

## APPENDIX A



National Institute of Standards &amp; Technology

## Certificate of Analysis

## Standard Reference Material® 2710

Montana Soil

Highly Elevated Trace Element Concentrations

This Standard Reference Material (SRM) is intended primarily for use in the analysis of soils, sediments, or other materials of a similar matrix. SRM 2710 is a highly contaminated soil that was oven-dried, sieved, and blended to achieve a high degree of homogeneity. A unit of SRM 2710 consists of 50 g of the dried material.

The certified elements for SRM 2710 are given in Table 1. The values are based on measurements using one definitive method or two or more independent and reliable analytical methods. Noncertified values for a number of elements are given in Table 2 as additional information on the composition. The noncertified values should not be used for calibration or quality control. Analytical methods used for the characterization of this SRM are given in Table 3 along with analysts and cooperating laboratories. All values (except for carbon) are based on measurements using a sample weight of at least 250 mg. Carbon measurements are based on 100 mg samples.

**NOTICE AND WARNINGS TO USERS**

**Expiration of Certification:** This certification of SRM 2710 is valid, within the measurement uncertainties specified, until 01 July 2015, provided the SRM is handled in accordance with instructions given in this certificate (see Instructions for Use). This certification is nullified if the SRM is damaged, contaminated, or modified.

**Maintenance of SRM Certification:** NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Return of the attached registration card will facilitate notification.

**Stability:** This material is considered to be stable; however, its stability has not been rigorously assessed. NIST will monitor this material and will report any substantive changes in certification to the purchaser.

**Instructions for Use:** A minimum sample weight of 250 mg (dry weight - see Instructions for Drying) should be used for analytical determinations to be related to the certified values on this Certificate of Analysis.

To obtain the certified values, sample preparation procedures should be designed to achieve complete dissolution. If volatile elements (i.e., Hg, As, Se) are to be determined, precautions should be taken in the dissolution of SRM 2710 to avoid volatilization losses.

The technical and support aspects involved in the original preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by T.E. Gills and J.S. Kane. Revision of this certificate was coordinated through the Standard Reference Materials Program by B.S. MacDonald.

Statistical consultation was provided by S.B. Schuller of the NIST Statistical Engineering Division.

The overall direction and coordination of the analyses were under the chairmanship of M.S. Epstein and R.L. Watters, Jr., of the NIST Analytical Chemistry Division.

**Instructions for Drying:** When nonvolatile elements are to be determined, samples should be dried for 2 h at 110 °C. Volatile elements (i.e., Hg, As, Se) should be determined on samples as received; separate samples should be dried as previously described to obtain a correction factor for moisture. Correction for moisture is to be made to the data for volatile elements before comparing to the certified values. This procedure ensures that these elements are not lost during drying. The weight loss on drying has been found to be in the range of 1.7% to 2.3%.

**Source and Preparation of Material:** The U.S. Geological Survey (USGS), under contract to the NIST, collected and processed the material for SRM 2710. The soil was collected from the top 10 cm (4 in) of pasture land located at Longitude 112° 47' and Latitude 46° 01' along Silver Bow Creek in the Butte, Montana area. The site is approximately nine miles east of the local Anaconda plant and 6.5 miles south of settling ponds that feed the creek. The creek periodically floods, depositing sediment with high concentrations of copper, manganese, and zinc at the collection site. The material was shoveled from a 6.1 m x 6.1 m (20 ft x 20 ft) area into polyethylene bags in cardboard cartons for shipment to the USGS laboratory for processing.

The material was spread on 30.5 cm x 61 cm (1 ft x 2 ft) polyethylene-lined drying trays in an air drying oven and dried for three days at room temperature. The material was then passed over a vibrating 2 mm screen to remove plant material, rocks, and large clumps of aggregated soil. Material remaining on the screen was deaggregated and rescreened. The combined material passing the screen was ground in a ball mill to pass a 74 µm screen and blended for 24 h. Twenty grab samples were taken and measured for the major oxides using x-ray fluorescence spectrometry and for several trace elements using inductively coupled plasma atomic emission analysis to provide preliminary assessment of the homogeneity of the material prior to bottling. The material was bottled into 50 g units and randomly selected bottles were taken for the final homogeneity testing.

**Analysis:** The homogeneity, using selected elements in the bottled material as indicators, was assessed using x-ray fluorescence spectrometry and neutron activation analysis. In a few cases, statistically significant differences were observed, and the variance due to material inhomogeneity is included in the overall uncertainties of the certified values. The estimated relative standard deviation for material inhomogeneity is less than 2% for those elements for which homogeneity was assessed.

