CHAPTER 1
INTRODUCTION

1.1 Arsenic

1.1.1 Information about Arsenic [1,2]

Arsenic has atomic symbol As, atomic number 33 and atomic weight 75. It is a metalloid element of group VA of the periodic table. It has three allotropes yellow, black and grey. The grey metallic form is the most stable and most common. Arsenic is a naturally occurring element in the environment. Many minerals contain arsenic but the most common sources are impurities in sulphide ores. Arsenic compounds are accumulative poisons.

Figure 1.1 Arsenic compounds

Arsenic is a naturally occurring element widely distributed in the earth's crust. In the environment, arsenic combines with oxygen, chlorine, and sulfur to form inorganic arsenic compounds. Arsenic in animals and plants combines with carbon and hydrogen to form organic arsenic compounds. Inorganic arsenic compounds are mainly used to preserve wood. Organic arsenic compounds are used as pesticides, primarily on cotton plants. The arsenic concentration in most potable waters seldom exceeds 10 μg/L, although values as high as 100 μg/L have been reported. Aqueous arsenic in the form of arsenite, arsenate and organic arsenic may result from mineral dissolution, industrial discharge or the application of herbicides. The toxicity of arsenic depends on its chemical form.

Despite arsenic's reputation as a poison, it actually has fairly low toxicity in comparison with some other metals, although with chronic exposure, there is some concern about arsenic's effect on chromosomes and its carcinogenicity. In fact, arsenic may even be essential and functional to humans in very small amounts. It has been shown to be essential in rats and other animals, though it is found at higher level than in human.

Organic arsenic as arsenates (+5 form of arsenic) and elemental arsenic both found naturally in the earth and in foods do not readily produce toxicity. In fact, they are handled fairly easily by the body and eliminated by the kidney. The inorganic arsenites or trivalent forms of arsenic, such as arsenic trioxide used industrially and found as a food contaminant, seem to create the problems. They accumulate in the body, particularly in the skin, hair, and nails, as well as in internal organs. On the average, there is about 10-20 mg. of arsenic in human body; higher levels may lead to problems. Arsenic can accumulate when kidney function is decreased. Luckily, absorption of arsenic is fairly low, usually less than 5 percent, so most of it is eliminated with the feces and some with urine. Hair and blood are currently the best indicator to evaluate arsenic levels in the body.

Sources: Arsenic is present in small amount in soil and therefore is present in our food. It is present in the ocean, so there is some arsenic in most seafood, especially the filtering mollusks, such as clams and oysters. Some arsenic is present as a contaminant in meat as well. Arsenic is also found in many fuel oils and coal, so it is added to the environment when these are burned. Weed killers and some insecticides (particularly the lead-arsenate sprays) are the main sources of arsenic contamination. This application is responsible for a twenty fold increase in the level found in human since ancient times.

Methods of toxicity: Though there is some suggestion that arsenic may be useful in human body, no clear biological function has yet been proved. In some studies, arsenic has been shown to promote longevity in rats. The importance of arsenic in cardiac function in humans is being studied. Though arsenic can displace phosphorus and phosphates in some reactions in the body, this is not known to lead to any definite physiological change.

Symptoms of toxicity: These are not clearly known. The average intake of arsenic is estimated at 1 mg per day, mainly from food, but this organic arsenic bound in food is generally well tolerated. Elemental arsenic can accumulate in the body and be a problem, the oxidized forms of arsenic are toxic in large amounts. Arsenic trioxide is used industrially and is the strongest poison of the arsenic species. Below 7-10 ppm of arsenic in hair is a relatively safe level.

Amounts leading to toxicity: There is no clear picture of arsenic deficiency or toxicity in human. Possible effects of arsenic toxicity include hair loss, dermatitis, diarrhea and other gastrointestinal symptoms, fatigue, headache, confusion, muscle pain, red and white blood cell problems, neurologic symptoms, and liver and kidney damage. Acute arsenic exposure may cause a rapid series of symptoms. Arsine gas exposure is very toxic to lung and kidney and is often fatal. Death from low-level, chronic arsenic exposure has the appearance of death from natural causes, very good for mystery books.

Susceptible: Exposure to insecticides, weed killers, contaminated meats, and fumes from the burning of arsenic-containing coals and oils may cause some toxicity problems. Miners, smelters, and vineyard workers may have a higher level of arsenic trioxide exposure and a higher incidence of lung cancer. The body does not eliminate trivalent arsenic as easily as it does with some other toxic minerals, so buildup can occur with regular exposure, generating chronic problems.

