

CHAPTER 2

EXPERIMENTAL

2.1 Apparatus and material

2.1.1 Apparatus

1) Nuclear Reactor Facility (Figure 2.1)

The Thai Research Reactor (TRR-1/M1), operated by the Office of Atomic Energy for Peace (OAEP), Bangkok, with the neutron flux at the irradiation position;

Epithermal neutron flux $2.2 \times 10^9 \text{ n cm}^{-2}\text{s}^{-1}$ (CA2 tube)

2) γ - Spectroscopy, manufactured by Canberra Instrument Inc., Nuclear Measurement Group, U.S.A., consisted of; HPGe detector (25% relative efficiency) (Figure 2.2) and relevant electronics;

a) High voltage power supply, Preamplifier and amplifier (Figure 2.3)

b) Data processing system, with the Gamma Acquisition Analysis program (Figure 2.4)

3) Vials and polyethylene irradiation container (rabbit) (Figures 2.5-2.6)

4) Agate mortar

5) pH meter

2.1.2 Chemicals and materials

1) Sodium arsenite (NaAsO_2), MW=129.91, lab grade, Fisher scientific company, U.S.A

2) Sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$), MW=312.01, AR grade, Merck, Germany

3) Lead(II) nitrate ($\text{Pb}(\text{NO}_3)_2$), MW=331.23, lab grade, May & Baker Ltd., England

4) Ammonium pyrrolidinedithiocarbamate ($\text{C}_5\text{H}_5\text{NS}_2 \cdot \text{NH}_4$), MW=164.29, lab grade, Fluka, Switzerland

5) Titanium(III) chloride, 15%(w/v) in HCl, lab grade

6) Hydrochloric acid, 37%(w/w), AR grade, Merck, Germany

7) Sodium hydroxide, MW=39.997, AR grade, Merck, Germany

8) Milli RX-20 water



Figure 2.1 The Thai Research Reactor (TRR-1/M1)



Figure 2.2 HPGe detector.

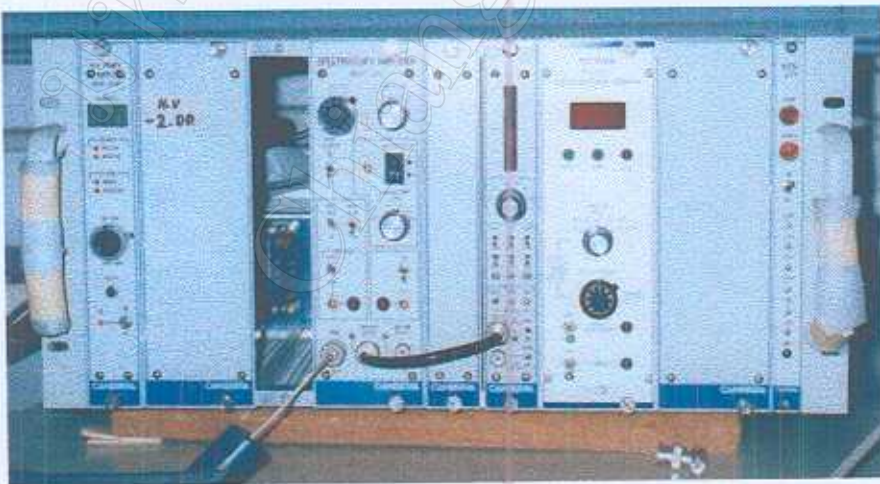


Figure 2.3 High voltage power supply, preamplifier and amplifier.



Figure 2.4 Computer with the Gamma Acquisition Analysis program.

