CHAPTER 3
RESULTS AND DISCUSSION

3.1 Preliminary study

3.1.1 Variation of pH

The pH effect for the coprecipitation of standard As(III) and As(V) was determined by varied pH range 1-11. Achieved using the following conditions : 15 minutes for irradiation times, 20 hr for cooling times and 100 s for measuring times.

The count rates of γ-spectra from radioactive arsenic – 76 induced from As(III)-Pb(PDC)$_2$ at elevated pH are shown in **Figures 3.1**
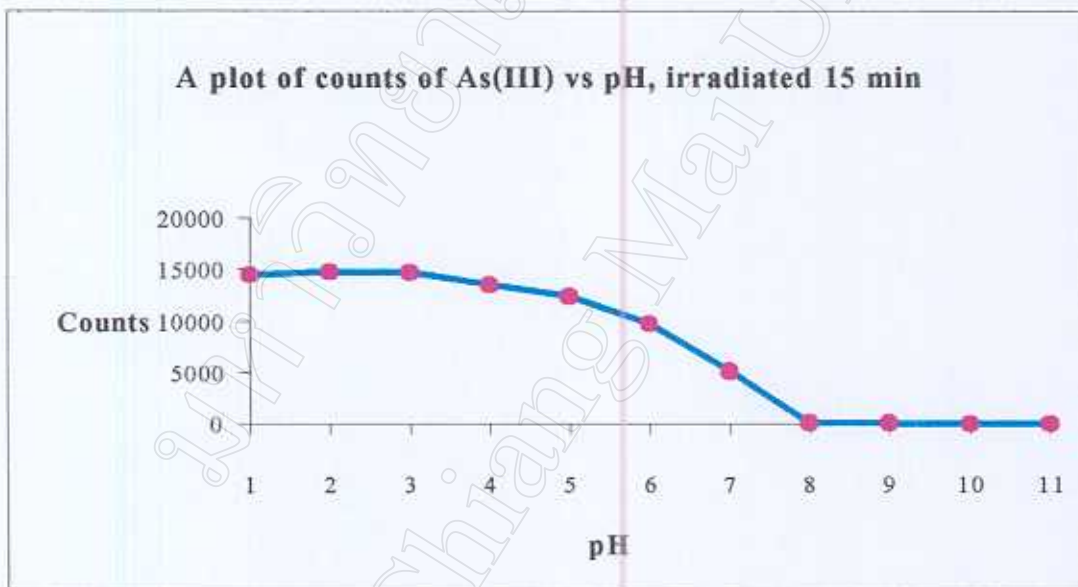

Figure 3.1 A plot of count rates of ^{76}As(III) vs. pH, irradiation times = 15 minutes, cooling times = 20 hr and measuring times = 100 s
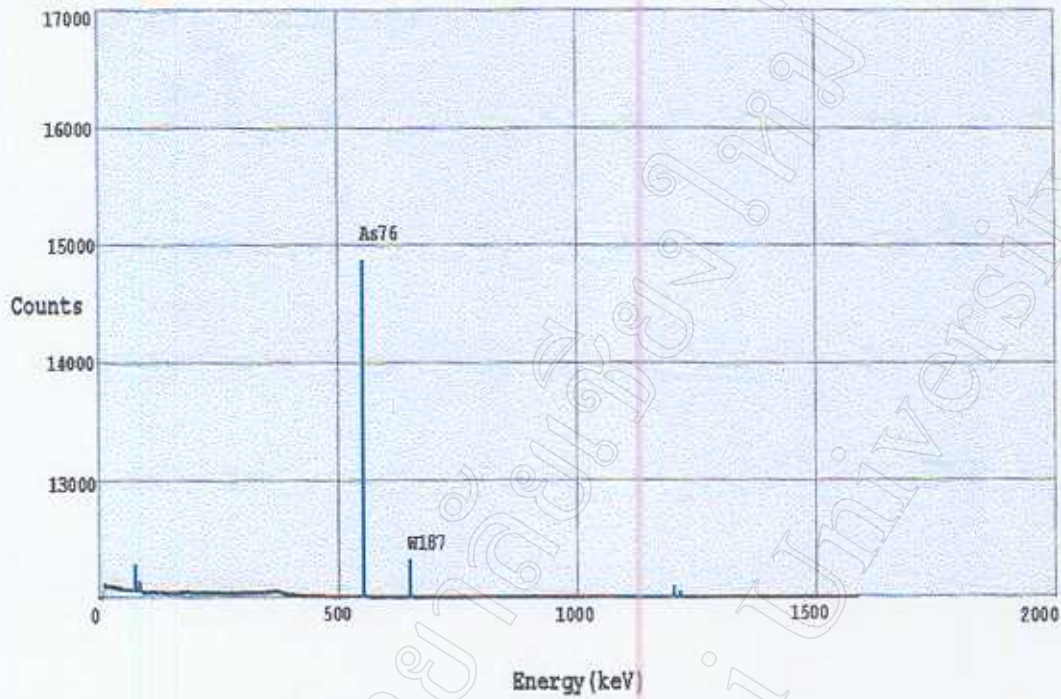
Figure 3.2 γ-spectra of ^{76}As(III) induced from epithermal neutron activation after irradiation in CA2 tube: standard As(III) = 500 ppm, irradiation times = 15 minutes, cooling times = 20 hr and measuring times = 100 s

