

CHAPTER 1

INTRODUCTION

1.1 Arsenic

1.1.1 General

Arsenic was discovered in 1250 A.D. by Magnus, and first prepared by Schroeder in 1649 [1]. Arsenic, which is a naturally-occurring element, is a grey metal-like material. An inorganic arsenic found is usually combined with other elements such as oxygen, chlorine, and sulfur such as arsenopyrite, orpiment, realgar, lollingite and tennantite. Arsenic combined with carbon and hydrogen is called organic arsenic. Due to the abundance of arsenic that occurs in the earth's crust-rock, soil, all natural sources of exposure includes weathering of rocks and erosion through deposition of arsenic in water bodies, and intake of this element by animals and plants [2]. General information of arsenic is shown in Table 1.1 [1, 3].

1.1.2 Arsenic pollution [4-6]

Arsenic is a nature part of the environment, low levels of arsenic are present in soil, water, air and many foods such as meat, fish, poultry, grain and cereals. Soil usually contains the most, with average level of about 5000 parts of arsenic per billion parts of soil (ppb), but in contaminated soil, level of arsenic may be up to 500 parts of arsenic per million parts of soil (ppm) or more. Levels in food, in water and in air are usually about 20-140 ppb, 2 ppb and 0.02-0.10 micrograms per cubic meter, respectively. Arsenic is often present in organic forms, which are less toxic than inorganic arsenic.

Arsenic is a toxic chemical and may pollute air, soil, sediments and water causing health hazards to both human and other living organisms. Air pollution by arsenic is caused through various industrial processes like smelting, manufacturing of insecticides and drugs. Contamination of leaching of arsenic waste from mining operation, industrial and agricultural processes have been found in some country. Arsenic is found to occur in nature as mineral from which, by way of erosion and deposition, soil may be contaminated. Water pollution by arsenic is attributed to both human activities and geohydrological phenomena.

Table 1.1 Physical and chemical information of arsenic

General Information				
Formula	As			
Atomic Number	33			
Relative Atomic Mass ($^{12}\text{C}=12.000$)	74.923			
Position in Periodic Table	VA			
Melting Point/K	1090			
Boiling Point/K	889			
Density/kg m ⁻³	5780 (293K)			
Ground State Electron Configuration	[Ar]3d ¹⁰ 4s ² 4p ³			
Electron Affinity(M-M ⁻)/kJ mol ⁻¹	77			
Enthalpy of Fusion/kJ mol ⁻¹	27.7			
Enthalpy of Vaporization/kJ mol ⁻¹	31.9			
Oxidation States	Main As ^{III} , As ^V Other As ^{-III}			
Type of arsenic compounds	<ul style="list-style-type: none"> • Inorganic (trivalent, e.g. arsenites, and pentavalent, e.g. arsenates) • Organic (mono and di-methyl arsenic acid) 			
Key Isotopes				
Nuclide	⁷³ As	⁷⁴ As	⁷⁵ As	⁷⁶ As
Atomic mass	72.924	73.924	74.922	75.922
Natural abundance(%)	0	0%	100%	0%

In Nakhonsrithammarat, the problem of arsenic contamination in soil episode in Ronpibul district has been known for many years. Primary and placer tin-tungsten-arsenic deposits have been worked in Ronpibul district for almost 100 years. Primary deposition lying in the mountain ranges is a high-grade vein typed tin mineral. However in the lowland mineral placers occur in many location. Arsenic species are scattered by acid during the process of mining dressing activity throughout the mining concession and these have increased the load of arsenic- rich in the environment. Arsenic in uncontaminated soil is present in concentrations from 0.2 to 40 ppb, with an average content of about 5 ppb [1] but the concentrations of arsenic in Ronpibul district soils were found in the range from 8.17 to 376 ppm [6,7].

1.1.3 Toxic effects of arsenic in human [4,8-9]

Arsenic is a poison and its lethal dose for human is 125 milligram. The amount of arsenic intake that is required to cause a harmful effect depends on the chemical and physical form of the arsenic. In general, inorganic forms of arsenic are more toxic than organic forms, and the forms that dissolve easily in water (soluble form of arsenic) tend to be more toxic than those that dissolve poorly in water. Also, toxic depends somewhere on the electric charge (the oxidation state or valence) of the arsenic. Toxicity of arsenic intake is classified into acute, sub-acute and chronic toxicity, respectively. Most of the ingested arsenic is excreted from the body through urine, stool, skin hair, nail and breath. In excessive intake, some amount of arsenic is deposited in tissues and inhibits cellular enzyme activities. Almost all organs are affected; but clinical symptoms appear insidiously after 6 months to 2 years or more depending upon the amount of arsenic intake. Chronic toxicity of arsenic is best discussed in term organ system (or "Systemic effects") affected, viz. skin, liver, nervous system, cardiovascular system and respiratory system as shown in Table 1.2. Figures 1.1 and 1.2 show the relationship between exposure to soluble forms of inorganic arsenic and known health effects.

