

CHAPTER 3

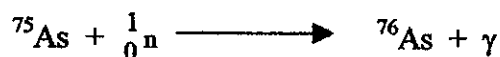
RESULTS AND DISCUSSION

The purpose of this study was to find out the simple method for arsenic determination in soil samples. Thus, neutron activation analysis was applied to analyze arsenic concentration with simpler, rapidly, more selective, and better than other methods. The sample can be analyzed in solid form and arsenic can be monitored in wide range of arsenic concentration due to the uncertainty from different sites. From the nature of instrument neutron activation, this method was non-destructive and no-time consuming separation work. It can be performed on any form of sample: solid, liquid, gas or any combination thereof, and used to determine elements at wide range of concentration since the calibration "curve" is actually a straight line [24,29-31]. In literatures, INAA had high sensitivity, and was used to measure elements within concentration ranges from nanograms to grams. Table 3.1 shows determination limits for arsenic element using NAA compared with other analytical techniques [24]. From these reasons, INAA method was chosen in this study to find out arsenic concentration in soil samples.

Table 3.1 Determination limits for arsenic element: a comparison of NAA (assuming a thermal neutron flux of $10^{18} \text{ n m}^{-2} \text{ s}^{-1}$) with other analytical techniques [24]

Method	Arsenic concentration
FAAS (mg dm^{-3})	0.003
ICP-AES (mg dm^{-3})	0.106
ICP-MS (mg dm^{-3})	0.0028
INAA (mg kg^{-1})	0.00001

In this experimental, (n,γ) reaction of ^{75}As was generated in both TNAA and ENAA. When the only stable isotope of arsenic is irradiated with neutron, an unstable isotope is produced in neutron capture. This reaction is represented by :



The nuclear data of arsenic is shown in Table 3.2 [33].

Table 3.2 Nuclear data of ^{76}As radionuclide

Isotope	Half-life	E_{γ} (keV)	Abundance (%)
^{76}As	26.32h	559.10	44.60
		563.23	1.20
		657.05	6.17
		1212.92	1.44
		1216.08	3.42
		1228.52	1.22

Thermal and epithermal neutrons in reactors are the most widely used for INAA because the neutron fluxes are greater and their cross section for (n, γ) reactions are largest. Epithermal neutron is however used to enhance the activation for some elements. The selection of thermal NAA and ENAA depends on the nature of the determinant. Most elements below copper in the periodic table have low cross-sections for epithermal neutron (resonance cross-section) and are best determined by thermal NAA, whereas most elements above copper have high resonance cross-sections and ENAA can be advantageous for their determination. In this study, however, both thermal and epithermal neutrons were used for arsenic determination. Another reason for using ENAA is due to the cadmium ratio, which is the ratio of activity of the element when it is irradiated without cadmium to that when irradiated under 1 mm of cadmium:

$$R_{\text{Cd}} = A_{\text{bare}} / A_{\text{epi}}$$

where A_{bare} is the activity in the bare tube and A_{epi} is the activity under 1 mm of cadmium.

The lower the cadmium ratio, the better is ENAA for an element. ENAA is often desirable because it reduces background activities, which results in enhanced sensitivity for an element [24,32]. ENAA is often desirable because it reduces background activities marked from γ -ray Compton distribution from the decay of interfering radionuclides, for example; ^{24}Na , ^{38}Cl and ^{82}Br etc, hence activity of ^{76}As is reduced. The cadmium ratios of these interfering radionuclides are higher than ^{76}As

for example, in a reactor position with a neutron energy distribution corresponding to a cadmium ratio of 2.4 for ^{197}Au , the advantage to be gained with respect to ^{76}As and ^{24}Na would be 2.9 and 27 respectively [32-33]. Hence, ^{75}As can absorb epithermal neutron more than ^{23}Na , and the activity of ^{76}As is higher than ^{24}Na , too.

3.1 Preliminary soil analysis

The aim for qualitative analysis was to investigate the natural elements and the interfering elements with arsenic in soil samples, and to quantitatively estimate the arsenic concentration in each soil sample. Suitable conditions from both samples and standard were selected from the data obtained in this section and applied to the comparative method.

3.1.1 Qualitative analysis

Preliminary qualitative analysis of soil samples was achieved using the conditions shown in Figure 2.4 (as mentioned in section 2.3.2.1). Radioisotopes induced from thermal neutron activation of natural elements present in soil samples and the γ spectra from these isotopes are shown in Table 3.3 and Figure 3.1. The gamma ray energies were applied to identify each element in the soil samples.

Table 3.3 Radioisotopes induced from thermal neutron activation of natural elements present in soil samples

Condition	Sample No	Isotope found and Energy in MeV											
		Al	As	Fe	In	K	La	Mg	Mn	Na	Sb	Sc	W
		1.78	0.56	1.10	0.42	1.52	1.59	1.01	1.81	1.37	0.60	0.89	0.48
CA3 :	S1	+	+	ND	+	ND	ND	+	+	+	ND	ND	ND
Ti=3 min	S2	+	+	ND	+	ND	ND	+	+	+	ND	ND	ND
Td=10 min	S3	+	+	ND	+	ND	ND	+	+	+	ND	ND	ND
	S4	+	+	ND	+	ND	ND	+	+	+	ND	ND	ND
	S5	+	+	ND	+	ND	ND	+	+	+	ND	ND	ND
CA3 :	S1	ND	+	ND	ND	ND	ND	ND	ND	+	ND	ND	+
Ti= 1 hr	S2	ND	+	ND	ND	ND	ND	ND	ND	+	ND	ND	+
Td= 1day	S3	ND	+	ND	ND	ND	ND	ND	ND	+	ND	ND	ND
	S4	ND	+	ND	ND	ND	ND	ND	ND	+	ND	ND	+
	S5	ND	+	ND	ND	ND	ND	ND	ND	+	ND	ND	+
A4:	S1	ND	+	ND	ND	+	ND	ND	+	+	ND	ND	+
Ti= 30 min	S2	ND	+	ND	ND	+	ND	ND	+	+	ND	ND	+
Td= 1day	S3	ND	+	ND	ND	+	ND	ND	+	+	ND	ND	+
	S4	ND	+	ND	ND	+	ND	ND	+	+	ND	ND	+
	S5	ND	+	ND	ND	+	ND	ND	ND	+	ND	ND	+
A4:	S1	ND	+	ND	ND	+	+	ND	ND	+	+	ND	+
Ti=1hr	S2	ND	+	ND	ND	+	+	ND	ND	+	+	ND	+
Td=3days	S3	ND	+	ND	ND	+	ND	ND	ND	+	+	ND	+
	S4	ND	+	ND	ND	+	+	ND	ND	+	+	ND	+
	S5	ND	+	ND	ND	+	+	ND	ND	+	+	ND	+
A4:	S1	ND	+	+	ND	+	+	ND	ND	+	+	+	+
Ti=5hr	S2	ND	+	+	ND	+	+	ND	ND	+	+	+	+
Td=7days	S3	ND	+	+	ND	+	+	ND	ND	+	+	+	+
	S4	ND	+	+	ND	+	+	ND	ND	+	+	+	+
	S5	ND	+	+	ND	+	+	ND	ND	+	+	ND	+