**Certified Values and Uncertainties:** The certified values are weighted means of results from two or more independent analytical methods, or the mean of results from a single definitive method, except for mercury. Mercury certification is based on cold vapor atomic absorption spectrometry used by two different laboratories employing different methods of sample preparation prior to measurement. The weights for the weighted means were computed according to the iterative procedure of Paule and Mandel [1] (NBS Journal of Research 87, 1982, pp. 377-385). The stated uncertainties include allowances for measurement imprecision, material variability, and differences among analytical methods. Each uncertainty is the sum of the half-width of a 95% prediction interval and includes an allowance for systematic error among the methods used. In the absence of systematic error, a 95% prediction interval predicts where the true concentrations of 95% of the samples of this SRM lie. The certified values were corroborated by analyses from nine Polish laboratories cooperating on the certification under the direction of T. Plebanski and J. Lipinski, Polish Committee for Standardization, Measures, and Quality Control. The Polish laboratory work was supported by the Maria Skłodowska-Curie Joint Fund.

Table 1. Certified Values

| Element    | Mass Fraction (in %) | Element  | Mass Fraction (in mg/kg) |
|------------|----------------------|----------|--------------------------|
| Aluminium  | 6.44 ± 0.08          | Antimony | 38.4 ± 3                 |
| Calcium    | 1.25 ± 0.03          | Arsenic  | 626 ± 38                 |
| Iron       | 3.38 ± 0.10          | Barium   | 707 ± 51                 |
| Magnesium  | 0.853 ± 0.042        | Cadmium  | 21.8 ± 0.2               |
| Manganese  | 1.01 ± 0.04          | Copper   | 2950 ± 130               |
| Phosphorus | 0.106 ± 0.015        | Lead     | 5532 ± 80                |
| Potassium  | 2.11 ± 0.11          | Mercury  | 32.6 ± 1.8               |
| Silicon    | 28.97 ± 0.18         | Nickel   | 14.3 ± 1.0               |
| Sodium     | 1.14 ± 0.06          | Silver   | 35.3 ± 1.5               |
| Sulfur     | 0.240 ± 0.006        | Vanadium | 76.6 ± 2.3               |
| Titanium   | 0.283 ± 0.010        | Zinc     | 6952 ± 91                |

**Noncertified Values:** Noncertified values are provided for information only. An element concentration value is not certified if bias is suspected in one or more of the methods used for certification, or if two independent methods are not available.

Table 2. Noncertified Values

| Element | Mass Fraction (in %) | Element    | Mass Fraction (in mg/kg) |
|---------|----------------------|------------|--------------------------|
| Carbon  | 3                    | Bromine    | 6                        |
|         |                      | Cerium     | 57                       |
|         |                      | Cesium     | 107                      |
|         |                      | Chromium   | 39                       |
|         |                      | Cobalt     | 10                       |
|         |                      | Dysprosium | 5.4                      |
|         |                      | Europium   | 1                        |
|         |                      | Gallium    | 34                       |
|         |                      | Gold       | 0.6                      |
|         |                      | Hafnium    | 3.2                      |
|         |                      | Holmium    | 0.6                      |
|         |                      | Indium     | 5.1                      |
|         |                      | Lanthanum  | 34                       |
|         |                      | Molybdenum | 19                       |
|         |                      | Neodymium  | 23                       |
|         |                      | Rubidium   | 120                      |
|         |                      | Samarium   | 7.8                      |
|         |                      | Scandium   | 8.7                      |
|         |                      | Strontium  | 330                      |
|         |                      | Thallium   | 1.3                      |
|         |                      | Thorium    | 13                       |
|         |                      | Tungsten   | 93                       |
|         |                      | Uranium    | 25                       |
|         |                      | Ytterbium  | 1.3                      |
|         |                      | Yttrium    | 23                       |