It was found from the results that, it was not possible to separate arsenic(III) from arsenic(V) by this method because a suitable pH for coprecipitation of arsenic with $Pb(PDC)_2$ was the same at pH 3 for both arsenic(III) and arsenic(V). Therefore, the total arsenic was determined instead. At high pH, arsenic can form easily soluble species and thus not coprecipitated with $Pb(PDC)_2$

In a mixture of arsenic (III) and arsenic(V), the arsenic(V) was reduced in aqueous sample solution by $TiCl_3$ at pH 2 for 5 min [30] to arsenic(III), and then all of the arsenic(III) was coprecipitated with $Pb(PDC)_2$ at pH 3.

Reduction of arsenic(V) to arsenic(III),will convert all of arsenic in water sample to oxidation state III, and can determine only total amount of arsenic in water sample.

In addition to being a rapid and simple way to increase the concentrations of the desired elements, the coprecipitation process provides a sample favorable for NAA. It is essential that in this procedure most of the alkaline metals, alkaline earth metals, and halogens are eliminated. This will also decrease the background level of radiation and the radiation dose received by personnel. Additionally, $Pb(NO_3)_2$ and $TiCl_3$ were chosen as the carrier and the reducing agent to avoid possible spectral interference.

3.1.2 Coprecipitation yield

The results of γ–energy measured at 559 keV from radioisotope ^{76}As induced after irradiation the coprecipitated As- $Pb(PDC)_2$ from 100 ml of 100, 50, 10 and 1 ppm standard As(III) with epithermal neutrons are shown in **Figure 3.3,** at various, irradiation, cooling and measuring times as shown in **Figure 2.9.**

It was found that the average percent coprecipitation were 76% and 82%, respectively, for addition of 100 ml of 100 ppm and 50 ppm of standard As(III) while the average percent coprecipitation were in the range 92-100% for addition of 100 ml of 10 ppm and 1 ppm of standard As(III)
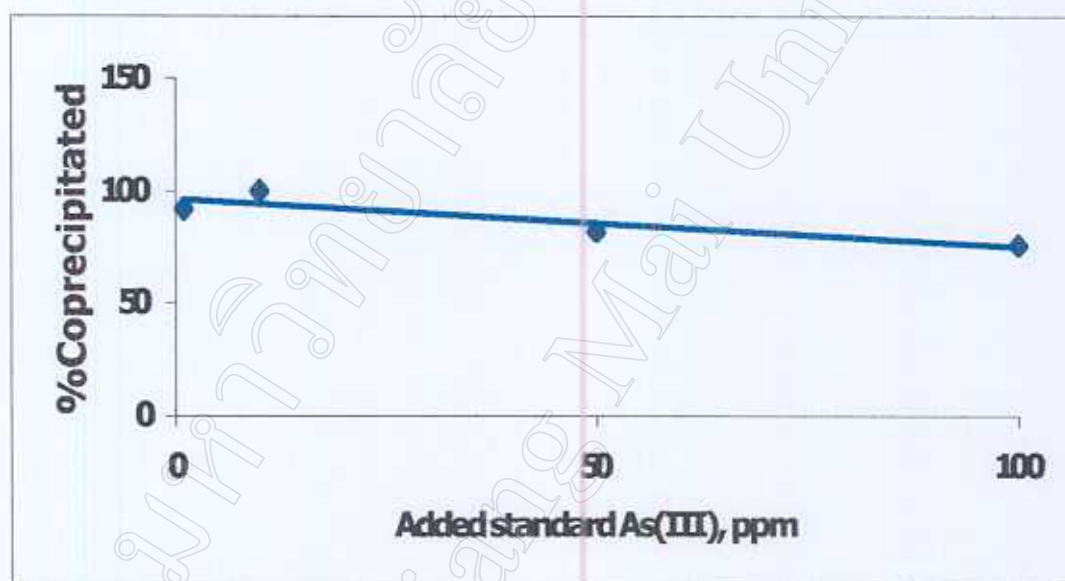

**Figure 3.3** A plot of percent coprecipitation vs added standard As(III)

It was found from the results that, if concentration of arsenic in water sample is less than 10 ppm, the range of chemical yield of coprecipitation was more than 90%, but if concentration of arsenic in water sample is higher than 10 ppm, the chemical yield of coprecipitation reduced to below 80% as shown in **Figure 3.3**.