+ = isotope found

ND = not detectable

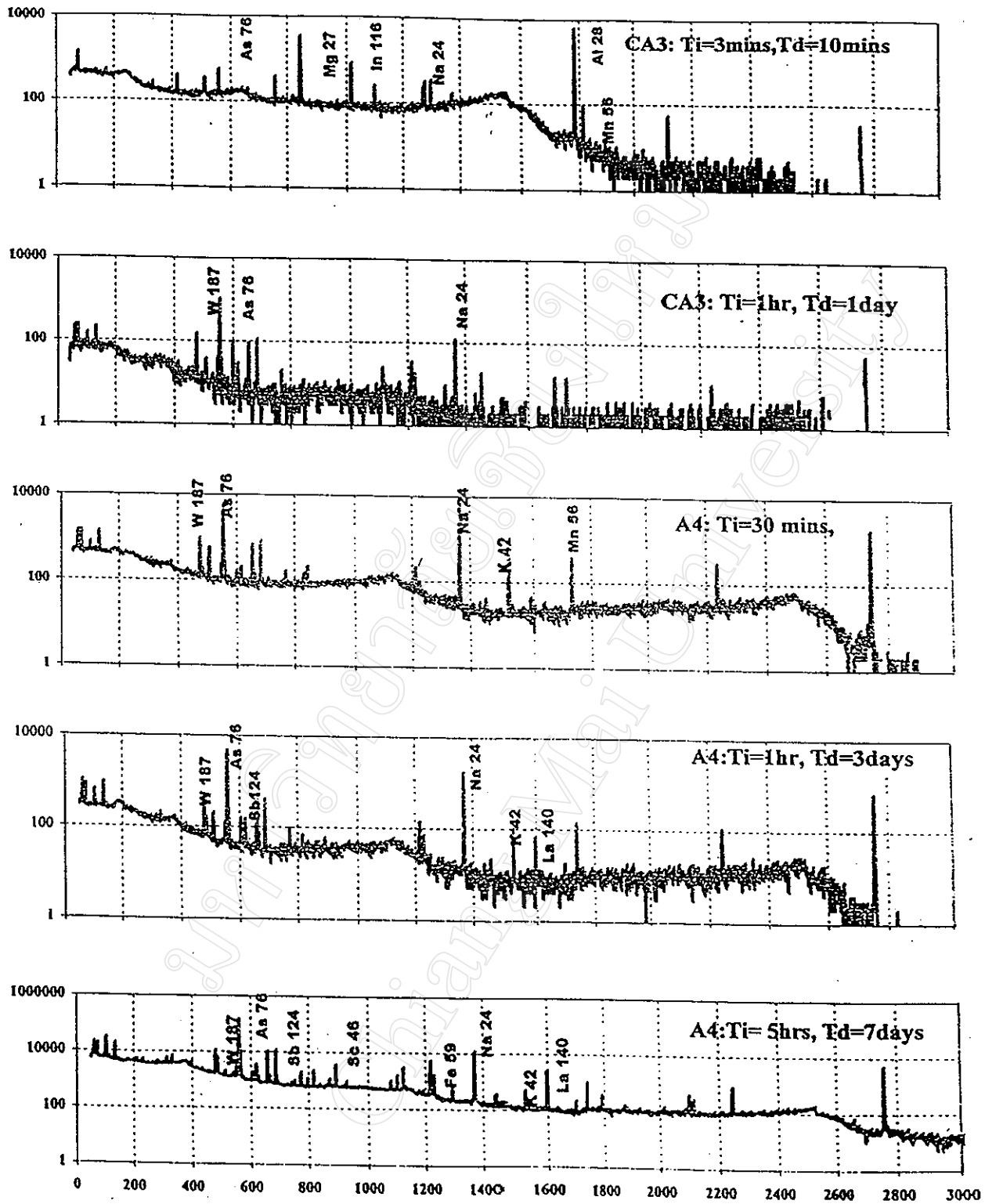


Fig 3.1 γ -spectra of radioisotopes induced from thermal neutron activation of natural elements present in soil samples for short-, intermediate-, and long time irradiation applied in both A4 and Ca3 core tubes.

3.2 Quantitative Analysis

3.2.1 Preliminary study

The arsenic concentrations in five samples from different locations were determined by thermal NAA described in section 2.3.2.2 (5 hours irradiation, about 7 days decay and 300 seconds counting), and the results obtained were shown in Table 3.4.

Generally, high contents of chlorine, bromine and sodium are the important interference with ^{76}As determination in soil samples, caused by high γ activities of ^{38}Cl , ^{82}Br , and ^{24}Na due to their large activity cross-section [30,34]. From Table 3.3 and Figure 3.1, ^{24}Na was the most important interfering element in this study. It was found in every period of irradiation (short-, intermediate- and long-term neutron irradiation) and cooling times. In addition, the grown up and decay of ^{24}Na (half-life 14.57h) were simultaneous with the grown up and decay of ^{76}As (half-life 26.3 h). In this case ^{76}As was interfered and masked from the sodium-24 Compton distribution by the 1368 and 2753 keV γ -ray from the ^{24}Na decay. The high sodium activity led to a high background at any energies lower than its γ -ray photopeaks, owing to the Compton scattering and high dead time, which forced the counting to be carried out at a large distance from the detector, so decreasing the counts due to arsenic species. From the results shown in Figure 3.2 and in Table 3.4, the SRM 2710 (Motana soil) was the most suitable standard material owing to its composition and chemical characteristic, which could be assumed to be very similar to those of the samples examined. Certified value of arsenic in SRM2710 ($626 \pm 38 \text{ mg kg}^{-1}$) was also enough to be a comparable standard in the comparative method. From the results, the amount of arsenic in soil No 5 was approximately the same range as in the standard SRM 2710 than that in the other soil sample. Thus, in the following section, soil No 5 was used for optimum condition study.