Table 3. Analytical Methods Used for the Analysis of SRM 2710

| Element | Certification Methods <sup>1</sup> | Element | Certification Methods <sup>1</sup> |
|---------|------------------------------------|---------|------------------------------------|
| Ag      | ID ICPMS, RNAA, INAA               | Mg      | XRF1, ICP                          |
| Al      | XRF1, XRF2, DCP, ICP               | Mn      | INAA, DCP, XRF2                    |
| As      | RNAA, HYD AAS, ICP, INAA           | Mo      | ID ICPMS                           |
| Au      | INAA, FAAS                         | Na      | INAA, FAES                         |
| Ba      | XRF2, FAES                         | Nd      | ICP                                |
| Br      | INAA                               | Ni      | ID ICPMS, ETAAS, INAA              |
| C       | COUL                               | P       | DCP, COLOR, XRF1, XRF2             |
| Ca      | XRF1, XRF2, DCP                    | Pb      | ID TIMS, POLAR, ICP                |
| Cd      | ID ICPMS, RNAA                     | Rb      | INAA                               |
| Ce      | INAA, ICP                          | S       | ID TIMS                            |
| Co      | INAA, ETAAS, ICP                   | Sb      | RNAA, ETAAS                        |
| Cr      | INAA, DCP, ICP                     | Sc      | INAA, ICP                          |
| Cs      | INAA                               | Si      | XRF1, XRF2, GRAV                   |
| Cu      | RNAA, FAES, ICP                    | Sr      | INAA                               |
| Dy      | INAA                               | Sr      | ID TIMS, INAA, ICP                 |
| Eu      | INAA                               | Th      | ID TIMS, INAA, ICP                 |
| Fe      | XRF1, XRF2, DCP, INAA, ICP         | Ti      | XRF1, XRF2, DCP                    |
| Ga      | INAA, ICP                          | Tl      | ID TIMS, LEAFS                     |
| Hf      | INAA                               | U       | ID TIMS, INAA                      |
| Hg      | CVAAS                              | V       | INAA, ICP                          |
| Ho      | INAA                               | W       | INAA                               |
| In      | INAA                               | Y       | ICP                                |
| K       | XRF1, XRF2, FAES, ICP              | Yb      | INAA                               |
| La      | INAA, ICP                          | Zn      | ID TIMS, ICP, INAA, POLAR          |

\*Methods in bold were used to corroborate certification methods or to provide information values.

COLOR - Colorimetry; lithium metaborate fusion

COUL - Combustion coulometry

CVAAS - Cold vapor atomic absorption spectrometry

DCP - Direct current plasma atomic emission spectrometry; lithium metaborate fusion

ETAAS - Electrothermal atomic absorption spectrometry; mixed acid digestion

FAAS - Flame atomic absorption spectrometry; mixed acid digestion except for Au, leached with HBr-Br<sub>2</sub>

FAES - Flame atomic emission spectrometry; mixed acid digestion

GRAV - Gravimetry; sodium carbonate fusion

HYD AAS - Hydride generation atomic absorption spectrometry

ICP - Inductively coupled plasma atomic emission spectrometry; mixed acid digestion

ID ICPMS - Isotope dilution inductively coupled plasma mass spectrometry; mixed acid digestion

ID TIMS - Isotope dilution thermal ionization mass spectrometry; mixed acid digestion

INAA - Instrumental neutron activation analysis

LEAFS - Laser enhanced atomic fluorescence spectrometry; mixed acid digestion

POLAR - Polarography

RNAA - Radiochemical neutron activation analysis; mixed acid digestion

XRF1 - Wavelength dispersive x-ray fluorescence spectrometry on fused borate discs

