using Z-score for comparison between experimental results and certified values. The Z-score value is defined by (liew, 2010):

$$Z = \frac{\left|X_{\exp} - X_{cert}\right|}{\sqrt{\left(\sigma^2_{\exp} + \sigma^2_{cert}\right)}} \quad (4)$$

where X_{exp} and X_{cert} are the experimental and certified value, respectively, σ_{exp} and σ_{cert} are the experimental and certifed uncertainty, respectively. The experimental uncertainty (σ_{exp}) is obtained from Equation 3. The criterion for evaluation Z-score is given in Table1.

Experimental

The neutron activation of soil-1 and soil-7 were carried out at irradiation positions 10, 22, 27 and 31. Approximately 30 mg of each sample was wieghted and irradiated in calibrated position of rotary rack facilities. The samples were sealed in a plastic and enclosed in polyethylene vial. The samples were then irradiated for 1 h. During the first period, after one day from the end of irradiation, nuclides As, La, Mn, Na, Sm, K, Sc and Ga were identified. Others were analysed after one week. A large number of gamma ray spectra were collected for the irradiated soil-1 and soil-7 samples that are placed at 2 cm from the calibrated detector. The samples irradiated at position 22 were measured using Canberra detector, while the rest of the irradiation positions were measured using Ortec detector. The quantitative analysis were carried out for radioisotopes using the most higher energy peaks which, have less interference than lower energy peaks and the statistical error in this case is lower. For each sample, measurement time was 1 h. Concentrations of elements were determined by measuring the

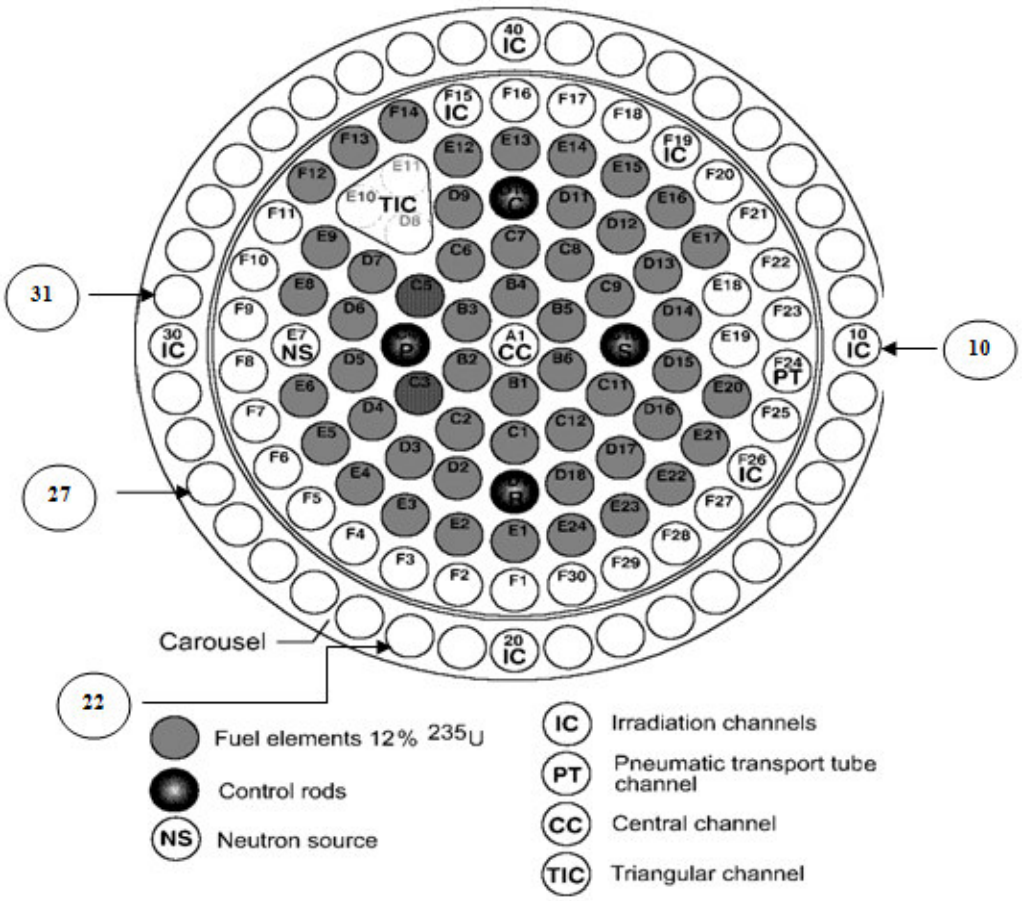

Figure 1. Reactor rotary racks with experimental irradiation facility.