Treatment: Chelation therapy with EDTA can eliminate some arsenic, but not as easily as it clears some of the other heavy metals. Dimercaprol is the treatment of choice for arsenic toxicity, but it should be given in the first 24 hours after exposure. Vitamin C protects the body somewhat from arsenic toxicity.

Prevention: Avoiding sources of contamination from arsenic.

General informations of arsenic are given in **Table 1.1**

Table 1.1 General Informations of Arsenic [3]

General Information				
Chemical formula	As			
Atomic Number	33			
Relative Atomic Mass (^{12}C=12.OOO)	74.9216			
Position in Periodic Table	VA			
Melting Point/K	1090			
Boiling Point/K	889			
Density/kg m	5780 (293K)			
Ground State Electron Configuration	$[Ar]3d^{10}4s^24p^3$			
Electron Affinity(M-M3/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	Inorganic : trivalent,e.g. arsenites, and pentavalent, e.g. arsenates Organic : mono and di-methyl arsenic acid			
Commonly occured with	Antimony, Arsenopyrite, Tennantite			
Nuclides	^{73}As	^{74}As	^{75}As	^{76}As
Atomic mass	72.924	73.924	74.922	75.922
Natural abundance	0%	0%	100%	0%

1.1.2 Arsenic in environment , exposed and effect of arsenic [1]

Arsenic enters the environment

Arsenic cannot be destroyed in the environment. It can only change its form. Arsenic in air will settle to the ground or is washed out of the air by rain. Many arsenic compounds can dissolve in water. Fish and shellfish can accumulate arsenic, but the arsenic in fish is mostly in a form that is not harmful.

Exposed to arsenic

- Eating food, drinking water, or breathing air containing arsenic.
- Breathing contaminated workplace air.
- Breathing sawdust or burning smoke from wood treated with arsenic.
- Living near uncontrolled hazardous waste sites containing arsenic.
- Living in areas with unusually high natural levels of arsenic in rock.

Arsenic in drinking water

Arsenic may enter the groundwater from erosion of natural sources, as well as contamination from industrial discharges from semiconductor manufacturing, from petroleum refining, and also from wood preservatives. It is also used as both inorganic and organic compounds in herbicides or pesticides.

Arsenic affect in health

Breathing high levels of inorganic arsenic can give a sore throat or irritated lungs. Ingesting high levels of inorganic arsenic can result in death. Lower levels of arsenic can cause nausea and vomiting, decrease production of red and white blood cells, abnormal heart rhythm, damage to blood vessels, and a sensation of "pins and needles" in hands and feet. Ingesting or breathing low levels of inorganic arsenic for a long time can cause a darkening of the skin and the appearance of small "corns" or "warts" on the palms, soles, and torso. Skin contact with inorganic arsenic may cause redness and swelling. Organic arsenic compounds are less toxic than inorganic arsenic

compounds. Exposure to high levels of some organic arsenic compounds may cause similar effects as inorganic arsenic.

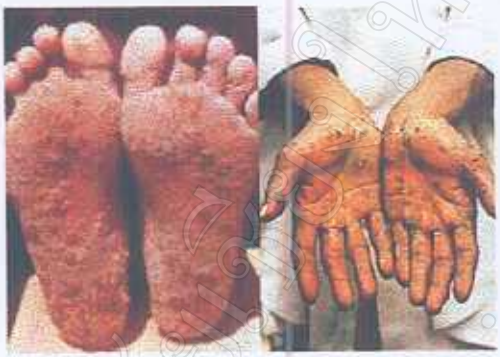

Figure 1.2 The effects of arsenic in drinking water. Skin damage of low arsenic poisoning in one victim

Arsenic to cause cancer

Several studies have shown that inorganic arsenic can increase the risk of lung cancer, skin cancer, bladder cancer, liver cancer, kidney cancer, and prostate cancer. The World Health Organization (WHO), the Department of Health and Human Services (DHHS), and the Environment Protection Agency (EPA) have determined that inorganic arsenic is a human carcinogen.

Medical test to show exposed to arsenic

There are tests to measure the level of arsenic in blood, urine, hair, or fingernails. The urine test is the most reliable test for arsenic exposure within the last few days. Tests on hair and fingernails can measure exposure to high levels or arsenic over the past 6-12 months. These tests can determine if you have been exposed to above-average levels of arsenic. They cannot predict how the arsenic levels in your body will affect your health.