3.2 Qualitative analysis

Qualitative analysis of water samples were achieved using the conditions as shown in **Figure 2.9**. The γ -ray energies, the γ-spectra and the radioisotopes induced from epithermal neutron activation of elements present in coprecipitated of water samples are given in **Table 3.1, Figures 3.4 - 3.6, Table 3.2** respectively.

Table 3.1 Gamma-ray energy of radioisotopes found [31]

| Element	Radioisotope	Half - life	Gamma-ray energy (keV)
As	^{76}As	27 hr	559(44.6), 657(6.4), 1216(3.7)
Sn	^{125m}Sn	9.7 minutes	332(99)
Na	^{24}Na	15 hr	1368(100), 2754(99)
Nb	^{94m}Nb	6.29 minutes	871(100)
W	^{187}W	24 hr	61(12.8), 134(10.1), 479(26.6), 686(32)
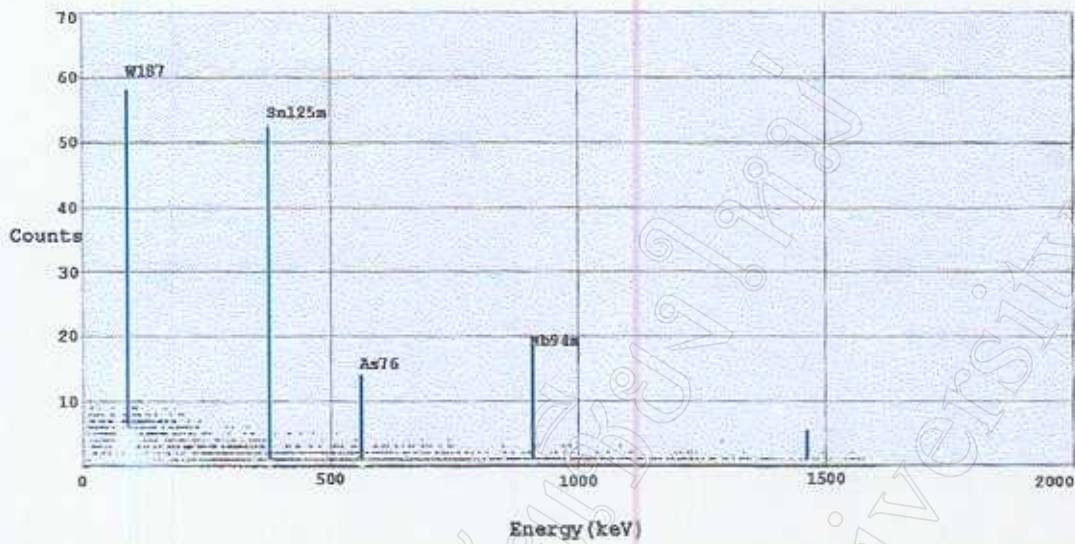
(a) Cooling times = 30 minutes
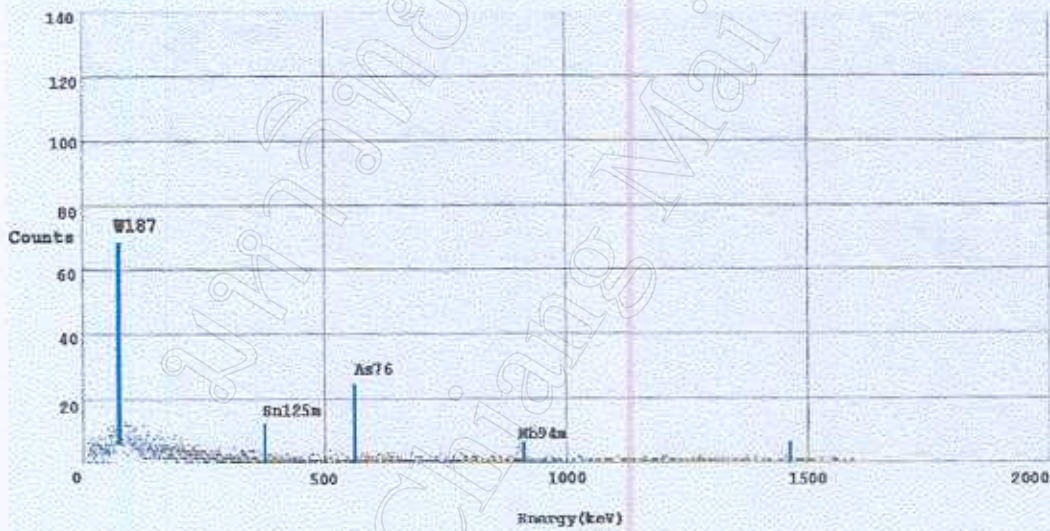
(b) Cooling times = 3 hr