It was proposed, in this work, to find out the method to reduce sodium matrix by varying irradiation and decay times when using thermal neutrons, and to use epithermal neutron to reduce the sodium-24 Compton continuum.

Table 3.4 Determination of arsenic concentrations in five samples from different locations where $\lambda = 4.389\text{E-}4 \text{ min}^{-1}$.

Sample No	Weight (g)	Count at time t_d (C)	t_d (min)	$\exp(-\lambda t_d)$	Initial count (C_0)	Weight of As (mg)	Net As (ppm)
SRM	0.19229	6475	10126	0.01174	5.515E+5	0.120	626
s1	0.21120	22511	10080	0.01198	1.879E+6	0.410	1942
s2	0.30673	26255	10087	0.01195	2.197 E+6	0.479	1565
s3	0.35566	1694	10111	0.01182	1.433 E+5	0.0312	88
s4	0.27194	3815	10132	0.01171	3.258 E+5	0.0711	262
s5	0.28348	7952	10138	0.01168	6.808 E+5	0.148	524

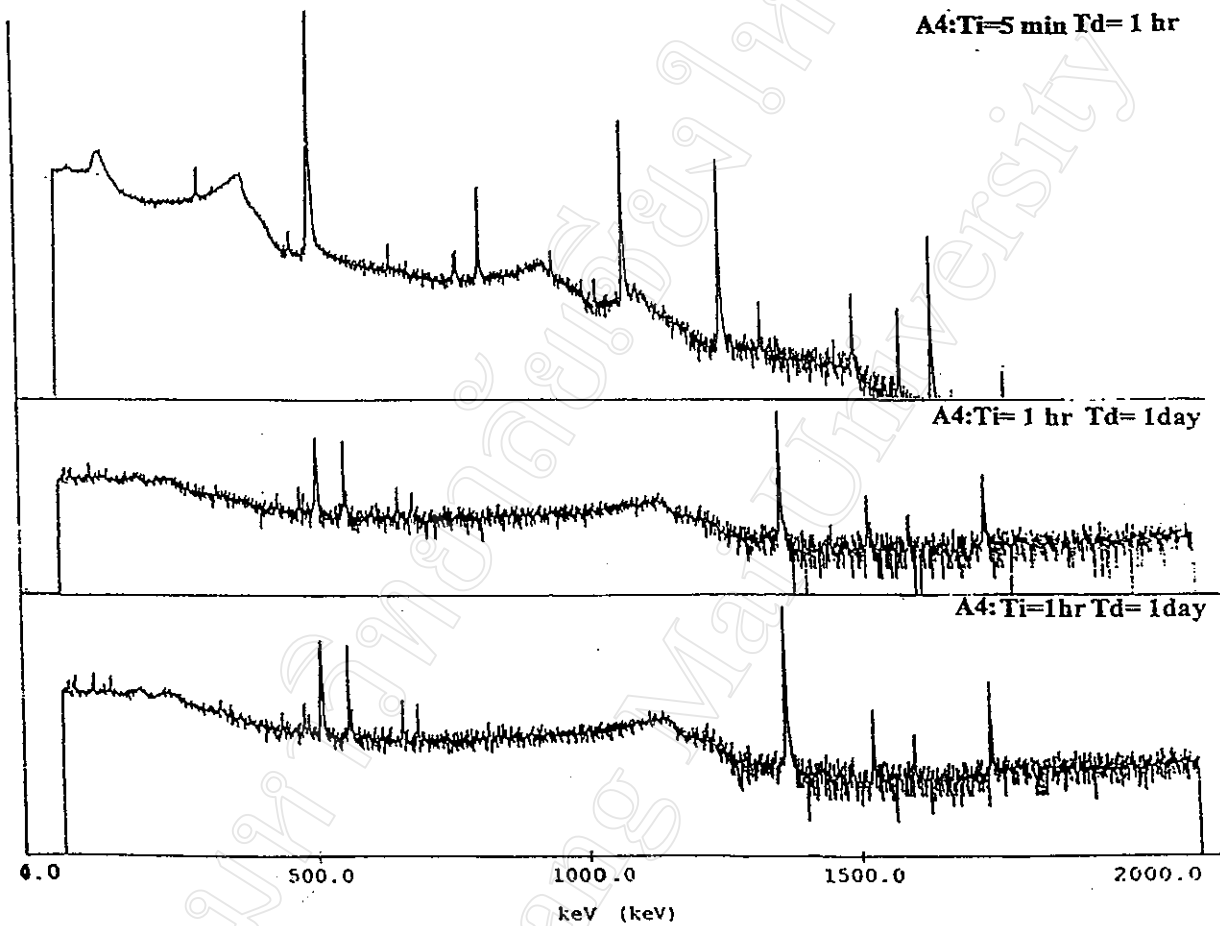


Fig 3.2 γ -spectra of radioisotopes induced from thermal neutron activation of elements present in SRM 2710 (Motana soil) for short-, intermediate-, and long time irradiation applied in A4 core tube.

3.2.2 Optimization conditions (irradiation and cooling times)

The position of measurement was fixed in this section and the followings to avoid the source-detector geometric error, which can be reduced by shaping samples and standards in the same dimension [35-37].

SRM and sample soil No 5 were used to investigate the optimum conditions by varying irradiation and cooling times in both A4-core tube and Ca3-core tube as indicated in Table 2.1 in section 2.3.3. The results of count rate, arsenic concentration, standard deviation of arsenic concentration and results of peak-to-background calculation obtained with various irradiation and cooling times were tabulated in Tables 3.5,3.6 (and Figure 3.3), and 3.7 respectively.