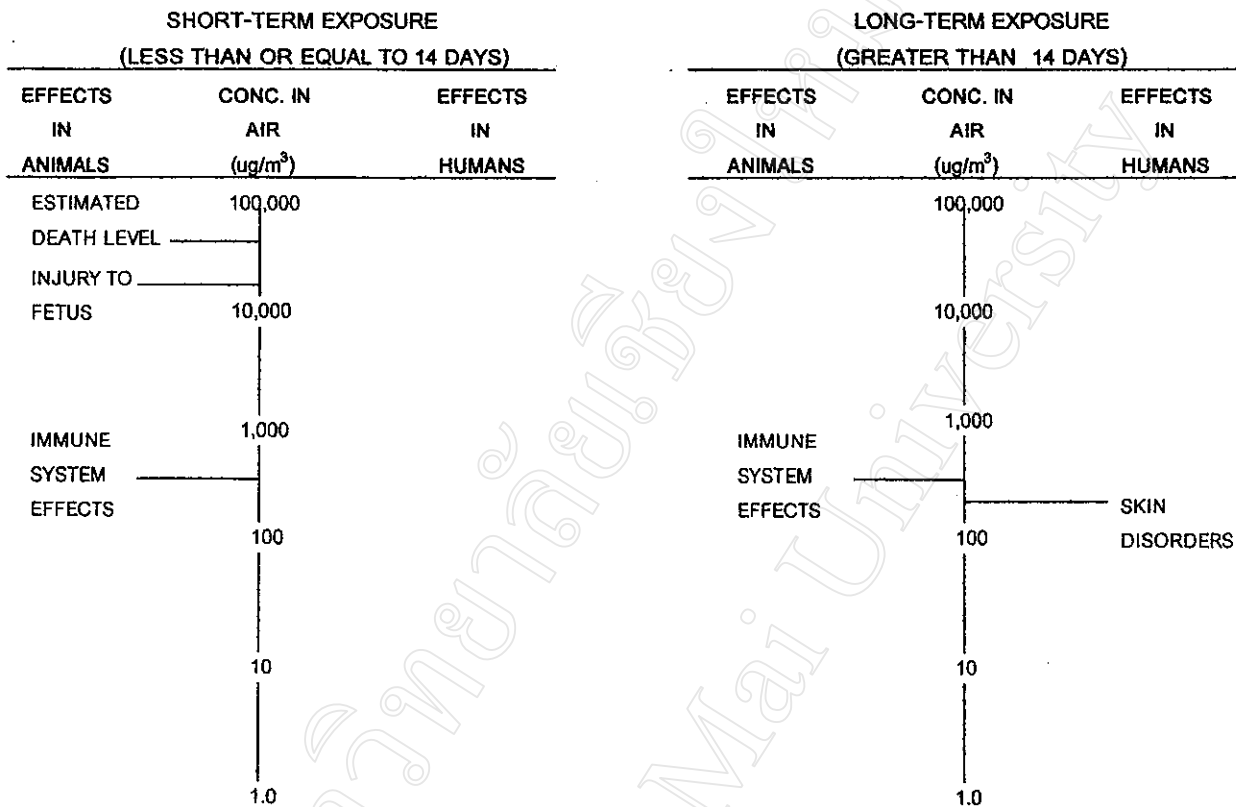


Fig.1.1 Health effects from breathing inorganic arsenic

Table 1.2 Arsenic toxic in different organ systems: systemic effects [4]

Organ System	Problems
Skin	Symmetric hyperkeratosis of palms and soles, melanosis or depigmentation, bowen's disease, basal cell carcinoma and squamous cell carcinoma
Liver	Enlargement, Jaundice, cirrhosis, non-cirrhotic portal hypertension
Nervous System	Peripheral neuropathy, hearing loss
Cardiovascular System	Acrocyanosis and Raynaud's Phenomenon
Hemopoietic System	Megaloblastosis
Respiratory System	Lung Cancer