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The recommendations to protect human health

United State Environment Protection Agency(EPA) has set limits on the amount of arsenic that industrial sources can release to the environment and has restricted or canceled many uses of arsenic in pesticides. EPA has set a limit of 0.05 parts per million (ppm) for arsenic in drinking water. The EPA arsenic drinking water standard of 0.01 ppm (10 ppb) reported in the Agency for Toxic Substances and Disease Registry(ATSDR) February 2001 Arsenic was based on the EPA final rule for arsenic in drinking water, published on January 22, 2001. However, the EPA is currently reviewing the science and cost estimate supporting this rule, and, in the interim, has reverted to the previous standard for arsenic. Thus, the current EPA arsenic drinking water standard remains at 0.05 ppm (50 ppb). The Occupational Safety and Health Administration United State has set limits of 10 microgram arsenic per cubic meter of workplace air (10 $\mu g/m^3$) for 8 hour shifts and 40 hour work weeks.

Table 1.2 Arsenic concentration in the environment [4]

Location	Concentration
Crust	1.5 ppm
Sea water	1.5 ppb
Fresh water:	
normal	1-10 ppb
polluted	10-1000 ppb
Soils:	
normal	1-10 ppm
contaminated	up to 200 ppm
Atmosphere	trace
Human body:	
average	0.25 ppm
hair	1 ppm

1.1.3 Chronic arsenic poisoning in Ronpiboon district, Nakhon Sri Thammarat province[5]

Ronpiboon district is 35 kilometers south-west of the central city in Nakhon Sri Thammarat province. Main water resources are from Ronna canal, an old mining swamp, underground and rain water. The environmental background of this area has 0.1 % arsenopyrite, 34.4% ferric compound, 40% arsenic compounds and 19.7% sulfur. These arsenic compounds are easily metabolized and highly soluble in low pH, so it can spread through surface water .

In August 1987, a female, living in the Ronpiboon district, was referred from Nakhon Sri Thammarat Regional Hospital to the Institute of Skin Diseases in Bangkok due to the problem of generalized chronic eczema. Skin biopsy showed cancerous change from chronic arsenic exposure. Cast investigation found clustering cases of chronic arsenic poisoning within the family and high concentrations (2.7 ppm) of arsenic in the drinking water. The Division of Epidemiology together with the Nakhon Sri Thammarat Provincial Health Office then conducted an epidemiological study in this area.

During a survey Rodcline and Metadilokkul (1988) conducted in 1987-1988, 824 cases of different stages of chronic arsenic poisoning (**Table 1.3**) were found from the Ronpiboon district and another 147 from neighbouring districts (**Table 1.4**)

Table 1.3 Classification of chronic arsenic poisoning using as standard diagnosis in Thailand, 1987-1994

Stage	Criteria of diagnosis
0	No skin lesion, high arsenic level in blood, urine, hair or nail
1a	Spotty dermal melanosis of palm and sole
1b	Pin-headed dermal less than 5 papules of palm and sole
2	Pin-headed dermal more than 5 papules of palm and sole
3	Pin-headed dermal papules with keratosis papules with crater size more than 0.5cm
4	Scaly erythematous or brownish patches of Bowen's disease, Basal cell epithelioma and squamous cell carcinoma, usually generalize

Table 1.4 Number of chronic arsenic poisoning in Ronpiboon District and other districts, by stage, 1987-1988

	Stage of diagnosis				
District	0	1	2	3	4
Ronpiboon	637	152	29	6	824
Others	124	21	2	-	147

Source: Institute of Skin Diseases, Department of Medical Services and Ronpiboon Hospital.

After reporting cases of chronic arsenic poisoning in 1987, locally named 'Kai Dam', in the newspaper, the Department of Geology (1988) investigated the source of environmental contamination of arsenic in the Ronpiboon district. It was postulated that contamination was from Arsenopyrite - FeAs, probably related to the

mining process that had taken place in this area for a hundred years. Study of the hydrogeology showed five main reasons of contamination;

1) High arsenic level in the natural background of this area.
2) Mining process, using acid to extract contamination from tin and wolfram, accelerated of arsenic through natural water resources.
3) Hydrogeology of this area allowed high accumulation and spreading of arsenic in the water resource.
4) Lack of a safe water supply for the inhabitants.
5) Belief and attitude of the southern people to consume deep well water rather than piped or rain water.

The adverse health effect from arsenic contamination of natural water sources in Ronpiboon district, Nakhon Sri Thammarat Province, southern part of Thailand, are extensive. However, no blackfoot disease was found here. Several interventions of the government, since 1987, have not improved the situation of chronic illnesses: the latest prevalence survey in 1994 showed a high prevalence of arsenic levels detected from nails and hair. Traditional belief and practice of villagers about water consumption affect the intervention of the government. For the past eight years the local government and local officers have been changedvery often, so any interventions could not be continued to make a dramatic change in this district.