Table 3.5 Count rates and arsenic concentrations in SRM and sample soil No 5 obtained from various irradiation (T_i) and cooling (T_d) times

a. $T_i = 5$ min in A4 core tube

Sample position in the rabbit	Weight (mg)	Count rate (cps) and As concentrations (ppm)			
		$T_d = 3$ hr	As (ppm)	$T_d = 21$ hr	As (ppm)
1	347.83	3.21	462	2.84	503
SRM	127.67	1.60	626	1.30	626
2	327.35	4.18	639	2.69	506
3	441.07	6.78	769	4.64	648
Average As (ppm)		623		553	

b. $T_i = 10$ min in A4 core tube

Sample position in the rabbit	Weight (mg)	Count rate (cps) and As concentrations (ppm)			
		$T_d = 1$ d	As (ppm)	$T_d = 4.6$ d	As (ppm)
1	358.66	4.14	570	1.79	1910
SRM	164.04	2.08	626	0.27	626
2	348.96	4.65	658	1.48	1630
3	334.59	5.66	835	2.36	2700
Average As (ppm)		688		2080	

c. $T_i = 30$ min in A4 core tube

Sample position in the rabbit	Weight (mg)	Count rate (cps) and As concentrations (ppm)			
		$T_d = 23$ hr	As (ppm)	$T_d = 4.6$ d	As (ppm)
1	393.98	13.43	524	3.21	557
SRM	107.22	4.37	626	0.98	626
2	378.17	16.10	654	3.72	673
3	345.39	21.93	975	5.08	1005
Average As (ppm)		745		718	

Table 3.5 (continued)

d. $T_i = 1$ hr in A4 core tube

Sample position in the rabbit	Weight (mg)	Count rate (cps) and As concentrations (ppm)			
		$T_d=45$ hr	As (ppm)	$T_d = 3$ d	As (ppm)
1	393.98	46.08	483	23.97	544
SRM	107.22	16.24	626	7.50	626
2	378.17	55.99	612	30.61	724
3	345.39	63.59	761	32.06	831
Average As (ppm)		619		700	

e. $T_i = 2$ hr in A4 core tube

Sample position in the rabbit	Weight (mg)	Count rate (cps) and As concentrations (ppm)			
		$T_d=43$ hr	As (ppm)	$T_d = 3$ d	As (ppm)
1	319.11	75.91	499	74.00	497
SRM	104.8	31.25	626	30.64	626
2	406.94	114.65	591	114.75	604
3	445.9	143.18	674	143.67	690
Average As (ppm)		633		647	

f. $T_i = 4$ hr in A4 core tube

Sample position in the rabbit	Weight (mg)	Count rate (cps) and As concentrations (ppm)	
		$T_d=70$ hr	As (ppm)
1	358.66	26.28	497
SRM	164.04	15.15	626
2	348.96	31.51	612
3	334.59	38.69	784
Average As (ppm)		631	

Table 3.5 (continued)

g. $T_i = 30$ min in Ca3 core tube

Sample position in the rabbit	Weight (mg)	Count rate (cps) and As concentrations (ppm)	
		$T_d = 4$ d	As (ppm)
1	358.66	3.12	450
SRM	164.04	1.99	626
2	348.96	2.86	424
3	334.59	3.36	519
Average As (ppm)		464	

h. $T_i = 1$ hr in Ca3 core tube

Sample position in the rabbit	Weight (mg)	Count rate (cps) and As concentrations (ppm)	
		$T_d = 4$ d	As (ppm)
1	319.11	4.31	612
SRM	310.48	1.45	626
2	406.94	5.48	609
3	445.9	6.34	643
Average As (ppm)		621	

Table 3.6 Arsenic average concentration in samples soil No 5 obtained with various irradiation and cooling times

Conditions, (T_d)	As average concentrations (ppm)
a. $T_i = 5$ min in A4 core tube	
3 hr	623
21 hr	553
b. $T_i = 10$ min in A4 core tube	
1d	688
4.6 d	2080
c. $T_i = 30$ min in A4 core tube	
23 hr	745
4.6 d	718
d. $T_i = 1$ hr in A4 core tube	
45 hr	619
3 d	700
e. $T_i = 2$ hr in A4 core tube	
43 hr	633
3 d	647
f. $T_i = 4$ hr in A4 core tube	
70 hr	631
g. $T_i = 30$ min in Ca3 core tube	
4 d	464
h. $T_i = 1$ hr in Ca3 core tube	
4d	621

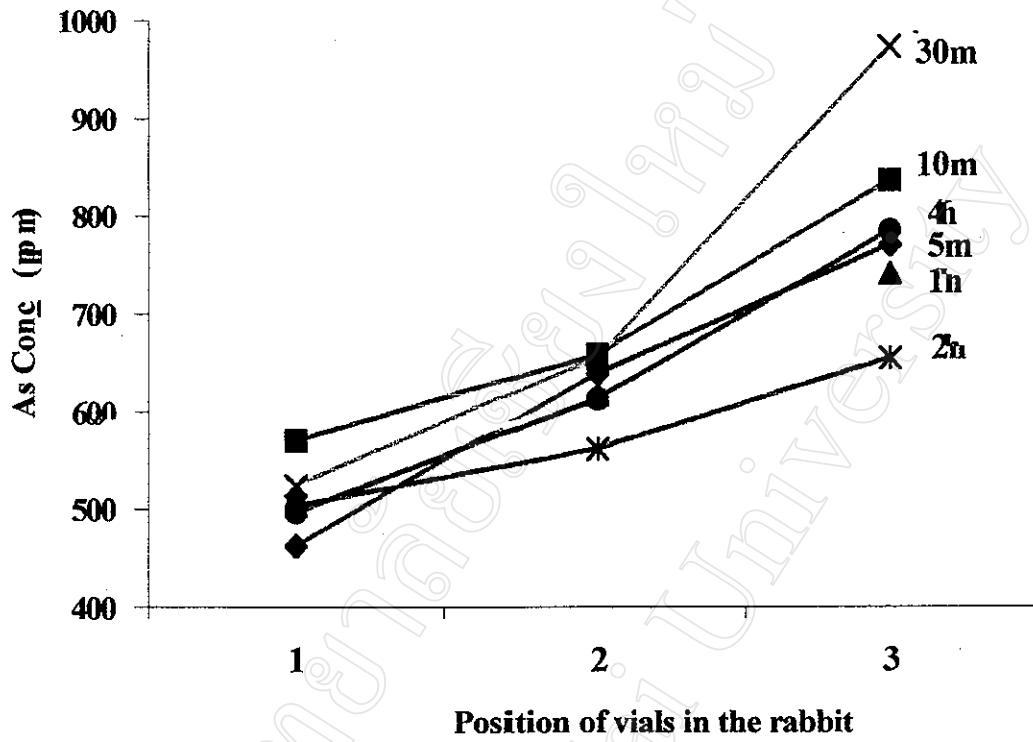


Fig 3.3 Arsenic concentration in soil samples No 5 obtained with various irradiation, cooling times and position vials in the rabbit