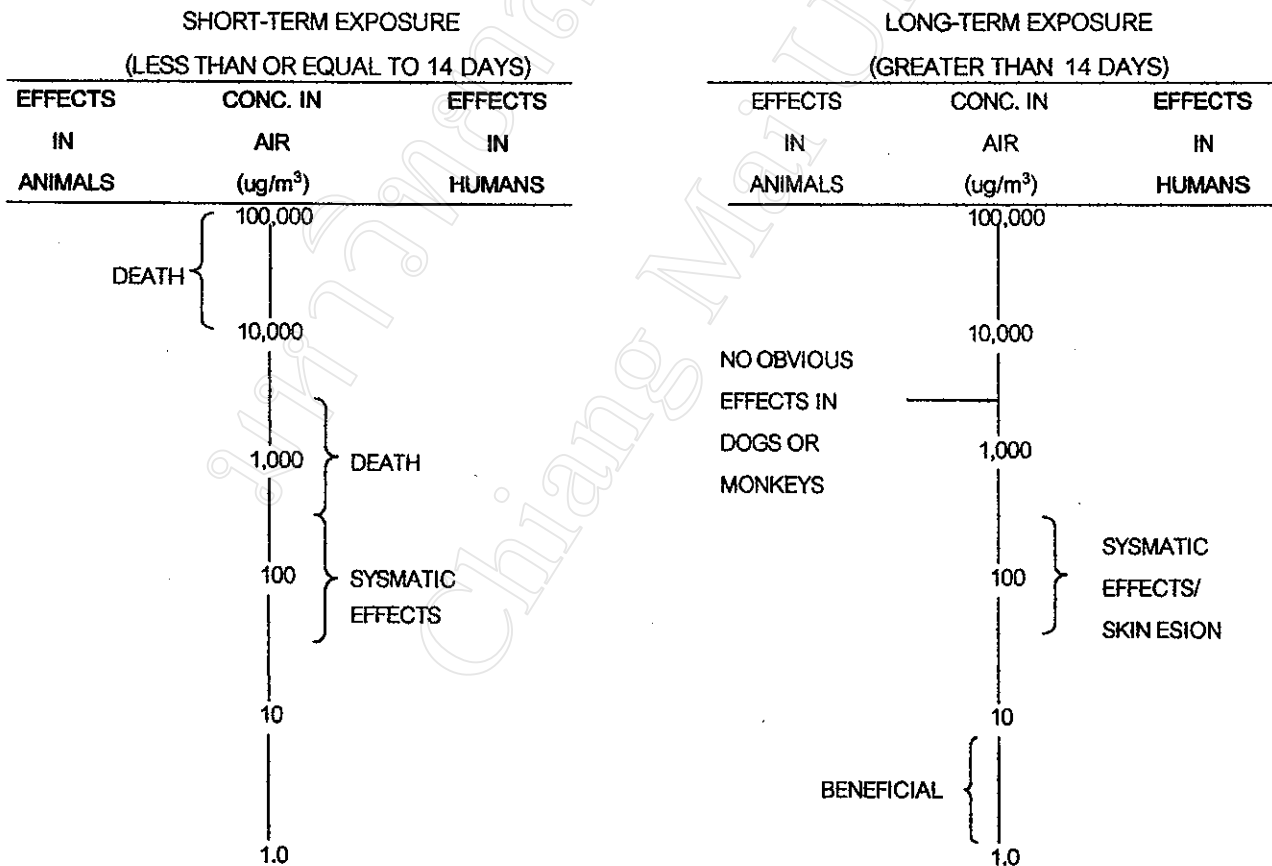


Fig 1.2 Health effects from ingesting inorganic arsenic

1.1.4 Arsenic determination

The review of 1161 scientific reports published during the last few years permitted to establish classification, as presented in Table 1.3, of the most important methods for arsenic determination. Some of them, such as the spectrophotometric analysis with silver diethyl-dithiocarbamate and certain modifications of the atomic absorption spectrometry (AAS) and the inductively coupled plasma (ICP) methods are generally standard methods [10,11].

Table 1.3 Classification of the methods for arsenic determination [11]

Method	Percentage of publications
Atomic absorption spectrometry (AAS)	25.84
Inductively coupled plasma-mass spectrometry (ICP-MS)	16.45
Neutron activation analysis (NAA)	15.68
Inductively coupled plasma-atomic emission spectrometry (ICP-AES)	19.65
X-ray fluorescence (XRF)	2.66
Molecular absorption spectrophotometry	5.77
Electrometric methods	5.25
Other methods ^a	8.70

^aSecondary ion mass spectrometry (SIMS), photon induced X-ray emission (PIXE), chemiluminescence, classical titrimetric determinations, etc.

There are a large number of techniques for determination of arsenic from various types of samples. The examples of techniques for arsenic determination are shown in Table 1.4.

Table 1.4 Examples of some techniques for arsenic determination

Sample	Technique	Analyte	Analytical Characteristic	Ref.
Soil	AFS	As(III), As(V)	LOD 0.015 $\mu\text{g l}^{-1}$ RSD 3%	12
	On-line extraction HGAAS	Total As	LOD 0.2 $\mu\text{g l}^{-1}$ for 212 μl Injection loop, corresponding to 7 ng g^{-1} in solid for 2.5 % mv^{-1} slurry in 25 ml.	13
Aqueous solution	GFAAS	As(III), As(V), DMMA,PAS	LOD 0.04-0.13 $\mu\text{g l}^{-1}$	14
	Electrochemical HG coupled with spectrophotometric	As(III)	LOD 0.05 $\mu\text{g l}^{-1}$	15
	HG electrostatic deposition GFAAS	Total As	RSD 4% at conc 40 fold above LOD 1 ml sample volume	16
	Sequential injection analysis coupled HGAAS	Total As	Linearity 2.5-50 $\mu\text{g l}^{-1}$ LOD ($3\sigma_{b,s^{-1}}$) 0.67 $\mu\text{g l}^{-1}$ RSD 1.8%	17
Natural water, biological material	ICP-MS after on- line separation and preconcentration	Total As (Cu, Se, Cd, In, Hg, Pb and Bi)	LOD varied from 0.43 ng l^{-1} to Bi 33 ng l^{-1} for Cu	18

Table 1.4 (continues)

Sample	Technique	Analyte	Analytical Characteristic	Ref.
Natural water, plant digest	Synchronized flow system with HG-ICP-MS	As(III),As(V) (Se (IV),Se (VI))	LOD 0.02 $\mu\text{g l}^{-1}$ As LOD 0.03 $\mu\text{g l}^{-1}$ Se	19
Environment, biological	Spectrophotometer	Total As	Beer's law obeyed in concentration 0.04-0.4 mg l^{-1} ϵ 3.24 $\times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$	20
Human hair	Microwave Digestion coupled AFS	Total As (Hg, Sb, Bi, Se)	Linear correlation coefficients 0.99984-0.99997 LOD 2-10 ng g^{-1}	21

1.2 Neutron activation analysis [22-24]

Neutron activation analysis (NAA) is a sensitive analytical technique useful for performing both qualitative and quantitative multi-element analysis of major, minor, and trace elements in samples from almost every conceivable field of scientific or technical interest. Neutron activation analysis was discovered in 1936 when Hevesy and Levi found that samples containing certain rare earth elements became highly radioactive after exposure to a source of neutrons.