Figure 3.4 γ-spectra of radioisotopes induced from epithermal neutron activation of elements present in coprecipitated of water samples with $Pb(PDC)_2$, irradiated in CA2 tube with irradiation times = 15 minute, cooling time are (a) 30 minutes and (b) 3 hr, measuring time = 100 s
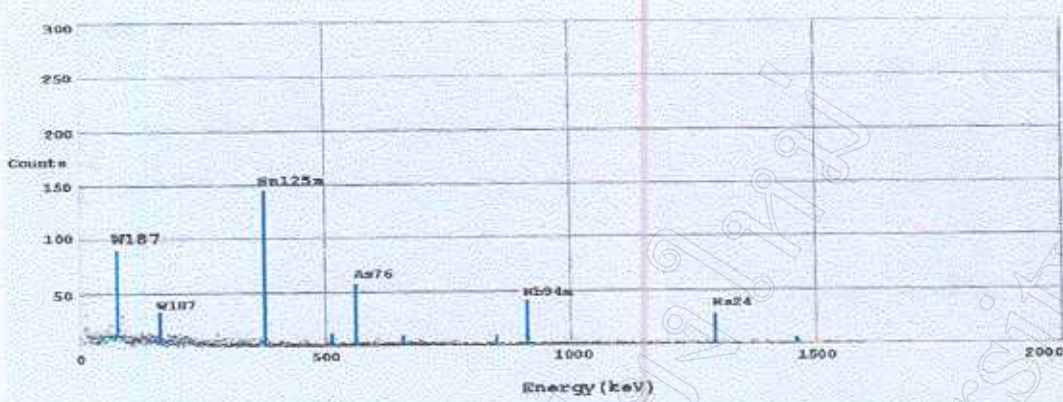
(a) Cooling times = 1 hr
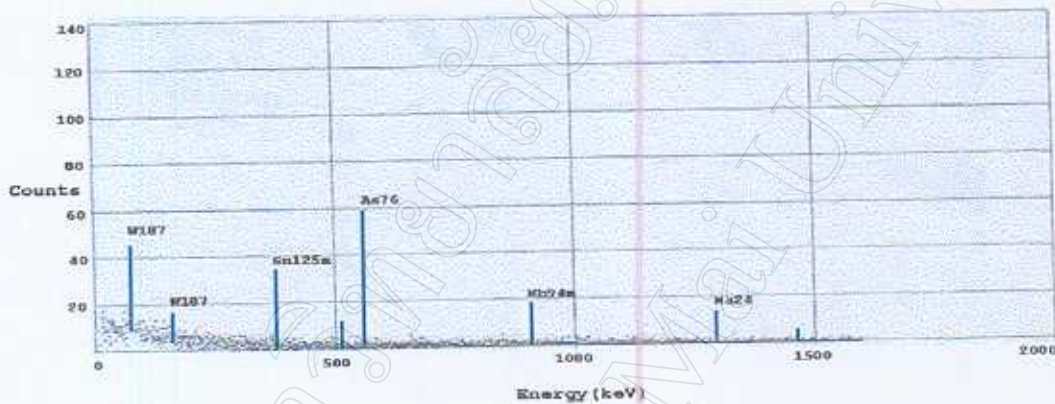

(b) Cooling times = 3 hr

(c) Cooling times = 20 hr

Figure 3.5 γ-spectra of radioisotopes induced from epithermal neutron activation of elements present in coprecipitated of water samples with Pb(PDC)$_2$, irradiated in CA2 tube with irradiation time = 1 hr, cooling time are (a) 1 hr and (b) 3 hr and (c) 20 hr, measuring time = 100 s.