Table 3.7 Photopeak to Compton scattering ratio of soil samples No 5 obtained with various irradiation and cooling times

a. $T_i = 5$ min in A4 core tube

Sample position in the rabbit	Photopeak to Compton scattering ratio	
	$T_d = 3$ hr	$T_d = 21$ hr
1	0.49	0.66
SRM	0.05	0.35
2	0.57	4.43
3	0.59	5.23

b. $T_i = 10$ min in A4 core tube

Sample position in the rabbit	Photopeak to Compton scattering ratio	
	$T_d = 1$ d	$T_d = 4.6$ d
1	7.67	8.52
SRM	2.60	4.70
2	7.05	7.05
3	11.79	13.11

c. $T_i = 30$ min in A4 core tube

Sample position in the rabbit	Photopeak to Compton scattering ratio	
	$T_d = 23.5$ hr	$T_d = 4.6$ d
1	10.17	29.75
SRM	2.43	10.91
2	10.95	24.83
3	8.31	22.92

Table 3.7 (continued)

d. $T_i = 1$ hr in A4 core tube

Sample position in the rabbit	Photopeak to Compton scattering ratio	
	$T_d = 45$ hr	$T_d = 3$ d
1	5.04	5.66
SRM	2.93	2.70
2	5.33	5.07
3	5.20	5.07

e. $T_i = 2$ hr in A4 core tube

Sample position in the rabbit	Photopeak to Compton scattering ratio	
	$T_d = 43$ hr	$T_d = 3$ d
1	8.63	8.06
SRM	5.57	5.75
2	7.32	8.02
3	6.89	7.53

f. $T_i = 4$ hr in A4 core tube

Sample position in the rabbit	Photopeak to Compton scattering ratio	
	$T_d = 70$ hr	
1	7.42	
SRM	4.03	
2	6.54	
3	7.14	

Table 3.7 (continued)

g. $T_i = 30$ min in Ca3 core tube

Sample position in the rabbit	Photopeak to Compton scattering ratio
	$T_d = 4$ d
1	1.47
SRM	1.46
2	1.15
3	1.28

h. $T_i = 1$ hr in Ca3 core tube

Sample position in the rabbit	Photopeak to Compton scattering ratio
	$T_d = 4$ d
1	6.81
SRM	2.56
2	5.27
3	6.89

The success of nondestructive activation analysis for element determination is a function of the total counts in the photopeak which used as a measure of an element, as well as the values of these photopeak counts relative to those of the Compton backgrounds below the photopeak. It is thus apparent that for the nondestructive determination of a certain element in a particular matrix by activation analysis, optimum irradiation and decay times should be chosen to obtain the best possible results. These optimum times obviously vary from one element to the next and are further dependent on the interfering characteristics of the matrices. Consequently it is necessary in practice to choose the best compromises regarding irradiation and decay times in order to determine simultaneously as many of the desired elements as feasible with an acceptable precision, while limiting or minimizing the number of the times of irradiation, decay, and counting.

In this study, the length of irradiation, which is attainable in practice, will depend on the way in which the reactor, or alternative neutron source, is operated [36-38]. The aim of this work was to develop a simple and rapid procedure for determining arsenic, therefore, it is essential to investigate the optimum time taken for each operation step to minimize the number of the times of irradiation and decay, and to minimize interference. However, the quantity of total arsenic found in soil No 5 showed the differences in concentrations with high standard deviation using both TNAA and ENAA. The standard deviation comprised a variety of experimental errors, which might arise from the following parameters [38]:

- 1) the irradiation conditions (uncertainties, regarding the position of the sample in the container, flux gradient, instability of the reactor and error on the irradiation time);
- 2) the measurement (cooling period, geometry, dead-time correction and stabilizer, stability of the detector);
- 3) counting statistics and peak area evaluation.

It can be ignored in this study the error by the measurement, counting statistics and peak area evaluation. The detector system was calibrated by radioisotope standards in every work and also in this experiment. The standard reproduced the geometry of the sample as closely as possible in the same size, shape of vial, the position of the sample vials on the detector. Moreover, Oxfordwin Assayer programs were used to find peaks, calculate count rates and then correct for dead time and evaluate the data in both standards and samples. Consequently, the results in Figure 3.3 showed that, the errors arose regarding the position of the sample in the container and flux gradient. The trends of arsenic concentration in the same sample under difference conditions were higher when the sample position was near the reactor core. The distribution of neutron flux within a neutron source is not necessarily constant. On the contrary, in a reactor the neutron flux is unlikely to remain constant even over relatively short distances. The neutron flux falls off with distance in both vertical and horizontal directions away from the center of the reactor core. The effect is a cosine curve with the maximum at the core centerline. The neutron fluxes in a particular irradiation site will depend on its distance from the reactor core. The higher the neutron fluxes in neutron activation, the better the activation of the sample, but the

activation of the background interference increases similarly, so this means that the improvement in the detection of the element of interest is not direct.

NAA is based on the principle that induced activity is proportional to neutron flux and therefore any quantitative measurements rely on the neutron flux being reproducible or quantifiable.

The calculation obtained from the results of photopeak-to-background with various irradiated and cooling times were tabulated in Table 3.7. It was found that suitable conditions for determination of arsenic by TNAA were 30 min for irradiation times and 1 day for cooling times to minimize the number of the times and to minimize interference as to maximize the ratio of the signal to background for the arsenic photopeaks.

For ENAA, it was found that ^{24}Na was the only important matrix element of arsenic in soil in this study. In a reactor position with a neutron energy distribution corresponding to a cadmium ratio of 2.4 for ^{197}Au , the advantage to be gained with respect to ^{76}As and ^{24}Na would be 2.9 and 27 respectively [33]. Gamma ray spectra were shown in Figure 3.4-3.5. As can be seen from Figure 3.5 the ratio of the signal to background for the photopeak of ^{76}As was very good by TNAA. In Figure 3.4, the background was very low as a result of the decrease in activity of ^{24}Na by ENAA.

This interference was decreased by an order of magnitude when using epithermal neutron. In using epithermal neutron, one can significantly reduce the contribution of the sodium radionuclide to the background continuum since that low I_0/σ_{th} value. The suitable conditions obtained from the results of photopeak-to-background for the epithermal neutron were 1 hour for irradiation times and 1 day for cooling times. The irradiation times of epithermal neutron are usually higher than those of thermal neutron because the epithermal neutron flux is lower than the thermal neutron flux in a TRIGA type reactor. Therefore, the irradiated time for ENAA in this study was longer than for TNAA due to the nature of reactor, which had the epithermal flux density about one order of magnitudes less than the thermal flux density.