Neutron activation is the irradiation of a nucleus with neutrons to produce a radioactive species, usually referred to as the radionuclide. The number of radionuclides produced depend on the number of target nuclei, the number of neutrons and on the factor called the cross section which defined the probability of activation occurring. If the activation product is radioactive, it will decay with a characteristic half-life. Consequently the growth of activity during irradiation will depend on the half-life of the product. The energy of the neutrons, which are bombarding the nucleus, will dictate the type of interaction that occurs and consequently the nature of the activation product. Therefore, if the nucleus is

irradiated in a neutron flux of both slow and fast neutrons, there may be more than one activation product. Similarly, interferences may occur as the result of the same radionuclide being produced by the activation of different target nuclei.

The basic essentials required to carry out an analysis of samples by NAA are a source of neutrons, instrumentation suitable for detecting gamma rays, and a detailed knowledge of the reactions that occur when neutrons interact with target nuclei. Brief descriptions of the NAA method, reactor neutron sources, and gamma-ray detection are given in section 1.2.1.

1.2.1 NAA method [23-25]

The sequence of events occurring during the most common type of nuclear reaction used for NAA, namely the neutron capture or (n, gamma) reaction, is illustrated in Figure 1.3. When a neutron interacts with the target nucleus via a non-elastic collision, a compound nucleus forms in an excited state. The excitation energy of the compound nucleus is due to the binding energy of the neutron with the nucleus. The compound nucleus will almost instantaneously de-excite into a more stable configuration through emission of one or more characteristic prompt gamma rays. The compound nucleus will almost instantaneously de-excite into a more stable configuration through emission of one or more characteristic prompt gamma rays.

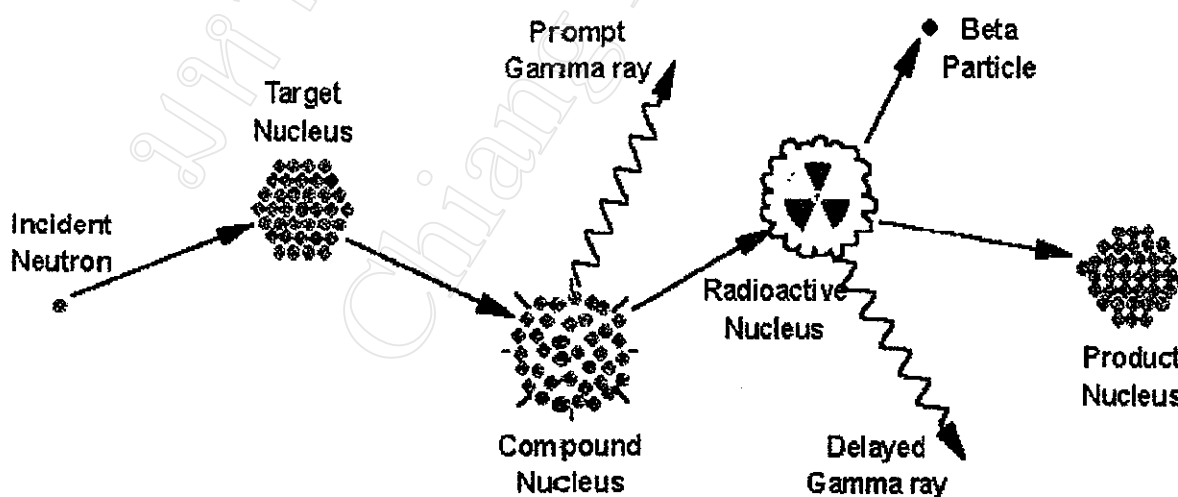


Fig. 1.3 The process of neutron capture by a target nucleus followed by the emission of gamma rays [24]

In principle, therefore, with respect to the time of measurement, NAA falls into two categories:

- (1) prompt gamma-ray neutron activation analysis (PGNAA), where measurements take place during irradiation,
- (2) delayed gamma-ray neutron activation analysis (DGNAA), where the measurements follow radioactive decay. The latter operational mode is more common; thus, when one mentions NAA it is generally assumed that measurement of the delayed gamma rays is intended.

1.2.2 Neutron sources [23]

There are several types of neutron sources (reactors, accelerators, and radioisotopic neutron emitters) one can use for NAA, nuclear reactors with their high fluxes of neutrons from uranium fission offer the highest available sensitivities for most elements. Different types of reactors and different positions within a reactor can vary considerably with regard to their neutron energy distributions and fluxes due to the materials used to moderate (or reduce the energies of) the primary fission neutrons. However, as shown in Figure 1.4, most neutron energy distributions are quite broad and consist of three principal components (thermal, epithermal, and fast).