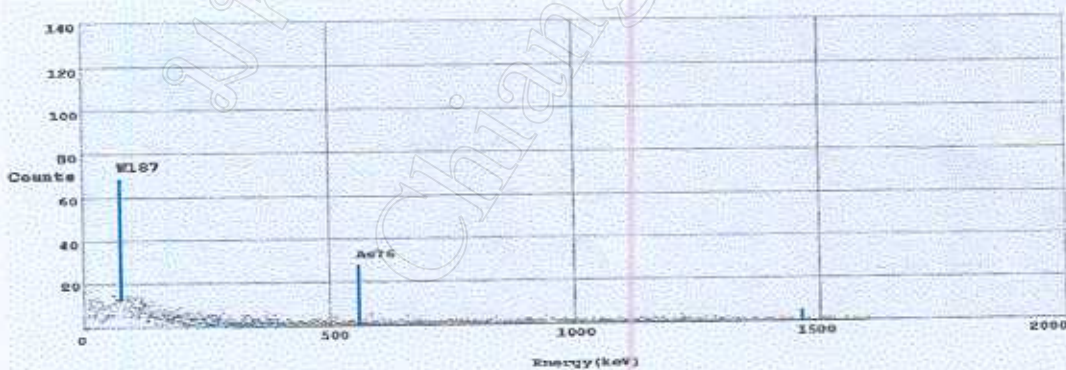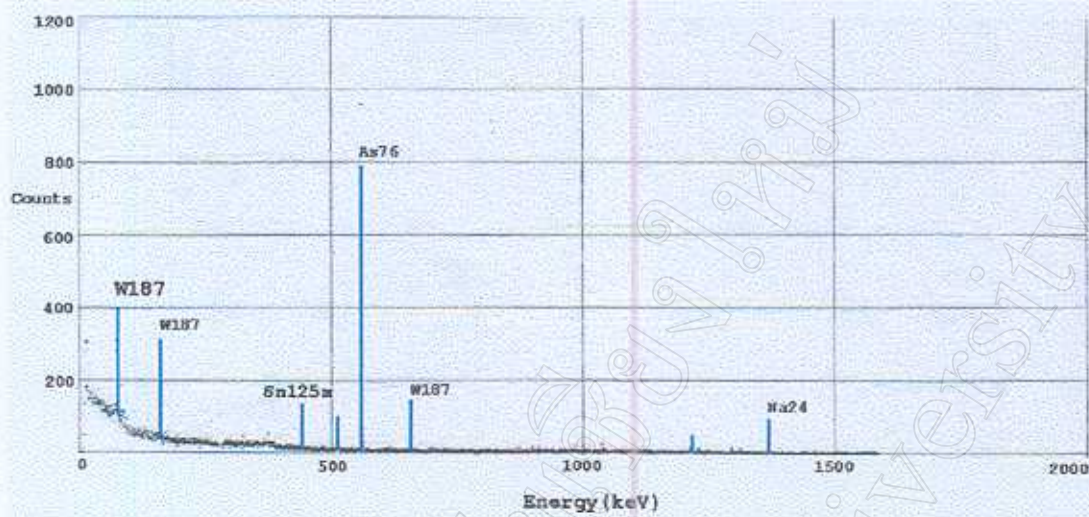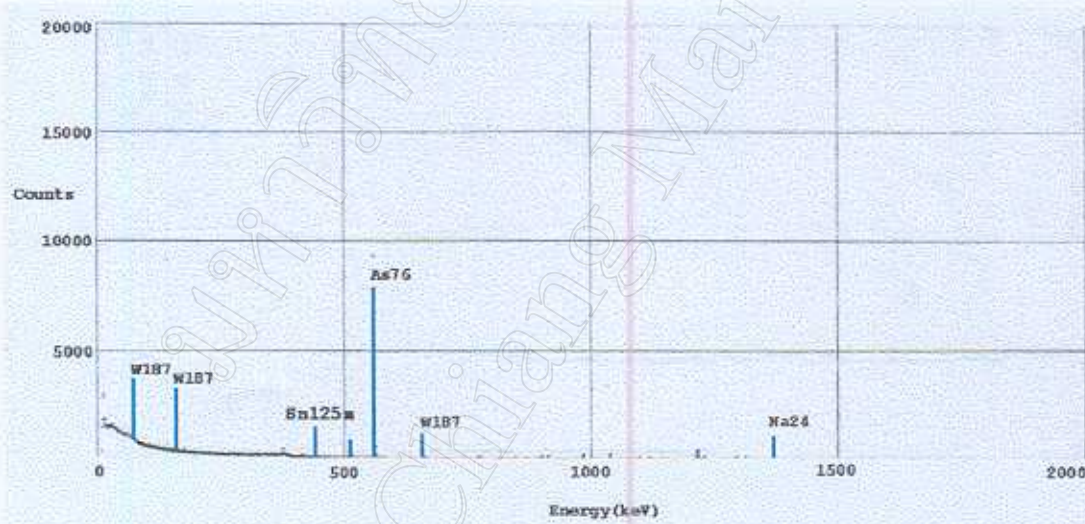(a) Measuring times = 100 s

(b) Measuring times = 1000 s

Figure 3.6 γ-spectra of radioisotopes of induced from epithermal neutron activation of elements present in coprecipitated of water samples with Pb(PDC)₂ irradiated in CA2 tube with irradiation time = 11 hr, cooling time = 13, measuring time are (a) 100 s and (b) 1000 s.