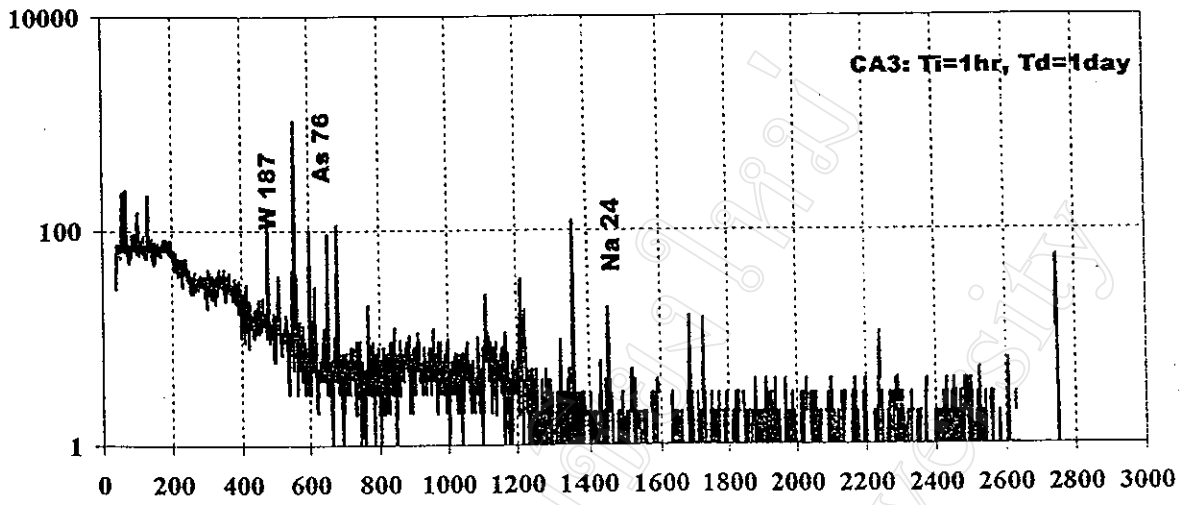


Fig 3.4 γ spectrum of soil No 1 using suitable conditions for ENAA

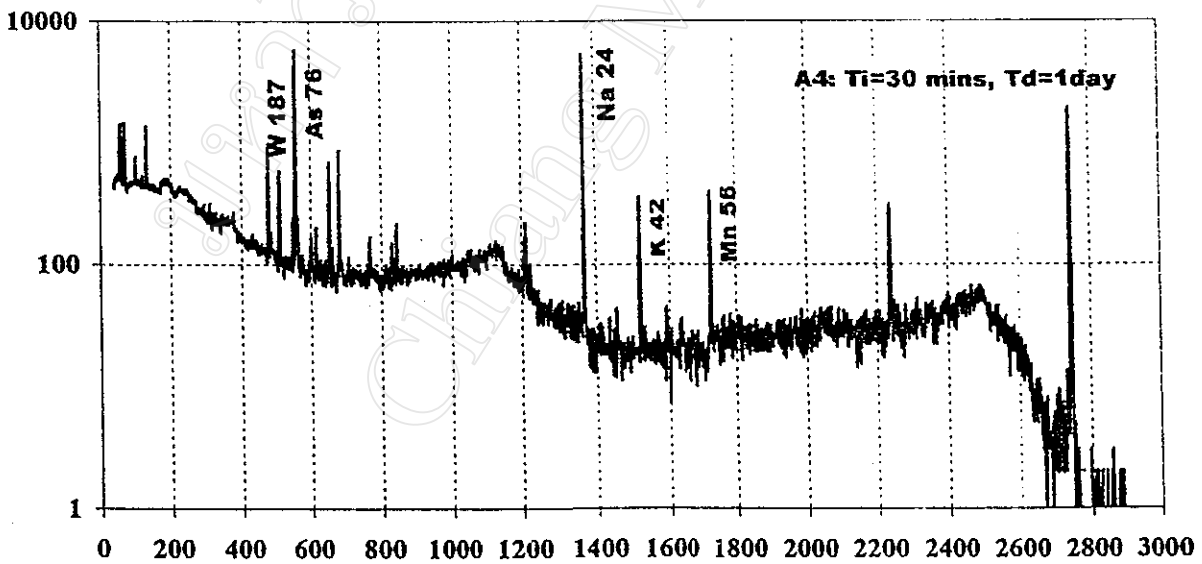


Fig 3.5 γ spectrum of soil No 1 using suitable conditions for TNAA

3.2.3 Analysis Validation Method and Flux Correction

3.2.3.1 Flux Correction

It is well known that neutron fluxes can vary markedly at different positions with an adjacent to the vertical direction of a TRIGA type reactor [39]. The Flux variation can cause serious biases and lack of reproducibility in activation analysis if not corrected.

Five standard vials and five copper wires (served as a flux monitor) were used for flux correction. The results of count and specific count from flux monitor by 5 copper wires were shown in Table 3.8 and the neutron flux variation shown in Figure 3.6. The flux correction data by both normalized with relative flux ratio of As/Cu and normalized with sample and standard position in the rabbit (for 3 vials sample sandwiches, together 2 vials standard) were shown in Table 3.9.

Table 3.8 Counts and specific counts in a copper monitor

Cu position in rabbit (height), (cm)	Count at 1345 keV (C)	Weight (mg)	Specific count (cpmg)
1	619	45.8	13.5
2	508	42.6	11.9
3	378	39.8	9.49
4	394	47.0	8.38
5	368	45.7	8.05
6	312	43.8	7.12

cpmg = counts per mg

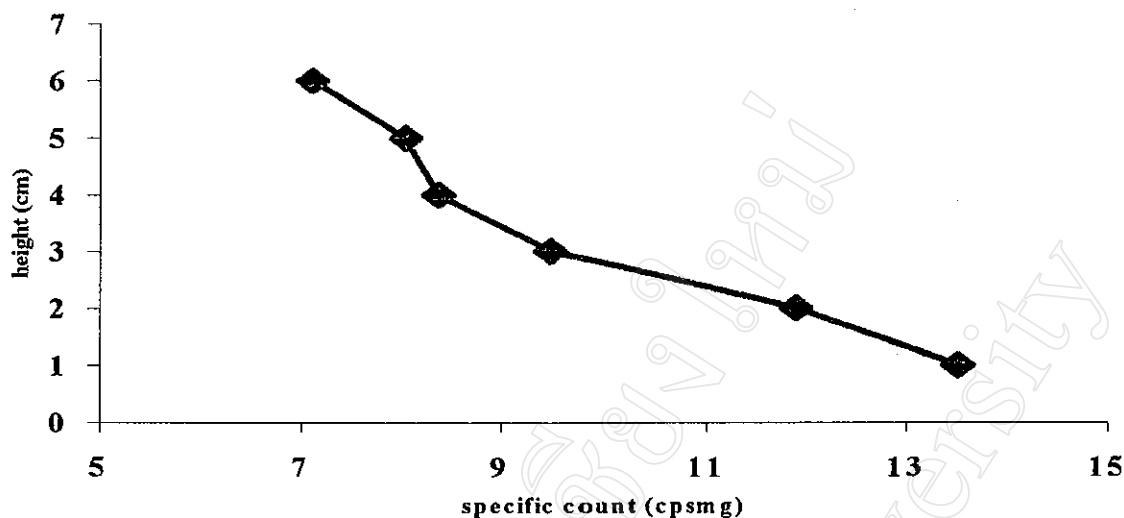


Fig 3.6 Neutron flux variation along an irradiation rabbit demonstrated by the specific count in a copper monitor