Table 2. The results of thermal and epithermal neutron flux of corresponding irradiation positions.

Irradiation positions	φ_{th}	φ_e
(rotary rack)	$10^{12}cm^{-2}s^{-1}$	$10^{10}cm^{-2}s^{-1}$
10	1.96 ± 0.05	9.92 ± 0.46
22	2.24 ± 0.21	11.01 ± 2.45
27	2.45 ± 0.01	12.16 ± 0.96
31	2.42 ± 0.05	11.16 ± 0.49

Where φ_{th} is sub-cadmium thermal neutron flux, φ_e is epithermal neutron flux per unit lnE.

reaction rate of the irradiated samples by using the absolute NAA method and the results were compared to the certified values (liew, 2010).The nuclear properties of radioisotopes requried for the absolute neutron activation technique were taken from the compiled literature data (De Corte et al., 2003).The thermal and epithermal neutron fluxes at irradiation positions 10, 22, 27 and 31 as shown in Figure 1 were determined from reaction rates measured from induced activities of the irradiated ^{198}Au, under bare and with cadmium cover. The efficiency at 411.97 kev (^{198}Au) is 0.00102 (performed using Ortec detector at 10 cm) and 0.00145 (performed using Canberra detector at 12 cm).

RESULTS AND DISCUSSION

Table 2 shows the measured thermal and epithermal neutron flux at the irradiation positions 10, 22, 27 and 31

Table 3. Relevant nuclear data required to calculate reaction rate.

Elements	Q_o	σo,barn	I_o, barn	$\bar{E}_r$, eV
As	13.6	3.85	52.4	106
La	1.24	9.39	11.6	76
Mn	1.05	13.2	13.9	468
Na	0.587	0.512	0 .302	3380
Sc	0.43	26.3	11.3	5130
Sm	14.4	202	2909	8.53
Ga	6.69	4.65	31.1	154
K	0.97	1.39	1.34	2960
Hf	2.52	13.5	34	115
Ba	24.8	8.53	211.5	69.9
Cr	0.53	15.1	8	7530
Sb	33	6.31	208	13.1
Ce	0.83	0.575	0.48	7200
Th	11.53	7.37	8.5	54.4
Fe	0.975	1.28	1.25	637
Co	1.993	37.1	37.9	136
Rb	14.8	0.502	7.43	839
Yb	0.46	63.4	29.2	602
U	103.4	2.68	277	16.9
Tb	17.9	24	430	18.1
Cs	12.7	30.8	391.1	9.27
Ca	0.45	1.13	0.51	1330000

Where Q_o = resonance integral (1/E) to 2200 ms^{-1} cross-section ratio (= I_0/σ_0), σo = thermal neutron capture cross-section at 2200 ms^{-1} (barn), 1 barn=$10^{-24}cm^2$, I_o = resonance integral for a 1/E epithermal spectrum (barn), $\bar{E}_r$ = effective resonance energy (eV).