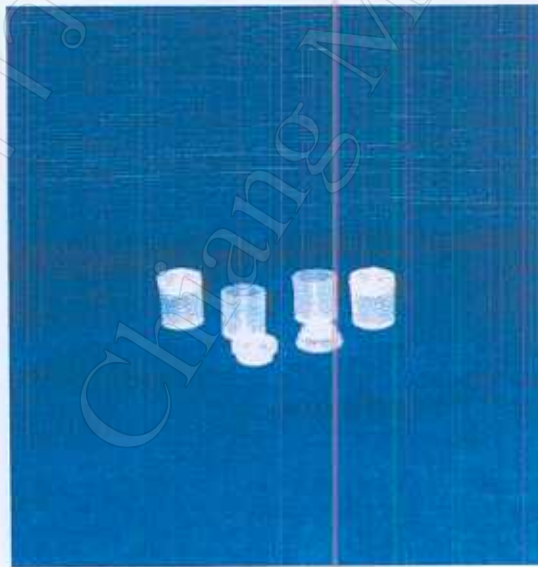


Figure 2.5 Vials

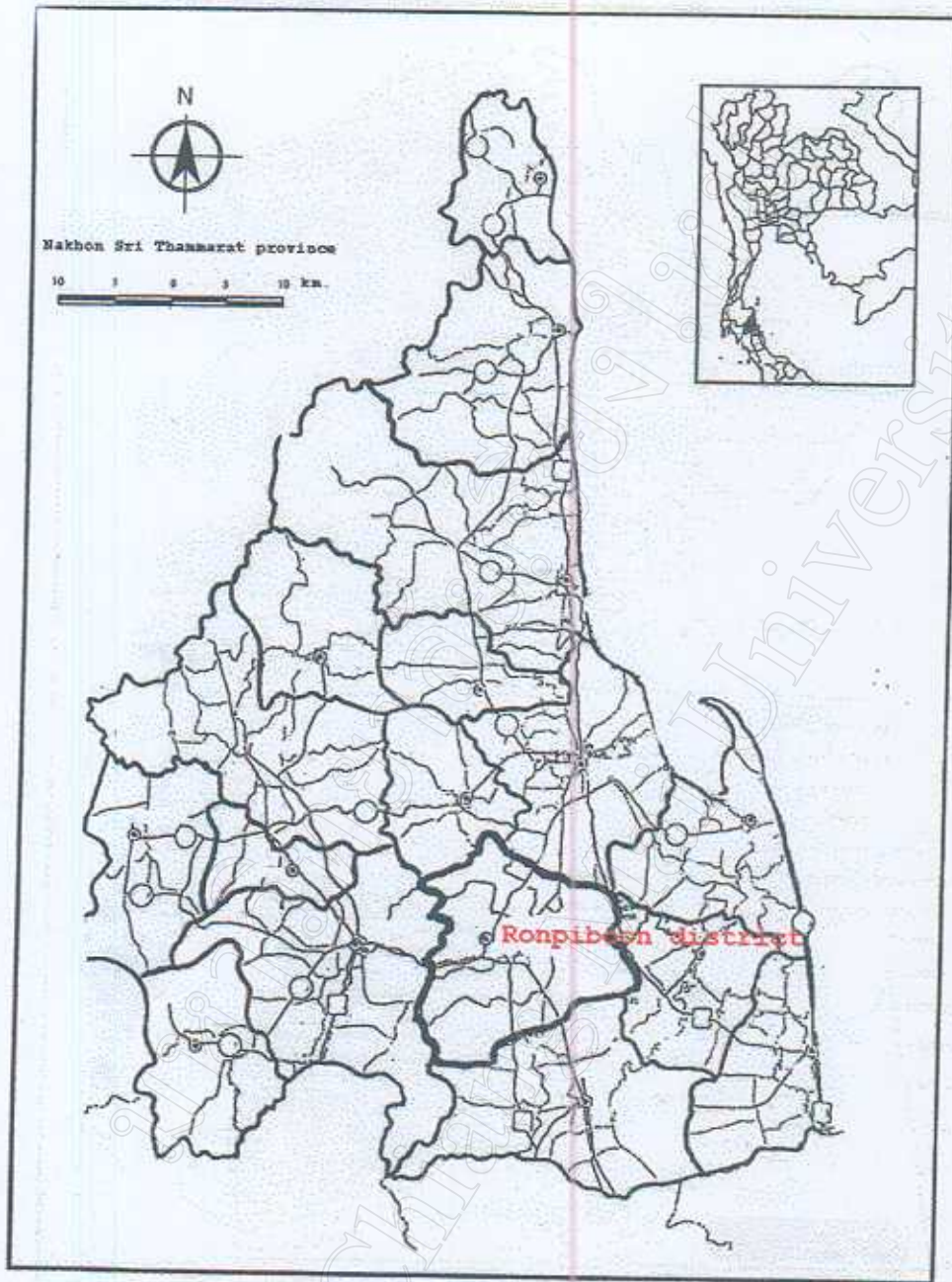


Figure 2.6 Rabbit

2.2 Sample material

Contaminate water samples from eight different sites were collected from Ronpiboon district, Nakhon Sri Thammarat province.