Table 3.9 Relative count values by sample position flux correction and relative flux ratio of As/Cu; counts of Cu ratios and normalized with sample and standard position in the rabbit

Position (cm)	Specific count of Cu (cpg)	Specific count of As (cpg)	Mean specific count of position value	Relative flux ratio of As/Cu
1	13500	9886		0.732
2	11900	8804	8664 ¹⁺³	0.740
3	9490	7442	7649 ²⁺⁴	0.784
4	8380	6493	6838 ³⁺⁵	0.775
5	8050	6233	5820 ⁴⁺⁶	0.774
6	7120	5146		0.723

cpg = counts per g

¹⁺³ = mean specific count from position 1 and 3

²⁺⁴ = mean specific count from position 2 and 4

³⁺⁵ = mean specific count from position 3 and 5

⁴⁺⁶ = mean specific count from position 4 and 6

The best way to do this is to keep the flux as constant and reproducible as possible. On the TRIGA®, in literature, this is achieved by using a rotating irradiation device, where the sample travel slowly round the perimeter of the core so that all the same integrated fluxes are obtained during an irradiation [39.]. The main disadvantage of equalization systems is that by their nature the samples will all see an average flux, obtained by traveling through regions of high and low neutron density. The compact nature of some reactor vessels means that there is little space available for equalization systems if maximum neutron fluxes are to be achieved.

The neutron flux distribution in a radiation sites can be characterized using a neutron flux monitor, either at the time of the experimental or in a separation measurement. The distribution of the neutron flux along the core tube from literature is shown in Figure 3.7 [24]. The activation follows the cosine curve expected for an irradiation site close to and along the length of the reaction core. The positions of the irradiation capsules are placed as indicated on the graph and clearly the variation is much less close to the centerline of the core. It is therefore extremely important that the variation is monitored and the proper correction made for the difference in the neutron flux experienced by adjacent samples.

In this study, the problem of flux variation due to distance was minimized. The flux corrections when normalized with relative flux ratio of As/Cu showed linear relationship as shown in Figure 3.8. The copper wire flux monitor utilized the nuclear reaction $^{63}\text{Cu} (n,\gamma) ^{64}\text{Cu}$. Copper-64 decays with a 1.345 MeV γ -ray and 0.511 MeV annihilation radiation from positron emission [33]. Normalized with sample position in therabbit was done by comparing the specific count of arsenic in the second position with mean values between specific count of arsenic in the first and third positions. From Figure 3.8, it was found that the plot between mean relative count value versus height shown better linearity than the plot between specific count value versus height. It was assumed that, the standards and samples were activated in the same irradiation sites and in the same position within an irradiation rabbit. The corrected amounts of arsenic in samples were calculated from the following equation:

$$\text{As (ppm)} = \frac{[\mu\text{g As in standard (R2)}](\text{photopeak area of sample}((R1+R3)/2))}{(\text{average weight of sample } ((R1+R3)/2)) (\text{photopeak area of standard(R2)})}$$

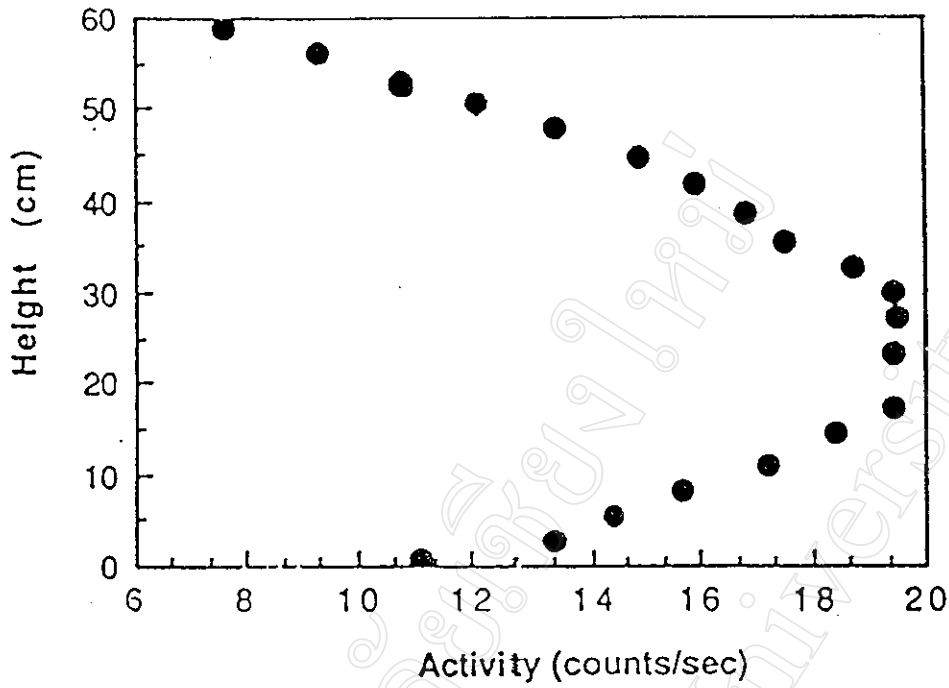


Fig 3.7 Neutron flux variation along an irradiation tube, demonstrated by the activity induced in a cobalt monitor [24].