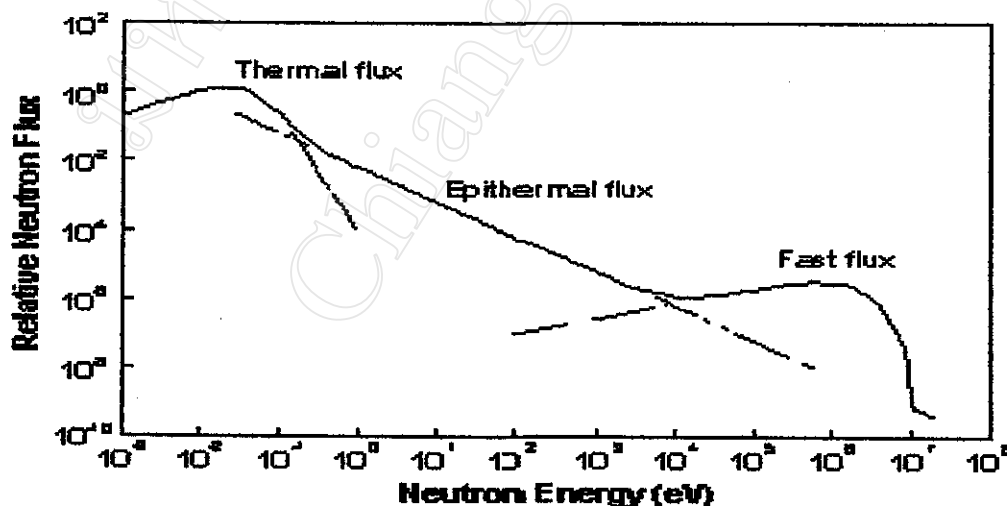


Fig. 1.4 A typical reactor neutron energy spectrum showing the various components used to describe the neutron energy regions

- The thermal neutron component consists of low-energy neutrons (energies below 0.5 eV) in thermal equilibrium with atoms in the reactor's moderator. The energy spectrum of thermal neutrons is best described by a Maxwell-Boltzmann distribution with a mean energy of 0.025 eV and the most probable velocity of 2200 m/s. In most reactor irradiation positions, 90-95% of the neutrons that bombard a sample are thermal neutrons.
- The epithermal neutron component consists of neutrons (energies from 0.5 eV to about 0.5 MeV) which have been only partially moderated. A cadmium foil 1 mm thick absorbs all thermal neutrons but will allow epithermal and fast neutrons above 0.5 eV in energy to pass through. In a typical unshielded reactor irradiation position, the epithermal neutron flux represents about 2% the total neutron flux. Both thermal and epithermal neutrons induce (n, gamma) reactions on target nuclei. An NAA technique that employs only epithermal neutrons to induce (n,gamma) reactions by irradiating the samples being analyzed inside either cadmium or boron shields is called epithermal neutron activation analysis (ENAA).
- The fast neutron component of the neutron spectrum (energies above 0.5 MeV) consists of the primary fission neutron, which still have much of their original energy following fission. Fast neutrons contribute very little to the (n, gamma) reaction, but instead induce nuclear reactions where the ejection of one or more nuclear particles - (n, p), (n, n'), and (n, 2n) - are prevalent. In a typical reactor irradiation position, about 5% of the total flux consists of fast neutrons. An NAA technique that employs nuclear reactions induced by fast neutrons is called fast neutron activation analysis (FNAA).

1.2.3 Activation with neutron [24–25]

In a neutron-induced reaction, the growth of the product is dependent on the size of the neutron flux. The larger the greater the rate at which interactions occur:

$$\text{Activation rate} \propto \text{neutron flux } (\phi)$$

The activation rate is also directly proportional to the number of target nuclei present:

$$\text{Activation rate} \propto \text{number of nuclei present } (N)$$

The number of target nuclei present will depend on the isotopic abundance of the particular isotope of interest. Avogadro's number (N_A) represents the total number of atoms in the atomic weight (A) of any element, Therefore the Avogadro's number, divided by the atomic weight gives the total number of atoms per gram:

$$N = N_A / A \quad (1.1)$$

and for a mass w , of the element, the total number of target nuclei will be:

$$N = wN_A / A \quad (1.2)$$

However, there may be more than one isotope of an element, such as in the case of calcium where there are six stable isotopes: ^{40}Ca , ^{42}Ca , ^{43}Ca , ^{44}Ca , ^{46}Ca , and ^{48}Ca . As an example, ^{48}Ca is only present as 0.185% of total. In such cases the number of target nuclei must be corrected for the isotopic abundance (θ):

$$N = wN_A \theta / A \quad (1.3)$$

The number of target nuclei is therefore proportional to the mass of element present and since the growth of the activation product is proportional to the number of target nuclei it follows that the activation rate is proportional to the mass of element:

$$\text{Activation rate} \propto \text{mass of element } (w)$$

It is therefore possible to deduce the mass of element present from the induced activity. This forms the basis of the neutron activation analysis technique. If the neutron flux remains constant then the "calibration curve" for an element can be determined by plotting the induced activity against the mass of the element.

- **Cross Section**

The relationship between activation rate, the number of target nuclei and neutron flux is expressed by the term "cross section" (σ). The cross section is simply a physical constant:

$$\text{Activation rate} = \sigma \phi N \quad (1.4)$$

where N is the number of target nuclei, in atoms

ϕ is the neutron flux, in neutrons $\text{m}^{-2} \text{s}^{-1}$

σ is the cross section, in m^2

activation rate is in events s^{-1} .

Substituting:

$$N = wN_A \theta/A \quad (1.5)$$

Into the expression for activation rate, it becomes:

$$\text{Activation rate} = \sigma \phi wN_A \theta/A \quad (1.6)$$

Cross section are usually expressed in barns which are 10^{-28} m^2 . As a rough guide, target nuclei with a cross section in the order of barns will activate well but a cross section in millibarns indicates poor activation. It is important to remember that each stable isotope of the same element will have different cross section. Consequently, one isotope may have a high cross section and become very active while another isotope of the same element may have a small cross section and be activated to a much smaller extent. It is therefore important to consider the cross sections when deciding which target nuclide to use in activation analysis.