Sample numbers 1-4 and 7 were collected from Moo 2, sample numbers 5-6 were collected from Moo 12 and sample number 8 was collected from Moo 7 (**Figer 2.7-2.8**).



Figur 2.7 Map of Rongpiboon district in Nakhon Sri Thammarat province

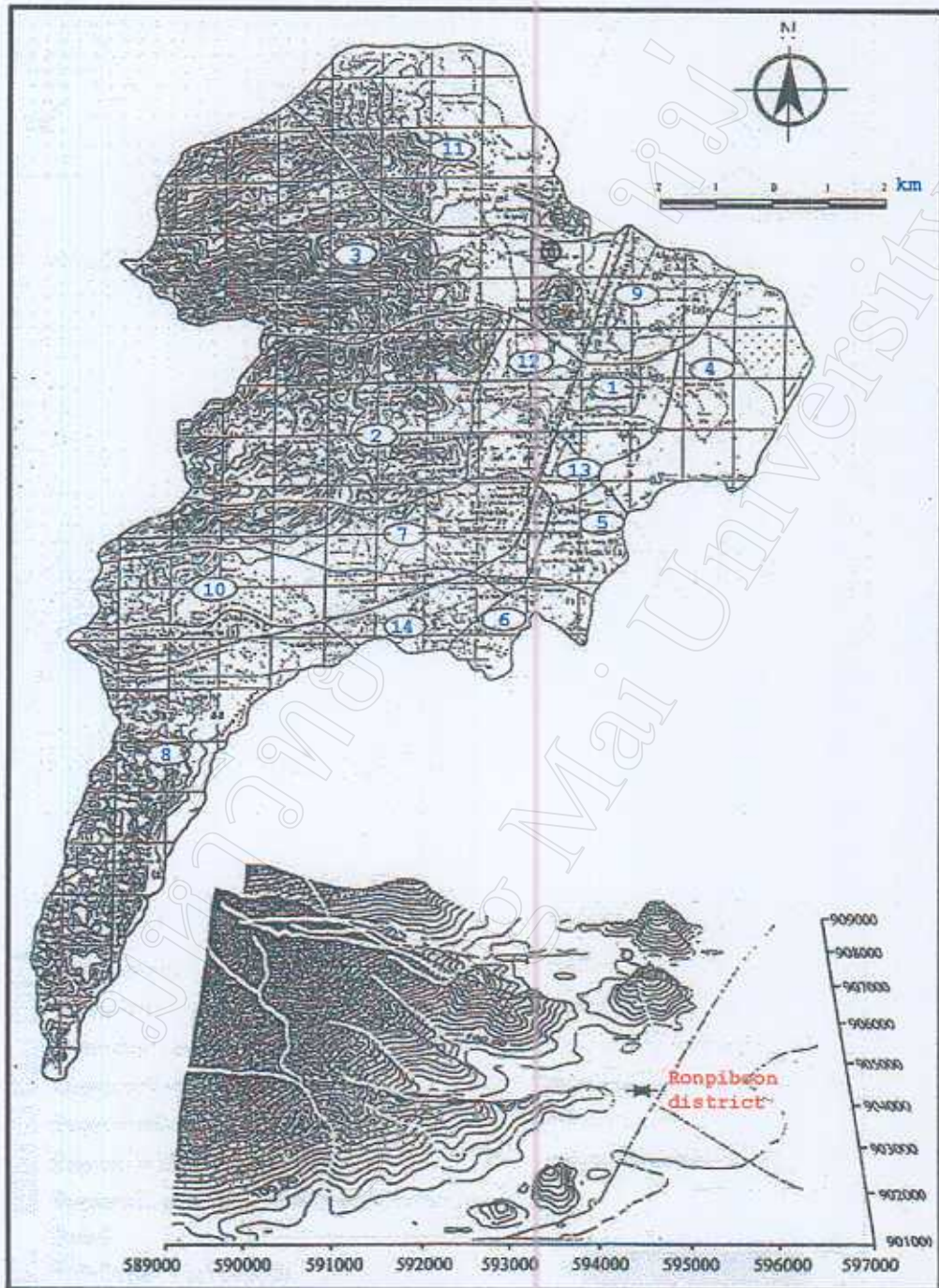


Figure 2.8 Map of Moo 1-14 of Ronpiboon district in Nakhon Sri Thammarat province

2.3 NAA experiment

2.3.1 Preliminary study

2.3.1.1 Variation of pH

Coprecipitation was accomplished by addition of 100 ml of APDC (1 g), 100 ml of $\text{Pb}(\text{NO}_3)_2$ (0.3 g), 100 ml Milli RX-20 water and 100 ml of 500 ppm As(III) or 500 ppm As(V). Sub-boiling purified HCl and NaOH were used to adjust the pH from 1-11. After 10 minutes of stirring and standing, the precipitates were collected on membrane filters, dried in a vacuum desiccator containing desiccant to complete dryness. About 0.05 g accurate weight of the coprecipitated was put into a polyethylene vial and heat-sealed for neutron irradiation.

The standard for comparative method were prepared by precipitation of $\text{Pb}(\text{APDC})_2$ in the same procedure as above except without arsenic. After 10 minutes of stirring and standing, the precipitates were collected on membrane filters, dried in a vacuum desiccator. Weighed about 0.05 g of the precipitate and put in a polyethylene vial. Pipet 50 μl containing 0.5 mg of standard As(III) (from 10,000 ppm arsenic stock solution) on the precipitate, then dried in a vacuum desiccator and heat-sealed for neutron irradiation.

The irradiation time, cooling time and measuring time were 15 minutes, 20 hr and 100 s, respectively.

2.3.1.2 Coprecipitation yield

a) Added 100 and 50 ppm standard As(III)