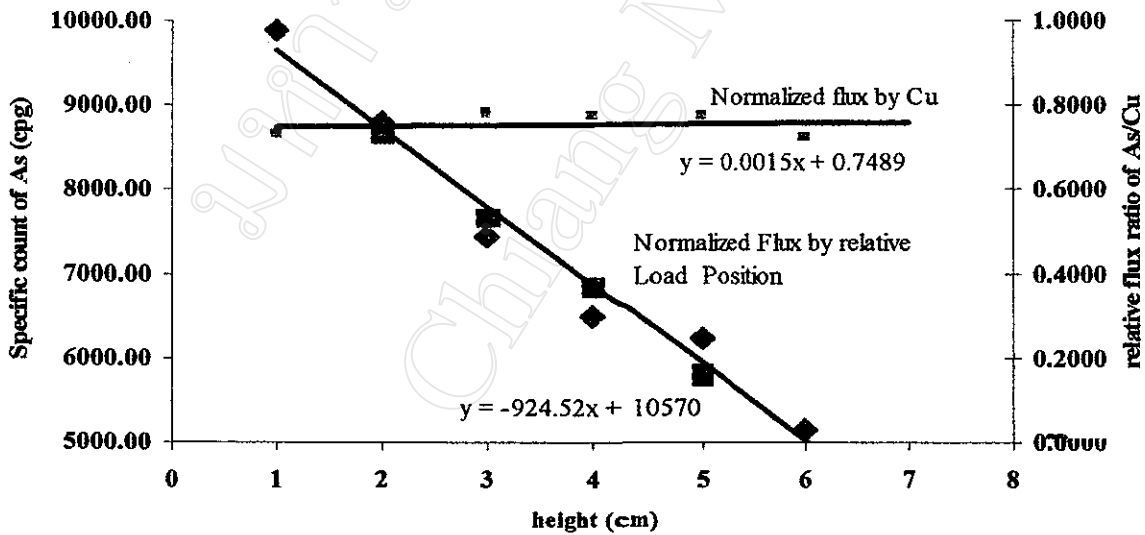


Fig 3.8 The flux corrections by both normalized with specific count of As/ specific count of Cu ratio and normalized with sample and standard position in rabbit

3.2.3.2 Validation Method

The SRM-2710 (certified value of arsenic in Motana was 626 ± 38 mg Kg⁻¹) were used to confirm the method in this study. The arsenic concentrations in 6 candidate's SRM were determined by INAA ($T_i = 30$ min, $T_d = 1$ hr and $T_m = 300$ s and position in the rabbit as shown in section 2.3.3.3) and the calculated results were shown in Table 3.10. The flux correction of SRM 2710 by sample position flux correction method is shown in Figure 3.9.

Table 3.10 Count rate and results of arsenic concentration in six candidate's SRM from different vial positions in the rabbit

Position (Height, (cm))	Weight (mg)	Count at 559.1 keV (C)	specific count (cpmg)	Mean relative count value	ppm of As
1 (R ₁)	0.14597	1443	9886		
2 (R ₂)	0.14402	1268	8804	8664 ¹⁺³	616 ^a
3 (R ₃)	0.16164	1203	7442	7648 ²⁺⁴	643 ^b
4 (R ₄)	0.18342	1191	6493	6837 ³⁺⁵	659 ^c
5 (R ₅)	0.17311	1079	6233	5819 ⁴⁺⁶	585 ^d
6 (R ₆)	0.15214	783	5146		
				Average =	626
				%SD=	5.24

a = ppm of As calculated from mean relative count value R1+R3 compared with R2

b = ppm of As calculated from mean relative count value R2+R4 compared with R3

c = ppm of As calculated from mean relative count value R3+R5 compared with R4

d = ppm of As calculated from mean relative count value R4+R6 compared with R5

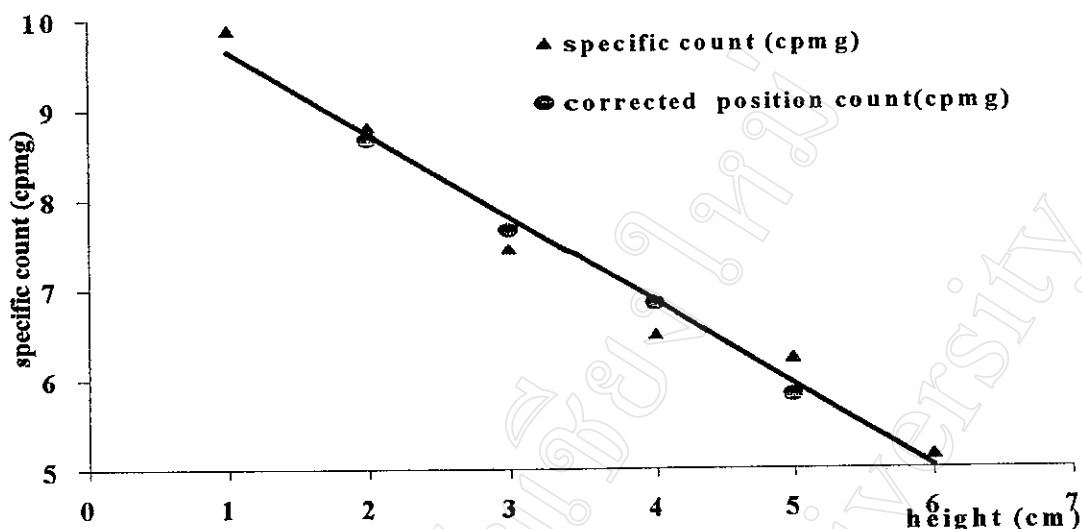


Fig 3.9 Flux correction of SRM 2710 by sample position flux correction method

To test the validity of the proposed standard, the Motana soil SRM 2710 of NIST, it appeared that there were no significant differences for the certified elements. The arsenic concentrations in SRM 2710 as obtained in this conditions together with the certified value were present in Table 3.11. Arsenic values were in acceptable agreement with certified value, and this determination indicated that the reproducibility of the INAA method is satisfactory. The precision was found better than 95% for arsenic element.

3.3 Analysis of soil samples

The arsenic concentrations in five candidate's sample from different location were determined by NAA (as indicated in section 2.4) and the results were tabulated in Table 3.11. These values were compatible with the results obtained from XRF(E-T) method for soil samples.

Table 3.11 Arsenic concentrations in 5 candidate's sample by TNAA and ENAA compared with XRF E-T method

Sample No.	Arsenic concentrations (ppm)		
	Thermal neutron (% SD)	Epithermal neutron (% SD)	XRF E-T method (% SD)
S1	2450 (1.31)	2405 (2.26)	2180 (1.92)
S2	1810 (2.61)	1740 (6.64)	1710 (4.97)
S3	115 (7.87)	117 (4.23)	119 (5.72)
S4	283 (1.96)	283 (7.04)	315 (4.62)
S5	669 (4.21)	572 (5.18)	621 (9.52)