The neutron cross section for a particular nucleus will depend on the energy of neutron. Many nuclei, particularly of low atomic number absorb thermal neutrons with cross sections which decrease linearly with increasing velocity of the neutron (known as $1/v$ absorbers). It is usual to refer to thermal cross sections for the absorption of neutron with an average velocity of 2200 m s^{-1} . Tables of cross section are available for activation with neutrons. In the tables the cross section may be expressed in different forms and the total cross section given for a particular target will be composed of a number of partial cross section, dependent on the activation process, including (n, γ) , (n, p) and (n, α) reactions. However for most thermal neutron activation the main process is the (n, γ) reaction involving the neutron radiation capture cross section (σ_γ).

Not all target nuclei are $1/v$ absorbers and there are many examples of nuclei, which preferentially absorb epithermal neutrons. At these higher energies the neutron cross section is referred to as the resonance integral and the radiative capture resonance integral (I_γ) is used. The values for capture cross sections and resonance integrals are given by Mughabhab *et al.* (1984) [26] and some typical examples are shown in Table 1.5.

Table 1.5 Capture cross section (σ_γ) and resonance integral (I_γ) (in barns) for some typical activation targets

Target	σ_γ	I_γ	Target	σ_γ	I_γ
23-Na	0.4	0.31	63-Cu	4.5	5.0
26-Mg	0.038	0.026	75-As	4.3	61
27-Al	0.23	0.17	81-Br	2.4	60
55-Mn	13.3	14.0	109-Ag	91	1400
59-Co	37.2	74	197-Au	98.7	1550

It can be seen from the cross section values that the lighter elements have thermal cross section and resonance integrals in the same order. They are the $1/v$ absorbers. On the other hand the isotopes ^{109}Ag , ^{152}Sm and ^{197}Au have very large resonance integrals compared to the thermal cross section, indicating that they are strong resonance in the region above the cadmium cutoff energy. In these cases it is important to include the resonance integral term in the calculation of the activation rate:

$$\text{Activation rate} = \sigma_\gamma \phi_{\text{th}} N + I_\gamma \phi_{\text{epi}} N \quad (1.7)$$

ϕ_{th} is thermal neutron flux

ϕ_{epi} is epithermal neutron flux

- **Decay rate**

If the product nuclide in a neutron-induced reaction is stable the number of nuclei produced is easily calculated from the activation equation by multiplying with the length of irradiation, t :

$$\text{Activation rate} = \sigma \phi N \quad (1.8)$$

$$\text{Number of nuclei} = \sigma \phi N t \quad (1.9)$$

However, if the product nuclide is radiative, it will have a decay rate, which must be taken into account. The radionuclide produced will decay with a characteristic half-life. If there are N^* radiative nuclei, the rate of decay of the nuclei is proportional to N^* .

$$\text{Decay rate, } dN^*/dt \propto -N^* \quad (1.10)$$

$$\text{Decay rate, } dN^*/dt = -\lambda N^* \quad (1.11)$$

where λ is the decay constant, which has a characteristic value for each radionuclide. If the equation is integrated between the limits N^*_o at time zero, and N^* remaining at time t :

$$N^* = N^*_o \text{ epx } (-\lambda t) \quad (1.12)$$

It is from the above expression which the term half-life ($T_{1/2}$), which is the time for half the nuclei to decay, is derived:

$$N^*_o/2 = N^*_o \text{ epx } (-\lambda T_{1/2}) \quad (1.13)$$

$$T_{1/2} = \ln 2 / \lambda = 0.693/\lambda \quad (1.14)$$

A semilogarithmic plot of the decay rate against time will give a straight-line graph with a slope of $-\lambda$. The half-life of the radionuclide can be read directly from the time taken for the decay rate to be reduced by a half. A table of the half-life from Brown and Firestone (1986) for some radionuclides commonly measured by neutron activation analysis are given in Table 1.6. Because the half-life is characteristic for a particular radionuclide it can be used to identify an unknown species or confirm the identity of the radionuclide being measured.

Table 1.6 Half-life values for typical activation products

Product	Half-life	Product	Half-life
24-Na	14.57 hr	64-Cu	12.70 hr
27-Mg	9.46 min	76-As	26.3 hr
28-Al	2.24 min	82-Br	35.3 hr
56-Mn	2.578 h	110-Ag	24.6 s
60-Co	5.27y	198-Au	2.69 d

- **Induced Activity**

If the activation product is radioactive and decays with its characteristic half-life, the radionuclide is being produced at the rate described by the activation equation

and decaying with the characteristic half-life. Consequently the growth of the activity is governed by the difference between them:

Production rate = activation rate – decay rate

$$dN^*/dt = \sigma \phi N - \lambda N^* \quad (1.15)$$

$$N^* = \sigma \phi N (1 - \exp(-\lambda t)) / \lambda \quad (1.16)$$

The activity or disintegration rate (A_o), at the end of the irradiation time t , is then:

$$A_o = \lambda N^* = \sigma \phi N (1 - \exp(-\lambda t)) \quad (1.17)$$

Consequently the growth of the induced activity with time is controlled by the half-life of the activation product, This is demonstrated in Figure 1.5 It can be seen that the majority of the activity is produced during the first two half-lives. When the irradiation time is very long the expression for activity become close to the maximum possible activity for a particular neutron flux, called the saturation activity (A_s):

$$A_s = \sigma \phi N \quad (1.18)$$

The saturation activity is independent of the half-life of the activation product and depends only on the value of the neutron flux and neutron cross section. Unless the activation product is relatively short-lived it is not convenient to allow the growth curve to reach saturation. The usual form of the equation for activity at the end of an irradiation for a time t is:

$$A_o = \sigma \phi N (1 - \exp(-\lambda t)) \quad (1.19)$$

It is possible to calculate the induced specific activity for particular length of irradiation, knowing the nuclear constants for the nuclide of interest and the neutron flux:

$$A_o = \sigma \phi w N_A \theta (1 - \exp(-\lambda t)) / A \quad (1.20)$$

Usually in neutron activation analysis, the activity of the radionuclide is measured experimentally in a sample to deduced the unknown mass of the element using the activation equation:

$$W = A_o A / (\sigma \phi N_A \theta (1 - \exp(-\lambda t))) \quad (1.21)$$

Corrections must also be made for the decay period t_d before counting:

$$W = A_o \exp(-\lambda t_d) A / (\sigma \phi N_A \theta (1 - \exp(-\lambda t))) \quad (1.22)$$