Coprecipitation of arsenic on $\text{Pb}(\text{APDC})_2$ was accomplished using the same procedure as described in 2.3.1.1, except that 100 ml of 100 and 50 ppm standard As(III) was used instead of 500 ppm As(III) or 500 ppm As(V), and the pH was adjusted to 3.

The standard for comparative method were prepared by precipitation of $\text{Pb}(\text{APDC})_2$ in the same procedure as described in 2.3.1.1, except that 10 μl (0.01 mg) of arsenic from 1,000 ppm standard As(III) stock solution was used instead of 50 μl (0.5 mg).

The irradiation and cooling times used were 5 minutes and 19 hr, respectively. The γ -peaks at energy of 559 keV were detected for 500 s.

b) Added 10 and 1 ppm standard As(III)

Coprecipitation of arsenic on $\text{Pb}(\text{APDC})_2$ was accomplished using the same procedure as described in 2.3.1.1, except that 100 ml of 10 and 1 ppm standard As(III) was used instead of 500 ppm As(III) or 500 ppm As(V), and the pH was adjust to 3

The standard for comparative method were prepared by precipitation of $\text{Pb}(\text{APDC})_2$ in the same procedure as described in 2.3.1.1, except that 10 μl (0.001 mg) of arsenic from 100 ppm standard As(III) stock solution was used instead of 50 μl (0.5 mg).

The irradiation and cooling time used were 4 hr and 12 hr, respectively. The γ -peaks at energy of 559 keV were detected for 200 s.

2.3.2 Qualitative analysis

Coprecipitation was accomplished by addition of 100 ml of APDC (1 g), 100 ml of $\text{Pb}(\text{NO}_3)_2$ (0.3 g), 100 ml Milli RX-20 water and 100 ml of water sample. The pH was adjust to 3.

In order to investigate optimum conditions for arsenic determination, as to minimize the interferences from other elements present in water which might be activated together with arsenic by epithermal neutrons, the proposed irradiation and cooling times were applied as shown in **Figure 2.9**.