Table 3.2 Radioisotopes induced from epithermal neutron activation of elements present in coprecipitated of water samples with Pb(PDC)$_2$ with irradiation times = 15 minutes, cooling times = 30 minutes and measuring times = 100 s

Irradiation times (hr)	Cooling times (hr)	Measuring times (s)	Radioisotopes				
			^{187}W	^{125m}Sn	^{76}As, counts	^{94m}Nb	^{24}Na
0.25	0.5	100	+	+	+, < 30	+	-
1	1	100	+	+	+, < 80	+	+
1	3	100	+	+	+, 40	+	-
1	20	100	+	-	+, 40	-	-
11	13	100	+	+	+, ≈ 800	-	+
11	13	1000	+	+	+, ≈ 8000	+	+

+ = found

- = not found

It can be concluded that, long irradiation time should be used to determination arsenic in natural water due to high counts of ^{76}As.

Table 3.3 The element found in water by NAA

Sample	Elements found	Reference
Contaminated water samples from Ronpiboon district	W, Sn, A.s, Nb, Na	This work
Tab water	Cr, Ag, Mn, Zn, Cd, Se, Fe	24

The other method such as Van Elteren et al [24], the elements found in tap water shown in **Table 3.3**. The sample were irradiated at a neutron flux of 5×10^{13} n cm^{-2} s^{-1} for 15 minutes. After cooling 1 day the sample were counted for 2000 s on a Ge(Li) detector. In tap water, Fe always present. The method that used to determine concentration of element from tap water and the method used in this work were precipitation methods or radiochemical neutron activation analysis (RNAA). Coprecipitation agent, Pb(PDC)$_2$, and pH 3 of precipitation were special conditions for elements that could form complexes under these conditions.

3.3 Precision of the method

The coprecipitated As-Pb(PDC)$_2$ from 100 ml of 2 ppm standard As(III) and the standard (added 0.029 mg standard As(III)) were irradiated simultaneously in the rabbit. Two vials of the coprecipitates were placed in the rabbit together with 3 vials of the reference. Irradiated for 1 hr in CA2 tube, cooled for 1 hr and measured for 100 s on HpGe detector at a distance of 4 cm from the detector.

The photopeak area of 559 keV γ-ray from [76]As was used to determine As concentration in the sample. Concentrations of arsenic calculated by comparision of photopeak area of sample with standard using the same irradiation periods and γ-ray energies are shown in **Table 3.4.**

Table 3.4 Counts of coprecipitated As-Pb(PDC)$_2$ and concentration of arsenic with irradiation times = 1 hr, cooling times = 1 hr and measuring time = 100 s

No.	Weight of precipitated (in vial), g	Average counts of coprecipitated	Average counts of standard	Concentration of As, ppm
1	0.05	3196	5002	1.842
2	0.05	3471	5289	1.878
3	0.05	3458	5297	1.853
4	0.05	3378	4864	1.958
5	0.05	3241	5072	1.892
6	0.05	3100	4625	1.928
Average oncentration of As =1.892 ppm				
% RSD = 2.35				

From data that shown in **Table 3.4,** the method in this work has relative standard deviation (RSD) = 2.35.

Concentration of arsenic added in the precipitated can be calculated as follows:

<u>No.1.</u> Irradiation times = 1 hr, cooling times = 1 hr and measuring times = 100 s

From equation: W_{sam} = (0.029 mg) x (3196/5002) = 0.0184 mg

Weight of coprecipitated in vial	= 0.0500	g	As	= 0.0184	mg
Weight of real sediment	= 0.4865	g	As	= 0.1790	mg

Chemical yield of coprecipitated	= 97.2%,		As	= 0.1790	mg
If chemical yield of coprecipitated	= 100% ,		As	= 0.1842	mg

Water sample	100	ml,	As	= 0.1842		mg
If water sample	1000	ml,	As	= (0.1842x1000)/100	= 1.8420	mg
					= 1.8420	ppm

(1) Equation of true standard deviation(s) :

$$S = \sqrt{\frac{\sum\limits_{i=1}^{i=N}(X_i - \overline{X})^2}{N-1}}$$

S = True standard deviation

N = Number of data

Xi = Observed value

$\overline{X}$ = Average value

(2) Equation of Relative standard deviation(RSD) :

$$\% \text{ RSD} = [\text{S/X}] \times 100$$

<u>Solution</u>

Calculation of true standard deviation(s). Give concentration of arsenic from **Table 3.4** instead in equation(1)

$$S = [0.009868833/5]^{1/2}$$
$$S = 0.0444$$

Give, S = 0.0444 instead in equation (2)

$$\% \text{ RSD} = (0.0444/1.8918) \times 100 = 2.35$$

∴ % Relative standard deviation(%RSD) = 2.35

3.4 Percent recovery

The standard and samples were placed in the rabbit with 2 vials of sample together with 3 vials of standard. They were irradiated for 1 hr in CA2 tube, cooled for 1 hr and measured for 100s on HPGe detector at a distance of 4 cm from the detector.