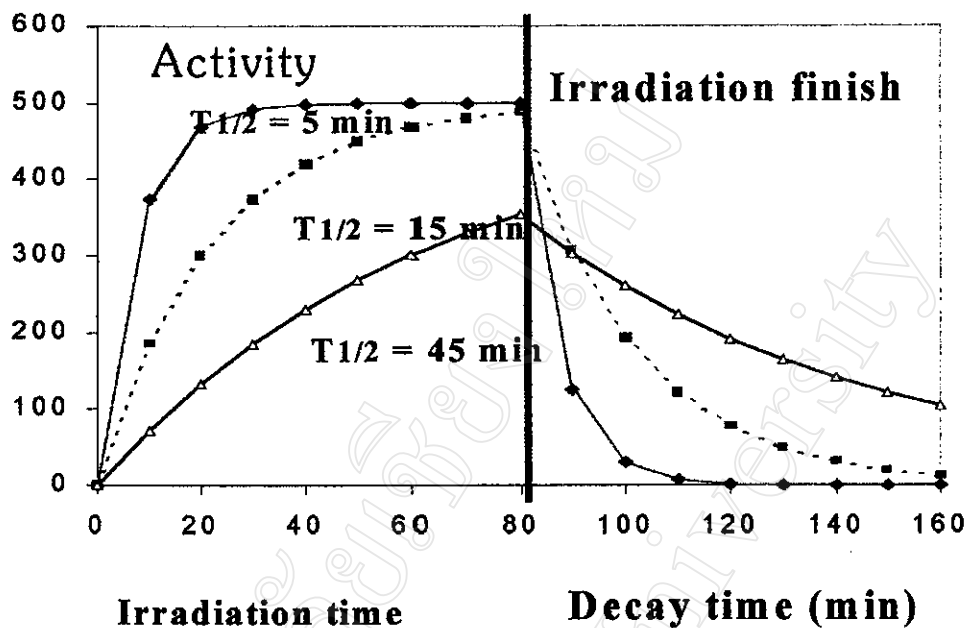


Fig1.5 Activation curve

1.2.4 Measurement of gamma ray [22,23]

The instrumentation used to measure gamma ray from radioactive samples generally consists of a semiconductor detector, associated electronics, and a computer-based, multi-channel analyzer (MCA/computer). Most NAA labs operate one or more hyperpure or intrinsic germanium (HPGe) detectors which operate at liquid nitrogen temperatures (77 degrees K) by mounting the germanium crystal in a vacuum cryostat, thermally connected to a copper rod or "cold finger". Although HPGe detectors come in many different designs and sizes, the most common type of detector is the coaxial detector which in NAA is useful for measurement of gamma-rays with energies over the range from about 60 keV to 3.0 MeV. The two most important performance characteristics requiring consideration when purchasing a new HPGe detector are resolution and efficiency. Other characteristics to consider are peak shape, peak-to-Compton ratio, crystal dimensions or shape, and price.

The detector's resolution is a measure of its ability to separate closely spaced peaks in a spectrum. In general, detector resolution is specified in terms of the full width at half maximum (FWHM) of the 122-keV photopeak of Co-57 and the

1332-keV photopeak of Co-60. For most NAA applications, a detector with 1.0-keV resolution or below at 122 keV and 1.8 keV or below at 1332 keV is sufficient.

Detector efficiency depends on the energy of the measured radiation, the solid angle between sample and detector crystal, and the active volume of the crystal. A larger volume detector will have a higher efficiency. In general, detector efficiency is measured relative to a 3-inch by 3-inch sodium iodide detector using a Co-60 source (1332-keV gamma ray) at a distance of 25 cm from the crystal face. A general rule of thumb for germanium detectors is 1 percent efficiency per each 5 cc of active volume. As detector volume increases, the detector resolution gradually decreases. For most NAA applications, an HPGe detector of 15-30 percent efficiency is adequate.

1.2.5 Quantitative determination of activity [23-24,26]

The activity of a sample can be measured by gamma ray spectrometry, provided that the efficiency of the detector is known for the counting position used. The activity is calculated from peak area of the gamma ray line. The peak area divided by the counting time gives activity in count per second, which must be corrected for detector efficiency at the energy to give the gamma per second. These have to be converted to disintegrations per second using the branching ratio (P) for the gamma ray of interest.

$$\text{Gammas per second} = (\text{count per second}) / E \quad (1.23)$$

$$\text{Disintegrations per second} = (\text{gammas per second}) / P \quad (1.24)$$

Finally, the activity at time 0 (A_0) in disintegrations per second must be corrected for decay time (t_d) prior to counting:

$$A_0 = (\text{disintegrations per second}) / \exp(-\lambda t_d) \quad (1.25)$$

To summarize,

$$A_0 = (\text{counts per second}) / E P \exp(-\lambda t_d) \quad (1.26)$$

If the half-life of the nuclide is short it may also be necessary to correct by the factor for decay during counting time (t_c):

$$\lambda t_c = (1 - \exp(-\lambda t_c)) \quad (1.27)$$

Any active source can be measured in this way on a gamma ray spectrometer. Environmental counting to monitor radioactivity in the environment requires only a further correction for the weight of sample to provide the Bq kg⁻¹ in an active sample.