in rotary rack. Obviously, it can be observed that the thermal neutron flux is the dominant neutron flux in the reactor (neutrons are well thermalized with about 95% of thermal over epithermal neutrons).Table 3 shows the relative nuclear data required by the Høgdahl method for calculating reaction rates in the irradiation positions.Table 4 shows the elements determined in soil-1 sample irradiated at positions 10, 22, 27 and 31, where Table 6 shows Z-score values for all irradiation positions. At position 10, the ratio of experimental to certified value was between 0.77 for (Rb) and 1.21 for (Hf) and Z-score (Z-score estimate from Figures 2 and 3 as the difference between the top of striaght line to start point ,e.g for Mn, in Figure 2, the straight line lies in point ~2.71, and start point is 1.12, then 2.71-1.12=1.59 and so on) maximum was 1.59 for (Mn) as shown in Figure 2, at position 22, the ratio of experimental to certified value was between 0.71 for (Ce) and 1.18, for Na and Sm, and the Z-score maximum is 1.33 (Na). For lanthanum (La), it revealed good results where the experimental concentration value is nearly the same as the certified value. The results at position 27 were between 0.74 for Hf and 1.14 for Cs, and Z-score maximum is 2.33 for Fe. At position 31, the ratio was between 0.75 for Yb and 1.26 for Co with Z-score maximum of 2.00 for Na.Table 5 shows elements that are identified in soil-7 sample irradiated at positions 10, 22, 27 and 31, where Table 6 shows Z-score values for all irradiation positions. At position 10, the ratio of experimental to certified value was from 0.80 (Ce) to 1.29 (Tb) and maximum Z-score was 2.27 (Na) as shown in Figure 3, at position 22, the ratio was between 0.86 (Sb) and 1.28 (Cr) and the Z-score value is less than 1 for all elements except Na (1.09). At position 27, the ratio was between 0.80 (Sc) and 1.27 (Co) with maximum Z-score of 1.39 (Na). At position 31, the ratio was between 0.87 (Th) and 1.30 (Sm) with maximum Z-score of 2.87 (Na). In general, the deviation between experimental and certified values are mostly less than ± 10%, except for elements Na, Mn, Sm, Sb, Fe, K and Th where large deviations were observed. The high energy γ-ray of most of these elements contribute a large Compton scattering continuum to background of low energy photopeaks, that can contribute additional error in the results.The ratio of experiment to certified values are mostly less than unity.

Table 4. IAEA soil-1 result at irradiation positions 10, 22, 27 and 31 by absolute method.

Elements	Certified value		Experimental value							
			10		22		27		31	
	µg/g	σ(%)	µg/g	σ(%)	µg/g	σ(%)	µg/g	σ(%)	µg/g	σ(%)
As	27.5	11	29.28	11	29.45	56	22.07	14	27.94	6
La	52.6	6	52.12	7	52.58	18	46.92	8	52.53	6
Mn	3460	5	3870	5	3788	12	3151	7	3431	33
Na	1720	6	1776	4	2037	11	1893	6	1970	4
Sc	17.3	6	17.06	20	16.87	37	17.89	32	16.94	11
Sm	9.25	6	10.16	7	10.90	15	9.74	16	6.66	23
Ga	24.0	22	23.94	27	24.53	19	25.55	16	26.44	11
K	14500	15	15049	6	14771	13	12406	8	13908	6
Hf	4.2	14	5.07	25	4.11	35	3.1	39	4.57	24
Ba	639	8	733.54	25	474.07	30	481.96	39	614.89	39
Cr	104	9	117.44	14	90.32	23	113.62	17	97.23	14
Sb	1.31	9	1.12	17	1.13	21	1.05	22	1.06	17
Ce	117	15	96.29	17	82.94	25	-	-	106.48	39
Th	14	7	12.13	10	14.58	39	12.80	13	12.33	9
Fe	67400	3	68467	10	60773	16	51582	13	59585	10
Co	19.8	8	21.14	17	-	-	20.77	17	24.88	13
Rb	113	37	86.96	33	100.62	44	-	-	-	-
Yb	3.42	19	3.41	32	3.94	48	3.02	38	2.56	35
U	4.02	8	3.30	26	3.80	30	4.13	28	4.11	21
Tb	1.4	33	-	-	1.31	45	-	-	1.53	50
Cs	7.0	13	6.36	25	6.30	32	8.01	84	6.11	29
Ta	1.58	37	-	-	-	-	1.72	60	-	-
Zn	223	5	-	-	-	-	235.12	33	-	-

Where µg/g = concentration of elements(µg is indicate to maicrogram, g is gram), σ(%) = percentage uncertainty.