The photopeak area at 559 keV of γ-ray from ^{76}As was used to determine As concentration in sample. Concentration of arsenic was calculated by comparision the photopeaks area of the samples with standard using the same irradiation periods and γ-ray energies. The percent recovery of each sample was then calculated (Table 3.5).

The Percent recovery could be calculated from the following equation:

(3) Equation of Percent recovery:

$$\% \text{ Recovery} = \frac{\text{Spiked sample value} - \text{Unspiked sample value}}{\text{Standard added value}} \times 100$$

Table 3.5 Percent recovery from spiked and unspiked samples from eight individual experiment. Irradiation time = 1 hr , cooling time = 1 hr and measuring time = 100 s

No.	Spiked sample value (ppm)	Unspiked sample value (ppm)	Standard added value (ppm)	Percent recovery
1	2.553	0.350	2.3500	94.7
2	2.711	0.419	2.419	94.8
3	2.643	0.374	2.374	95.6
4	3.005	0.599	2.599	92.6
5	1.974	0.047	2.047	94.1
6	2.561	0.354	2.354	93.8
7	2.325	0.223	2.223	94.6
8	2.030	0.072	2.072	94.5
Average percent recovery = 94.3%				

Percent recovery of this method when spike all eight water samples with 2 ppm standard arsenic, then coprecipitated with APDC - $Pb(NO_3)_2$ at pH 3. The percents recovery of eight samples range from 92.6% - 95.6%.

3.5 Quantitative analysis .

The standard and samples were placed in the rabbit with 2 vials of each sample together with 3 vials of standard and then irradiated for 11 hr in CA2 tube, cooled for 13 hr and the photopeak area of 559 keV γ-ray from ^{76}As was counted for 100s on HPGe detector at a distance of 4 cm from the detector. **Figure 3.7** show the γ-spectrum from sample no. 4. Concentrations of arsenic were calculated by comparision of photopeak areas of the samples with standard using the same irradiation periods and γ-ray energy and the resulting data given in **Table 3.6** and shown in **Figure 3.8**.
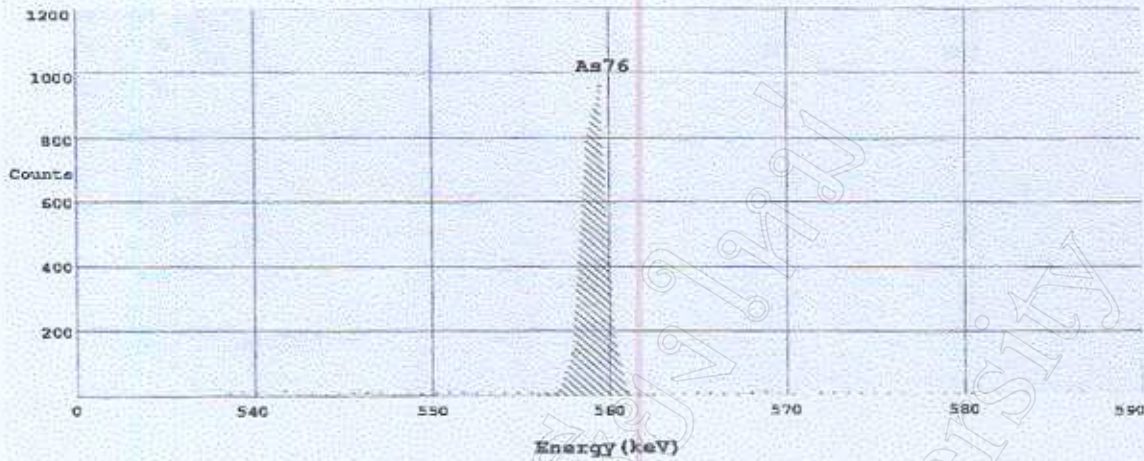
Figure 3.7 Gamma-spectra of induced radioisotopes after irradiation the coprecipitate As- Pb(PDC)$_2$ from water sample no. 4 with epithermal neutrons in CA2 tube. Irradiation time = 11 hr, cooling time = 13 hr and measuring time = 100 s.

Table 3.6 Concentration of arsenic in contaminated water samples from Ronpiboon district with irradiation time =11 hr, cooling time = 13 hr and measuring time = 100 s