1.1.4 The method for arsenic determination

Arsenic The review of 1161 scientific reports published during the last few years permitted to establish classification, as presented in **Table 1.5**, 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 [6,7].

Table 1.5 Classification of the methods for arsenic determination

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

[a]Secondary 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 1.6.** The activation analysis compared to other analytical techniques for trace elements are shown in **Table 1.7.**

1.1.5 Treatment technologies/removal from water

Because arsenic in drinking water is responsible for most medical problems and it is very dangerous, many techniques have been introduced for its removal from water. Some of them are: coagulation/filtration, lime softening, activated alumina, ion exchange, reverse osmosis and electrodialysis reversal.

Table 1.6 Examples of some techniques for arsenic determination

Sample	Technique	Analyte	Analytical Characteristic	Ref.
Soil	AFS	As(III), As(V)	LOD 0.015 μg l^{-1} RSD 3%	7
	On-line extraction HGAAS	Total As	LOD 0.2 μg l^{-1} for 212 μl Injection loop,corresponding to 7 ng g^{-1} in solid for 2.5 % mg^{-1} slurry in 25 ml	8
Aqueous solution	GFAAS	As(III), As(V), DMMA,PAS	LOD 0.04-0.13 μg l^{-1}	9
	Electrochemical HG coupled with spectrophotometric	As(III)	LOD 0.05 μg l^{-1}	10
	HG electrostatic deposition GFAAS	Total As	RSD 4% at conc. 40 fold above LOD 1 ml sample volume	11
	Sequential injection analysis coupled HGAAS	Total As	Linearity 2.5-50 μg l^{-1} LOD 0.67 μg l^{-1} RSD 1.8%	12
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	13
Natural water, plant digest	Synchronized flow system with HG-ICP-MS	As(III),As(V) (Se (IV),Se (VI))	LOD 0.02 μg l^{-1} As LOP 0.03 μg l^{-1} Se	14

Table 1.7 Activation analysis compared to other analytical techniques for trace elements[a] [15]

Methods	Detection: Necessary quantity of element	Sample size: Necessary quantity of element	Possibility of nondestructive analysis	Possibility of multielement analysis	*Analysis time
1.Activation analysis	$>10^{-12}$ g	mg - g	Yes	Yes	min to weeks
2.Spark mass spectrometry	10^{-3}-10^{-9} g	mg	No	Yes	hours
3.Molecular absorption spectrometry	10^{-5}-10^{-7} g	10 mg-1 g	No	No	hours
4.Emission spectrometry	10^{-5}-10^{-6} g	10-100 mg	No	Yes	1-2 hr
5.Flam emission and atomic absorption spectrometry	10^{-6}-10^{-7} g	0.1-1 g	No	No	1-2 hr
6.Flamless atomic absorption spectrometry	10^{-11}-10^{-12} g	0.1-2 mg	No	No	1-2 hr
7.X-ray fluorescence	10^{-3}-10^{-5} g	0.1-2 g	Yes	Yes	1 hr
8.Polarography	10^{-6}-10^{-7} g	0.01-1 g	No	No	1-2 hr

*The analysis time represents the complete analysis, including dissolution. In fact, analyses by atomic and molecular absorption, emission and polarography require only a few minutes.

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1.2 Activation Analysis [15]

Neutrons, gamma rays and energetic charge particles can react with isotopes of various elements and produce radioactive nuclides. The characteristic radiation emitted by the nuclides produced can be used for qualitative detection and quantitative determination of various elements. Often elements in parts per million or parts per billion level can be analyzed by this technique.

1.2.1 Neutron activation analysis[16]

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. For many elements and applications, NAA offers sensitivities that are superior to those attainable by other methods, on the order of parts per billion or better. In addition, because of its accuracy and reliability, NAA is generally recognized as the "referee method" of choice when new procedures are being developed or when other methods yield results that do not agree. Worldwide application of NAA is so widespread. It is estimated that approximately 100,000 samples undergo analysis each year.

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. From this observation, they quickly recognized the potential of employing nuclear reactions on samples followed by measurement of the induced radioactivity to facilitate both qualitative and quantitative identification of the elements present in the samples.

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 below.

The sequence of events occurring during the most common type of nuclear reaction used for NAA, namely the neutron capture or (n,γ) 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. In many cases, this new configuration yields a radioactive nucleus which also de-excites (or decays) by emission of one or more characteristic delayed gamma rays, but at a much slower rate according to the unique half-life of the radioactive nucleus. Depending upon the particular radioactive species, half-lives can range from fractions of a second to several years.