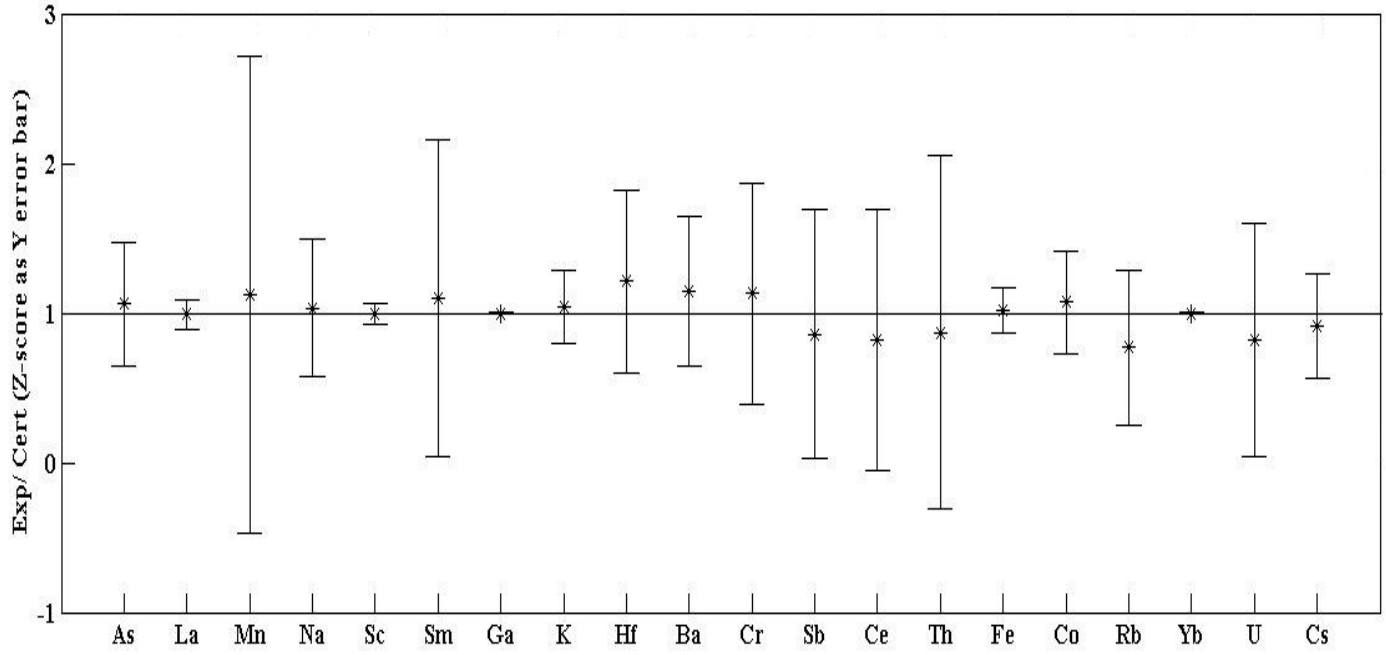

Figure 2. Soil-1 elements at irradiation position of 10 in rotary rack.

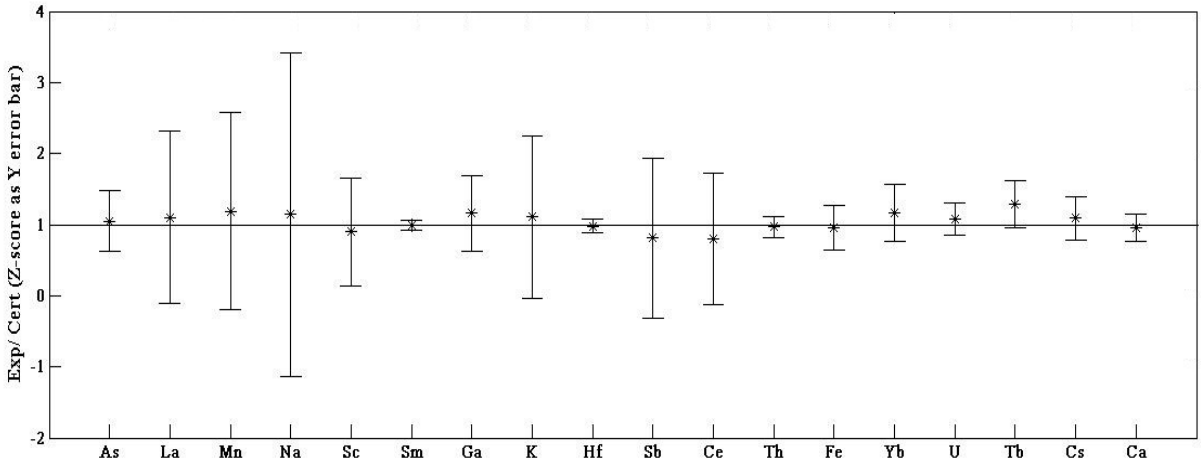

Figure 3. Soil-7 elements at irradiation position of 10 in rotary rack.

Table 5. IAEA Soil-7 result at irradiation positions 10, 22, 27 and 31 by absolute method.