After cooling, the irradiated coprecipitated was transferred to clean counting containers, measured for 100s on HpGe detector at a distance of 4 cm from the detector. The γ -peaks at energy of 559 keV were detected for 100s. NAA recorded spectra were evaluated with the Gamma acquisition analysis program. Various radionuclides were identified from their characteristic γ -ray energies.

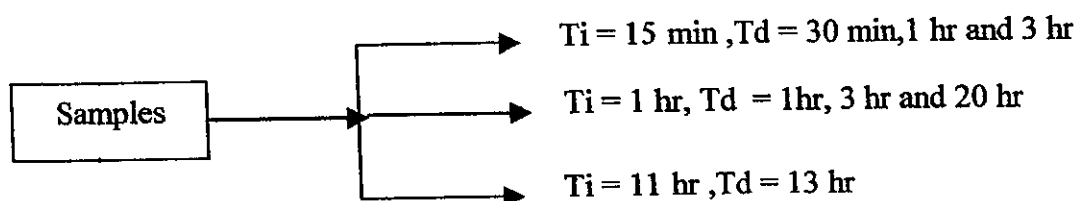


Figure 2.9 Irradiation times (Ti) and cooling times (Td) for qualitative analysis of samples

2.3.3 Precision of the method

Coprecipitation of arsenic on $\text{Pb}(\text{APDC})_2$ was accomplished by using the same procedure as described in 2.3.1.2 except that 100 ml of 2 ppm standard As(III) was used instead of 100 ppm and 50 ppm As(III), and the pH was adjust to 3. About 0.05 g accurate weight of coprecipitated was put into a polyethylene vial and heat-sealed for neutron irradiation.

The standard for comparative method were prepared by precipitation of $\text{Pb}(\text{APDC})_2$ in the same procedure as described in 2.3.1.1, except that 10 μl (0.1 mg) of arsenic from 10,000 ppm standard As(III) stock solution was used instead of 50 μl (0.5 mg).

The irradiation and cooling times used were both 1 hr. The γ -peaks at energy of 559 keV were detected for 100 s.

2.3.4 Percent recovery

a) Spiked 2 ppm standard As(III) in each sample

Coprecipitation of arsenic on $\text{Pb}(\text{APDC})_2$ was accomplished using the same procedure as described in 2.3.2, and 100 ml of 2 ppm standard As(III), the pH was adjust to 3. About 0.05 g accurate weight of coprecipitated was put into a polyethylene vial and heat-sealed for neutron irradiation.

b) Unspiked 2 ppm standard As(III) in each sample

Coprecipitation of arsenic on $\text{Pb}(\text{APDC})_2$ was accomplished using the same procedure as described in 2.3.2, but not added 100 ml of 2 ppm standard As(III) in the samples, the pH was adjust to 3. About 0.05 g accurate weight of coprecipitated was put into a polyethylene vial and heat-sealed for neutron irradiation.

The standard for comparative method were prepared by precipitation of $\text{Pb}(\text{APDC})_2$ in the same procedure as described in 2.3.1.1, except that 10 μl (0.1 mg) of arsenic from 10,000 ppm standard As(III) stock solution was used instead of 50 μl (0.5 mg).

The irradiation and cooling times used were both 1 hr. The γ -peaks at energy of 559 keV were detected for 100 s.

Percent recovery can be calculated by:

$$\text{Percent recovery} = \frac{[\text{Spiked sample value} - \text{Unspiked sample value}] \times 100}{\text{Standard added value}}$$

2.3.5 Quantitative analysis

The standard and eight samples from different locations were irradiated simultaneously in the rabbit. The standard and samples were placed in the rabbit with 2 vials of each sample together with 3 vials of standard as shown in **Figure 2.10**. Irradiated for 11 hr in CA2 tube, cooled for 13 hr, counted for 100s and 1000s 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. Concentration of arsenic was calculated by comparison of photopeak area of sample with standard using the same irradiation periods and γ -ray energies.