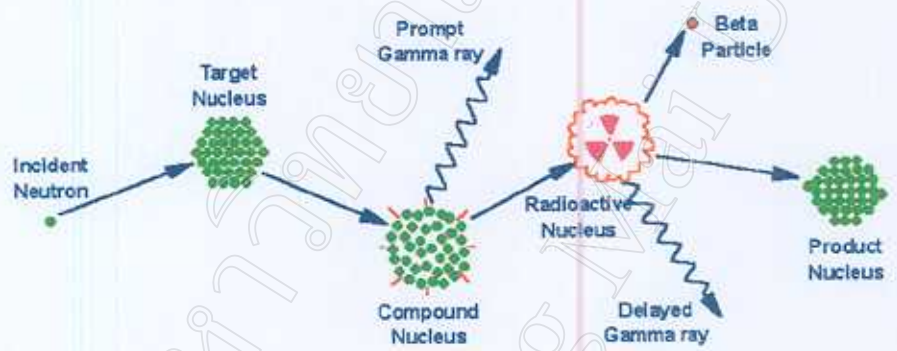

Figure 1.3 Diagram illustrating the process of neutron capture by a target nucleus followed by the emission of gamma rays

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, or (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. About 70% of the elements have properties suitable for measurement by NAA.

1.2.2 Neutron source [15-16]

The most powerful neutron source is nuclear reactor. The neutron fluxes ranges from 10^{12} n cm^{-2} s^{-1} to 10^{14} n cm^{-2} s^{-1}. Reactors provide an abundant flux of thermal neutrons. Higher energy neutrons are available at special energies are obtained as a result of various nuclear reactions. The following paragraphs give an outline of these reactions.

Nuclear reaction

Fission of radioisotope (^{235}U, ^{239}Pu) is accompanied by a radiation containing γ-rays, neutrons, electrons and α-particles. In modern reactors, thermal neutron fluxes of 10^{11}-10^{13}n cm^{-2} s^{-1} are obtained, also accompanied by fast neutron

Although 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).

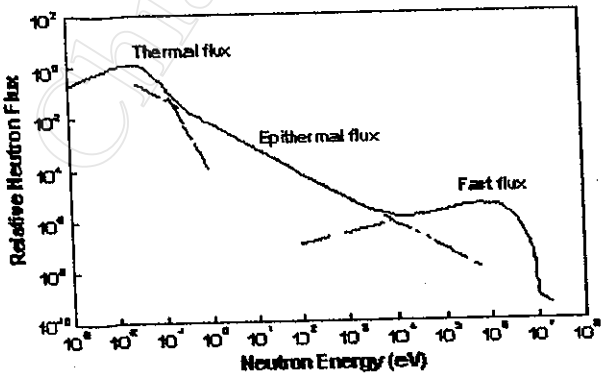

Figure 1.4 A typical reactor neutron energy spectrum showing the various components used to describe the neutron energy regions

The thermal neutron component consists of low-energy neutrons (energies below 0.5 eV) in thermal equilibrium with atoms in the reactor's moderator. At room temperature, the energy spectrum of thermal neutrons is best described by a Maxwell-Boltzmann distribution with a mean energy of 0.025 eV and a most probable velocity of 2200 m/s. In most reactor irradiation positions, 90-95% of the neutrons that bombard a sample are thermal neutrons. In general, a one-megawatt reactor has a peak thermal neutron flux of approximately 10^{13} n cm^{-2} s^{-1} .

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,γ) reactions on target nuclei. An NAA technique that employs only epithermal neutrons to induce (n,γ) 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 neutrons which still have much of their original energy following fission. Fast neutrons contribute very little to the (n,γ) 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 Principle of activation analysis [17-20]

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 :

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

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

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

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:

$$N = N_A/A$$

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

$$N = wN_A/A$$

However, there may be more than one isotope of an element, such as in the ease 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):

$$N = wN_A\,\theta/A$$

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:

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

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". The cross section is simply a physical constant:

$$\text{Activation rate} = \sigma\phi N$$

where

N is the number of target nuclei, in atoms

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

σ is the cross section, in m^2

activation rate is in events s^{-1}

Substituting:

$$N = wN_A\,\theta/A$$

into the expression for activation rate, it becomes:

$$\text{Activation rate} = \sigma\phi\, wN_A\,\theta/A$$

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 ms^{-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 rediative capture resonance integral (I_γ) is used. The values for capture cross sections and resonance integrals are given by Mugbabhab *et. al* (1984) and some typical examples are shown in **Table 1.8**