Elements	Certified value		Experimental value							
	µg/g	σ(%)	10		22		27		31	
			µg/g	σ(%)	µg/g	σ(%)	µg/g	σ(%)	µg/g	σ(%)
As	13.4	6	14.07	9	13.26	14	11.29	19	13.49	9
La	28	4	30.75	7	29.53	19	26.92	29	29.94	7
Mn	631	4	750.16	11	728.87	19	645.05	11	749.27	12
Na	2400	4	2727	4	2727	10	2651	6	2813	4
Sc	8.3	13	7.44	6	8.42	31	6.66	9	7.65	27
Sm	5.1	7	5.06	10	5.06	14	6.30	20	6.65	8
Ga	10	20	11.59	19	12.24	25	11.33	25	12.01	20
K	12100	6	13427	7	12951	13	12236	8	13099	6
Hf	5.1	7	4.98	28	4.76	33	4.37	27	4.49	33
Ba	159	20	-	-	-	-	180.26	83	-	-
Cr	60	21	-	-	77.10	23	-	-	-	-
Sb	1.7	12	1.38	14	1.45	19	1.98	96	1.57	13
Ce	61	11	49.06	23	55.46	27	60.36	25	54.44	63
Th	8.2	13	7.96	13	7.95	17	6.62	18	7.14	12
Fe	25700	2	2462	14	27639	18	21423	16	25798	12
Co	8.9	10	-	-	-	-	11.34	23	-	-
Rb	51	9	-	-	-	-	-	-	53.98	40
Yb	2.4	15	2.80	34	2.17	45	3.02	50	2.85	32
U	2.6	21	2.82	28	-	-	2.47	31	2.87	23
Tb	0.6	33	0.78	63	-	-	0.52	76	-	-
Cs	5.4	14	5.90	24	6.14	35	4.93	33	-	-
Ca	163000	5	156084	22	148384	28	183959	19	156080	21

Conclusions

Most of the analytical results have Z-score within $0< |Z|< 2$, hence the results are coherent with certified values. The accuracy of the analytical results for each element in soil-1 and soil-7 may be awarded to uncertainties of the involved nuclear properties and thus varied from element to element. However, the calculated concentrations for sodium (Na) obtained by absolute NAA method were high compared to the certified value. Overall the accuracies of the absolute method adopted in the analysis of the soil-1 and soil-7 are in good agreement. These encouraging

Table 6. Z-score results for soil-1 and soil-7 at irradiation positions 10, 22, 27 and 31.

Elements	Soil-1				Soil-7			
	10	22	27	31	10	22	27	31
As	0.41	0.21	1.29	0.31	0.43	0.07	0.91	0.06
La	0.10	0.00	1.13	0.02	1.21	0.27	0.14	0.86
Mn	1.59	0.70	1.18	0.03	1.39	0.71	0.19	1.32
Na	0.46	1.33	1.17	2.00	2.27	1.09	1.39	2.87
Sc	0.07	0.07	0.10	0.17	0.76	0.04	1.34	0.28
Sm	1.06	0.94	0.30	1.60	0.07	0.05	0.93	2.51
Ga	0.01	0.08	0.24	0.41	0.53	0.62	0.38	0.64
K	0.24	0.10	0.90	0.26	1.14	0.47	0.11	0.91
Hf	0.61	0.06	0.81	0.29	0.09	0.21	0.59	0.40
Ba	0.50	1.07	0.81	0.10	-	-	0.14	-
Cr	0.74	0.61	0.45	0.42	-	0.78	-	-
Sb	0.83	0.67	1.01	1.17	1.12	0.73	0.15	0.45
Ce	0.87	1.29	-	0.24	0.93	0.34	0.04	0.19
Th	1.18	0.10	0.61	1.09	0.15	0.14	0.99	0.75
Fe	0.15	0.65	2.33	1.30	0.31	0.39	1.23	0.03
Co	0.34	-	0.26	1.46	-	-	0.88	-
Rb	0.52	0.20	-	-	-	-	-	0.13
Yb	0.01	0.26	0.30	0.77	0.40	0.22	0.40	0.45
U	0.78	0.19	0.09	0.09	0.22	-	0.13	0.31
Tb		0.12	-	0.14	0.33		0.18	-
Cs	0.35	0.32	0.15	0.44	0.31	0.33	0.26	-
Ta	-	-	0.12	-	-	-	-	-
Zn	-	-	0.16	-	-	-	-	-
Ca	-	-	-	-	0.19	0.34	0.59	0.20

results can form a strong basis for future use of absolute method NAA at the MNA research reactor.

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