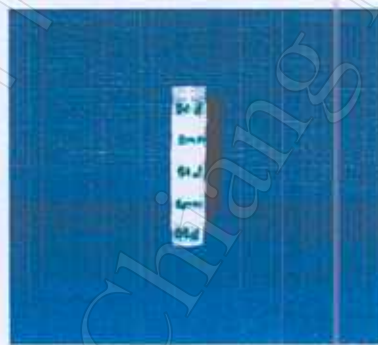


Figure 2.10 The standard and samples in the rabbit with 2 vials of each sample together with 3 vials of standard

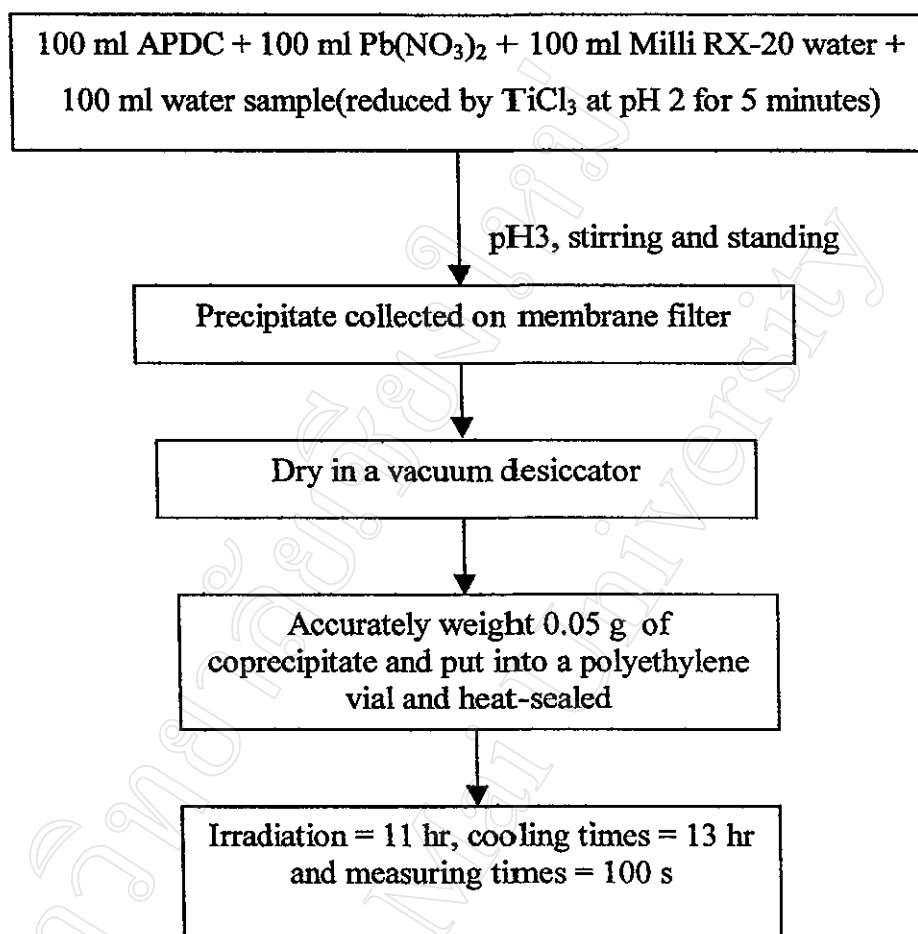


Figure 2. 11 Schematic diagram for coprecipitation of sample

2.3.6 Detection limit

Coprecipitation of arsenic on Pb(APDC)₂ was accomplished using the same procedure as described in 2.3.1.1 but not added 100 ml of 500 ppm standard As(III) or 500 ppm As(V). The pH was adjusted to 3. After 10 minutes of stirring and standing, the precipitates were collected on membrane filter, dried in a vacuum desiccator. About 0.05 g accurate weight of coprecipitated was put into a polyethylene vial and heat-sealed for neutron irradiation.

The irradiation times were 4 hr. The γ -peaks at energy of 559 keV were detected for 200 s.

2.4 Calculation of results

The concentration of arsenic in sample can be calculated by the equation for comparative NAA as follow :

$$W_{\text{sam}} = [W_{\text{std}}] \times [C_{\text{sam}} / C_{\text{std}}]$$

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.