Table 1.8 Neutron 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	3	74	197-Au	98.7	1550

It can be seen from the cross section values that the lighter elements have thermal neutron 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 string 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:

$$\text{Activation rate} = \sigma\phi_{th}N + I_\gamma\phi_{epi}N$$

were

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:

$$\text{Activation rate} = \sigma\phi N$$

$$\text{Number of nuclei} = \sigma\phi N\, t$$

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^* radioactive nuclei, the rate of decay of the nuclei is proportional to N^*.

$$\text{Decay rate, } dN^*/dt \ \alpha \ -N^*$$

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

where λ is the decay constant, which has a characteristic value for each radionuclide. If the equation is integrated between the limits N^*_0 at time zero, and N^* remaining at time t:

$$N^* \ N^*_0 \exp(-\lambda t)$$

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:

$$N^*_0 /2 = N^*_0 \exp(-\lambda t_{1/2})$$

$$t_{1/2} = \ln 2/\lambda = 0.693/\lambda$$

A semilogarithmic plot of the decay rate against time will give a straight-line graph with a slope of - λ. 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 1.9** 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 1.9 Half life values for typical activation products

Product	Half-life	Product	Half-life
24-Na	14.57 hr	64-Cu	12.7O hr
27-Mg	9.46 mm	76-As	26.3 hr
28-Al	2.24 mm	82-Br	35.3 hr
56-Mn	2.578 h	110-Ag	24.6 s
60-Co	5.27 y	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

$$dN^*/dt = \sigma\phi N - \lambda_i N^*$$

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

The activity or disintegration rate (A_0), at the end of the irradiation time t, is then:

$$A_0 = \lambda N^* = \sigma\phi N (1 - \exp(-\lambda t))$$

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):

$$A_s = \sigma\phi N$$

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:

$$A_0 = \sigma\phi N (1 - \exp(-\lambda t))$$

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:

$$A_0 = \sigma\phi\, wN_A\theta (1 - \exp(-\lambda t))/A$$

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

$$w = A_0 A/(\sigma\phi\, N_A\theta (1 - \exp(-\lambda t))$$

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

$$w = A_0 \exp(-\lambda t_d) A/(\sigma\phi N_A \theta (1 - \exp(-\lambda t))$$

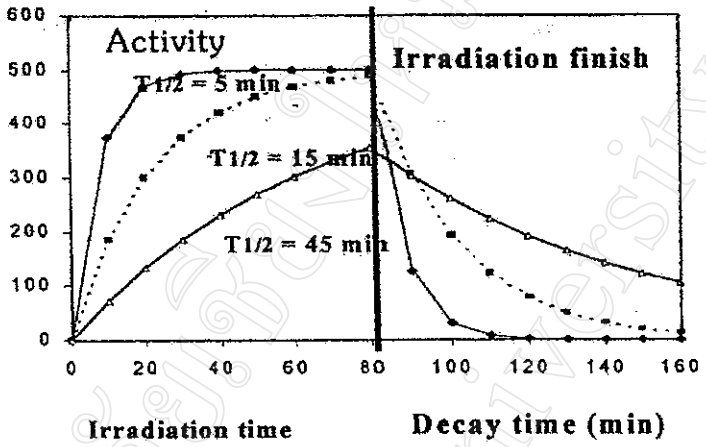

Figure 1.5 Activation curve

1.2.4 Measurement of gamma ray [16]

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 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 cm^3 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 [16,19-20]

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.

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

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

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

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

To summarize,

$$A_0 = (\text{counts per second}) / E\,P \exp(-\lambda t) \tag{1.26}$$

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):

$$\lambda t_c = (1 - \exp(-\lambda t_c)) \tag{1.27}$$

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:

$$w = A_0 A/(\sigma\phi N_A\theta (1- \exp (-\lambda t)) \qquad (1.28)$$

and since: A_0 = (counts per second) / $E P \exp (-\lambda t_d)$

then w = (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 crosssection, 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[16]

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

$$\frac{A_{sam}}{A_{std}} = \frac{W_{sam}(\exp\text{-}\lambda t_d)_{sam}}{W_{std}(\exp\text{-}\lambda t_d)_{std}}$$

where A_{sam}, A_{std} = activity of the sample and standard, w_{sam}, w_{std} = mass of the element in the sample and standard, 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

$$W_{sam} = [W_{std}] x [C_{sam}/ C_{std}]$$

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

1.2.6 Sensitivities for determination of elements by NAA [16]

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. The approximate sensitivities for determination of elements assuming interference free spectra and the elements which

can be analyzed by neutron activation analysis technique are shown in **Tables 1.10 and 1.11.**