In The case of neutron activation analysis the original sample is inactive and only becomes activated by irradiation in a neutron source. The activity is measured to deduce the amount of the element in the sample, using the activation equation.

- **Absolute activation analysis**

The activation equation derived in section 1.23 can be solved to give the mass of the element using the measured count rate, knowing the value of the other factors:

$$W = A_o A / (\sigma \phi N_A \theta (1 - \exp(-\lambda t))) \quad (1.28)$$

And since:

$$A_o = (\text{counts per second}) / E P \exp(-\lambda t_d)$$

$$W = (\text{counts per second}) A \exp(\lambda t_d) / E P (\sigma \phi N_A \theta (1 - \exp(-\lambda t)))$$

The atomic weight, Avogadro's number and isotopic abundance are all well-known constants. The cross section, on the other hand, is evaluated using measurement of a known mass of an element and the activation equation above. Uncertainties can be quite high particularly for some radionuclides with short half-lives. The decay constants and the branching ratio are usually known precisely but they also are precise in the case of short half-life radionuclides. Determination of the neutron flux and detector efficiency terms can only be made locally.

The value of the neutron flux is often the factor in the equation that is least well known, since it varies not only from source to source but also within the source itself.

Clearly, elemental analysis using the parametric method is only as accurate as the nuclear data on which the analysis is based; thus, the accurate measurement of pertinent nuclear data is imperative.

- **Comparative Method**

The procedure generally used to calculate concentration (i.e., ppm of element) in the unknown sample is to irradiate the unknown sample and a comparator standard containing a known amount of the element of interest together in the reactor. If the unknown sample and the comparator standard are both measured on the same

detector, then one needs to correct the difference in decay between the two. One usually decay corrects the measured counts (or activity) for both samples back to the end of irradiation using the half-life of the measured isotope. The equation used to calculate the mass of an element in the unknown sample relative to the comparator standard is

$$\frac{A_{sam}}{A_{std}} = \frac{m_{sam} (e^{-\lambda T_d})_{sam}}{m_{std} (e^{-\lambda T_d})_{std}} \quad (1.29)$$

where A_{sam}, A_{std} = activity of the sample (sam) and standard (std), m_{sam}, m_{std} = mass of the element, λ = decay constant for the isotope and T_d = decay time. When performing short irradiation, the irradiation, decay and counting times are normally fixed the same for all samples and standards such that the time dependent factors cancel. Thus the above equation simplifies into

$$C_{sam} = C_{std} \frac{W_{std} A_{sam}}{W_{sam} A_{std}} \quad (1.30)$$

where C_{sam}, C_{std} are concentrations of the element in sample and standard, W_{sam}, W_{std} are weights of the sample and standard.

1.2.6 Instrumental and radiochemical NAA [22-23]

With the use of automated sample handling, gamma-ray measurement with solid-state detectors, and computerized data processing it is generally possible to simultaneously measure more than thirty elements in most sample types without chemical processing. The application of purely instrumental procedures is commonly called instrumental neutron activation analysis (INAA).

If chemical separations are done to samples after irradiation to remove interference or to concentrate the radioisotope of interest, the technique is called radiochemical neutron activation analysis (RNAA).

1.2.7 Sensitivities for determination of elements by NAA [22-23]

The sensitivities for NAA are dependent upon the irradiation parameters (i.e., neutron flux, irradiation and decay times), measurement conditions (i.e., measurement time, detector efficiency), nuclear parameters of the elements being measured (i.e., isotope abundance, neutron cross-section, half-life, and gamma-ray abundance). The accuracy of an individual NAA determination usually ranges between 1 to 10 percent of the reported value. Table 1.7 lists the approximate sensitivities for determination of elements assuming interference free spectra.

Table 1.7 Estimated detection limits for INAA using decay gamma rays, assuming irradiation in a reactor with neutron flux of $1 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$

Sensitivity (picograms)	Elements
1	Dy, Eu
1 – 10	In, Lu, Mn
$10 - 10^2$	Au, Ho, Ir, Re, Sm, W
$10^2 - 10^3$	Ag, Ar, As, Br, Cl, Co, Cs, Cu, Er, Ga, Hf, I, La, Sb, Sc, Se, Ta, Tb, Th, Tm, U, V, Yb
$10^3 - 10^4$	Al, Ba, Cd, Ce, Cr, Hg, Kr, Gd, Ge, Mo, Na, Nd, Ni, Os, Pd, Rb, Rh, Ru, Sr, Te, Zn, Zr
$10^4 - 10^5$	Bi, Ca, K, Mg, P, Pt, Si, Sn, Ti, Tl, Xe, Y
$10^5 - 10^6$	F, Fe, Nb, Ne
10^7	Pb, S

1.3 Aims of the research

The aims of this research work can be summarized as follows:

1.3.1 To study and obtain the optimum INAA conditions for arsenic analysis in soil sample,

1.3.2 To determine the arsenic content in contaminated soil samples by INAA.