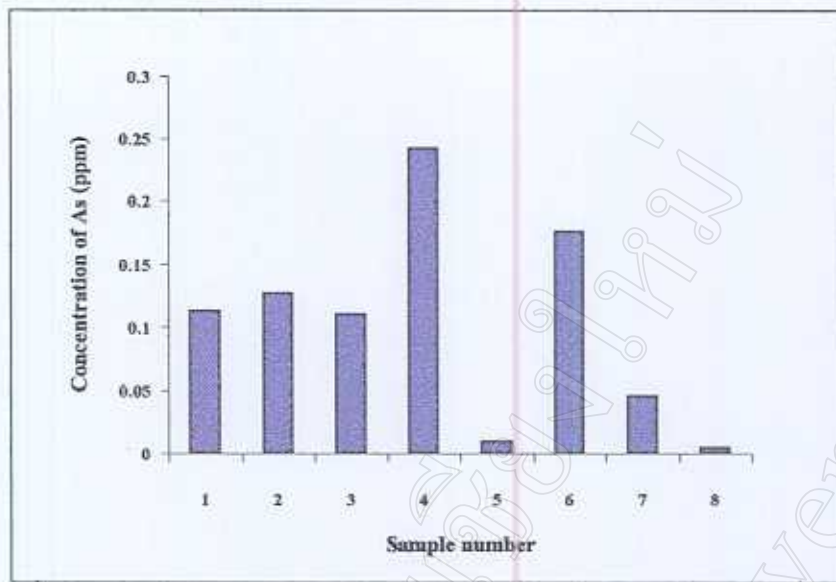| Sample No.	Average area of standard	Average area of samples	Average concentration of As (ppm)	%Relative standard deviation (%RSD), n = 3
1	100832	887	0.11	1.20
2	122444	1155	0.13	5.34
3	83517	994	0.11	1.25
4	104706	1862	0.24	4.15
5	107697	95	0.01	5.74
6	102470	1696	0.18	5.37
7	1111240	3803	0.05	1.73
8	105861	37	0.005	5.07

Figure 3.8 Chart represents concentration of arsenic in eight contaminated water samples from Ronpiboon district, Nakhon Sri Thammarat province with irradiation time = 11 hr, cooling time = 13 hr and measuring time = 100 s .

The concentrations of arsenic found in water samples from Ronpiboon District which is 35 kilometers south-west of the central city in Nakhon Sri Thammarat province are shown in **Table 3.6** and **Figure 3.8.** 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 [32]. These arsenic compounds are easily metabolized and highly soluble in low pH, It can spread through surface water .

From information about source of sample, it was postulated that contamination was from arsenopyrite (FeAsS), probably related to the mining process that had taken place in this area for a hundred years [5]. In Moo 2 Ronpiboon district, high arsenic level was reported by Abernathy et al in 1997 [5]. It was also found in this work that arsenic content in water in this area, especially creek water from Moo 2 (sample number 4) was higher than that present in normal water (see Table 1.2).

It has been reported that water in wells and old alluvial mining pits in this area [32] had arsenic concentrations higher than WHO drinking water limits (0.05 mg/l). The water from this area is not safe for drinking.

Concentration of arsenic in the samples can be calculated as follows:

Sample no. 1, irradiation time = 11 hr, cooling time = 13 hr and measuring time = 100 s

$$W_{som} = (0.1mg) \times (876/101855) = 8.689 \times 10^{-4} \quad mg$$

Weight of precipitated in vial	=	0.0504	g	As =	8.689×10^{-4}	mg
Total weight of precipitated	=	0.6357	g	As =	0.01096	mg

Precipitation	= 96.7% ,	As	= 0.01096	mg
Precipitation	= 100 % ,	As	= 0.01128	mg

Water sample   100 ml , contains As =   0.01128   mg

If water sample 1000 ml, contains As =   (0.01128×1000)/100 = 0.1128 mg

$$= 0.1128 \quad ppm$$

Table 3.7 Concentration of arsenic in contaminated water samples from Ronpiboon district compared with other water samples from literatures

Sample	Concentration of As (ppm)	Reference
Contaminated water samples	0.005 - 0.24	This work
River water	0.004	[26]
Mine water	0.004-0.080	
Ground and mine water	0.003-0.440	[33]
Ground water	0.002	[34]
Mine drainage samples	0.017	
Ground water	0.050	[35]
River water	0.001	[36]

As shown in Table 3.7, the concentrations of arsenic in river water and ground water were in the range of 0.001-0.050 ppm, while in mine water, the range of 0.004-0.440 ppm was reported.

In this work, however, arsenic level in water were from 0.005 ppm to 0.24 ppm, which are similar to the results from Mok et al [26]. Concentration of arsenic in mine water were higher than river water and ground water.

It can be concluded coprecipitation of arsenic in contaminated water sample from Ronpiboon District with Pb(PDC)$_2$ and determination by neutron activation analysis was very sensitive, with high selectivily and can be applied for analysis of non-contaminated as well as contaminated water samples.

3.6 Detection limit

Detection limit of the work studied have was obtained by measuring the background counts at 559 keV of As phothopeak. Blank sample was irradiated for 4 hr and measured for 100 s. The detection limit was then calculated at 3σ of this background count. For the irradiation time of 4 hr in a flux of 2.2 x 10^9 n cm^{-2} s^{-1} and measuring time 100 s, the detection limit as low as 8 x 10^{-4} ppm can be obtained.