Table 1.10 Estimated detection limits for INAA using decay gamma rays. Assuming irradiation in a reactor neutron flux of $1x10^{13}$ n cm^{-2} 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

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Table 1.11 The elements which can be analyzed by neutron activation analysis technique

Aluminum	Gadolinium	Neodymium	Sodium
Antimony	Gallium	Nickel	Strontium
Arsenic	Germanium	Niobium	Tantalum
Barium	Gold	Osmium	Tellurium
Bromine	Hafnium	Palladium	Terbium
Cadmium	Indium	Platinum	Thorium
Cerium	Iodine	Potassium	Thulium
Cesium	Iridium	Praseodymium	Tin
Chloride	Iron	Rhenium	Titanium
Chromium	Lanthanum	Rubidium	Tungsten
Cobalt	Lutetium	Ruthenium	Uranium
Copper	Magnesium	Samarium	Vanadium
Dysprosium	Manganese	Scandium	Ytterbium
Erbium	Mercury	Selenium	Zinc
Europium	Molybdenum	Silver	Zirconium

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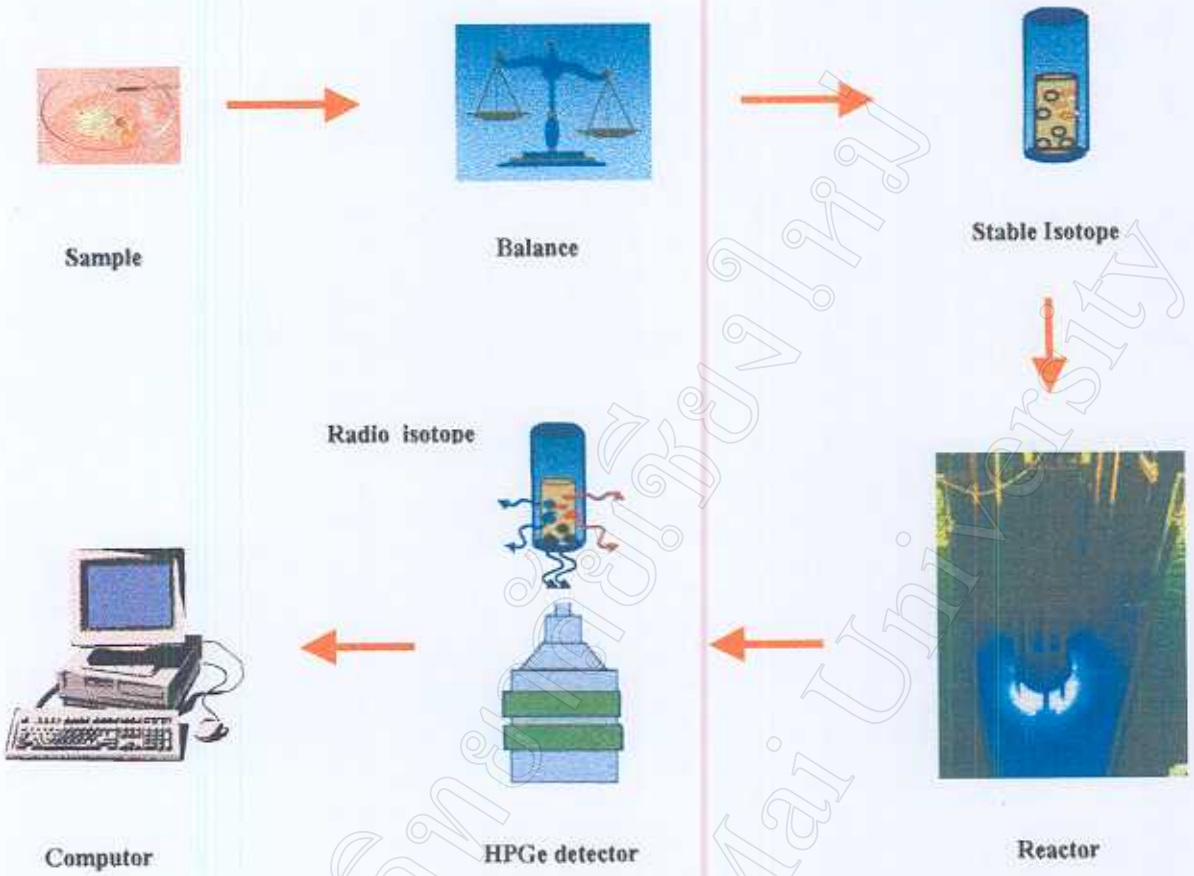


Figure 1.6 Diagram shown neutron activation analysis method

1.2.7 Preconcentration of Arsenic for NAA

The aims of this research were to study and obtain the optimum RNAA conditions for arsenic analysis in water sample and to determine concentration of arsenic in water samples from Ronpiboon district, Nakhon Sri Thammarat province. For the study of arsenic in natural waters, it is necessary to find a method to determine arsenic down to the part per million level [21]. Neutron activation analysis (NAA) is a sensitive analytical technique useful for performing both qualitative and quantitative multi-element analyses. It is one of the most sensitive techniques for arsenic analysis. Under interference-free conditions, neutron activation analysis (NAA) can easily detect nanogram levels of arsenic in a sample with good accuracy [22]. It can be performed on any form of sample (solid, liquid and gas). From these reasons,

radiochemical neutron activation analysis (RNAA) method was chosen in this research to determine arsenic in natural water samples. Epithermal neutron activation analysis is often desirable because it reduces background activities, which results in enhanced sensitivity for an element [23].

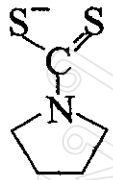
Determination of the total arsenic content of aqueous samples is not sufficient as environmental risk depend on the valency and chemical form of the element, As(III) is appreciably more toxic than As(V), whereas organoarsenic species such as monomethylarsenic acid (MMAA) and dimethylarsenic acid (DMAA) are the lest toxic. These organoarsenic species are likely to be found in water with a high microbial activity, as several microorganisms are capable of biomethylation of inorganic arsenic. However, As(III) and As(V) are the most often determined specie in environmental water. Usually the concentration of these species is in the sub-micrograms per litre range, which necessitates a preconcentration step because present detectors still lack the sensitivity for direct determination [24].

Using published thermodynamic data for arsenic species and the assumption of redox equilibrium, Cherry *et al* [25] have shown that the apparent redox condition, as pH, can be computed from measured concentrations of As(III) and As(V) species in water.

Because of its toxicity and possible carcinogenicity, arsenic is one of the most widely measured trace metals in many environmental monitoring programs. The concentration of total arsenic in the most natural water systems are in the range of 10^{-6}-10^{-7} g/L[26]. The concentration of total arsenic in ground waters and in mine waters generally vary from ppb to ppm levels.[25].

From recent report[34], it can be found that studies concerning the simultaneous determination of As is focused on the total elemental determination. Determining the extraction of As(III) in the presence of As(V) with an ammonium pyrrolidinedithiocarbamate(APDC) was developed by Mok and Wai [27]. During the past few years, a simple solvent extraction method for the separation of As(III) and As (V) has been developed using ammonium pyrrolidinedithiocarbamate(APDC) as a chelating agent. The derivatives of dithiocarbamic acid are known to chelate with a large number of metal ions to form complexes which are soluble in organic solvent.

Ammonium pyrrolidinedithiocarbamate (APDC) is one of the dithiocarbamate derivatives which have been widely used as chelating agents for preconcentration and separation of trace metals from aqueous solutions.



Pyrrolidine dithiocarbamate (PDC)

One unique feature of this method is that the alkali metals, the alkaline earth metals, the halogens, aluminum, sulfate, and phosphate which do not complex with dithaiocarbamates can be simultaneously removed during the extraction. The extraction method, therefore, not concentrates trace metals but also eliminates interfering matrix species present in natural water systems.

As(III) can be extracted by dithiocarbamates, reduction of As(V) to As(III) is necessary in order to determine total As in water [28].

In this experiment, nuclear reactor was used to generate neutrons. The neutron flux was 2.2×10^9 n $cm^{-2}s^{-1}$ (epithermal neutron) . The (n, γ) reaction of ^{75}As, the only stable isotope of arsenic, was irradiated by neutron and unstable isotope of arsenic (^{76}As) was produced in neutron capture as follows:

$$^{75}As + {}^{1}_{0}n \longrightarrow {}^{76}As + \gamma$$

The radioisotope ^{76}As produced has a half-life of 27 hours and emits a gamma ray of 559 keV which can be used for its identification and quantification. Another gamma energies of ^{76}As is shown in **Table 1.12**.

Table 1.12 γ-energies of radioisotope ^{76}As [29].

Element	Radioisotope	Half - Life	γ-ray Energy (keV)	Percent Intensity
As	^{76}As	27 hr	559	100
			657	14
			768	1
			868	1
			1216	10
			1229	3

1.3 Objectives of this research

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

(1) To study and obtain the optimum RNAA conditions for arsenic analysis in water samples.

(2) To determine the arsenic concentration in water samples by RNAA.

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