XRF2 - Wavelength dispersive x-ray fluorescence spectrometry on pressed powder

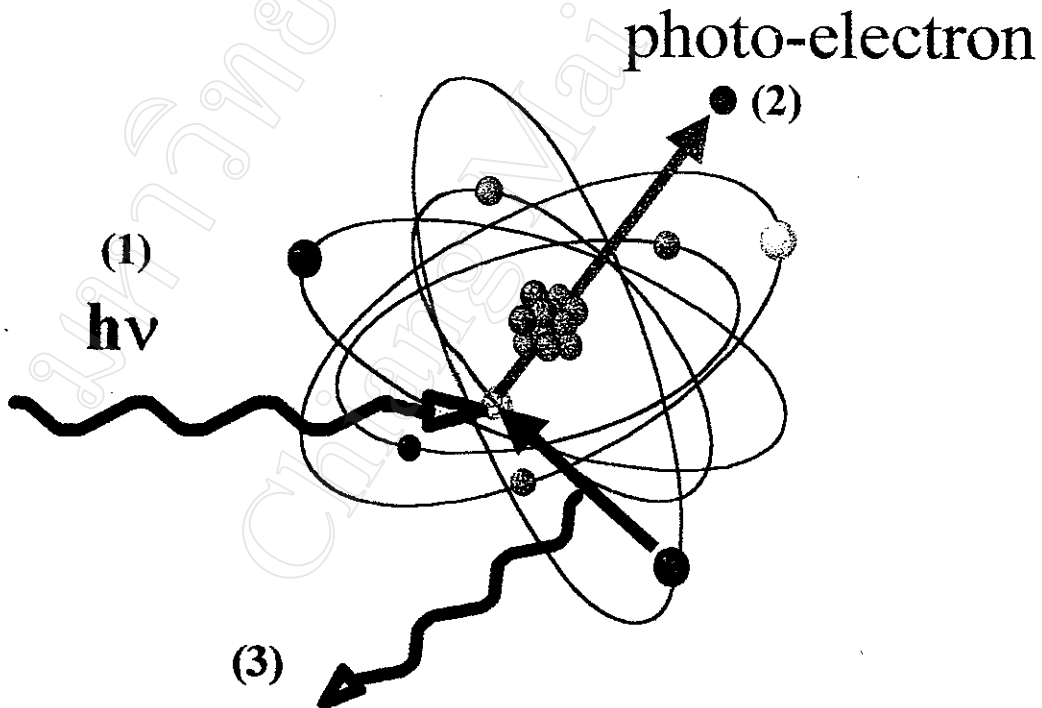
## APPENDIX B

### B.1 Energy Dispersive X-ray Fluorescence Technique (EDXRF) [40-43]

#### B.1.1 EDXRF method

When the atoms in a sample material are irradiated with high-energy primary x-ray photons, electrons are ejected in the form of photoelectrons. This creates electron 'holes' in one or more of the orbitals, converting the atoms into ions - which are unstable.

To restore the atoms to a more stable state, electrons from outer orbitals fill the holes in inner orbitals. Such transitions may be accompanied by an energy emission in the form of a secondary X-ray photon a phenomenon known as 'fluorescence'.



## Characteristic X-ray

Fig B.1.1 The production of characteristic X-ray

From the Figure B.1.1 the characteristic X-ray is produced from excitation atom after electron is ejecting from the K shell by electron bombardment or by the absorption of photon. A certain amount of energy of excited atom is emitted in form of electromagnetic radiation due to electron transfer process from higher energy level to lower energy level. The various electron orbitals are called K, L, M, etc., where K is closest to the nucleus. Each corresponds to a different energy level - and the energy (E) of emitted fluorescent photons is determined by the difference in energies between the initial and final orbitals for the individual transitions followed the selection rule. The selection rule shown in Figure B.1.2

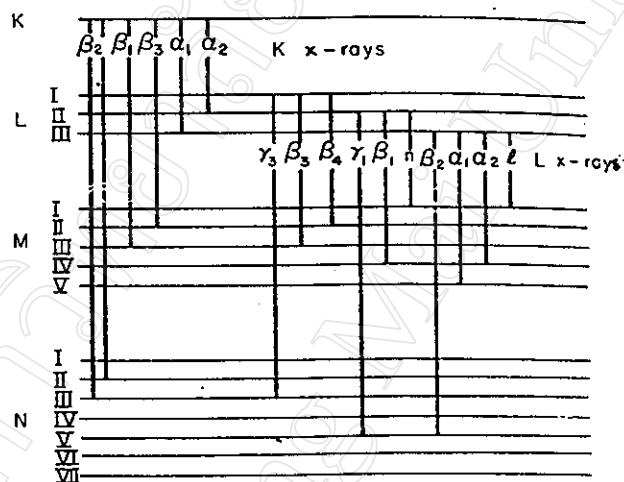


Fig B.1.2 The selection rule [40,41]

## B.1.2 Source of the primary radiation of EDXRF [44]

### B.1.2.1 Radio isotope source

$^{238}\text{Pu}$  isotope is used as the radio isotope source in this research. The simplified decay scheme of this isotope and X-ray spectrum from  $^{238}\text{Pu}$  is presented in Figure 1.8 and Figure 1.9 respectively.

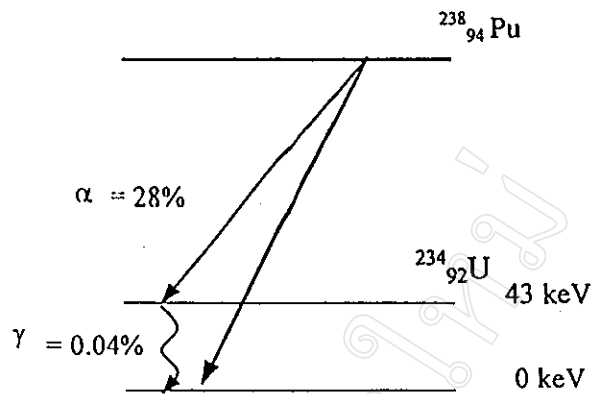


Fig B.1.3 Decay scheme of the principle transition in  $^{238}\text{Pu}$

From Figure B.1.3, 28% of  $^{238}\text{U}$  nuclei resulting from alpha decay of  $^{238}\text{Pu}$  are in an intermediate state with energy equal to 43.5 keV. For such a low energy and high atomic number of nucleus the transition to ground state yields practically no gamma radiation. The emitted X-rays are the L-series radiation of uranium, which are used for excited radiation. The L-series of uranium observed from X-ray spectra are shown in Fig B.1.4

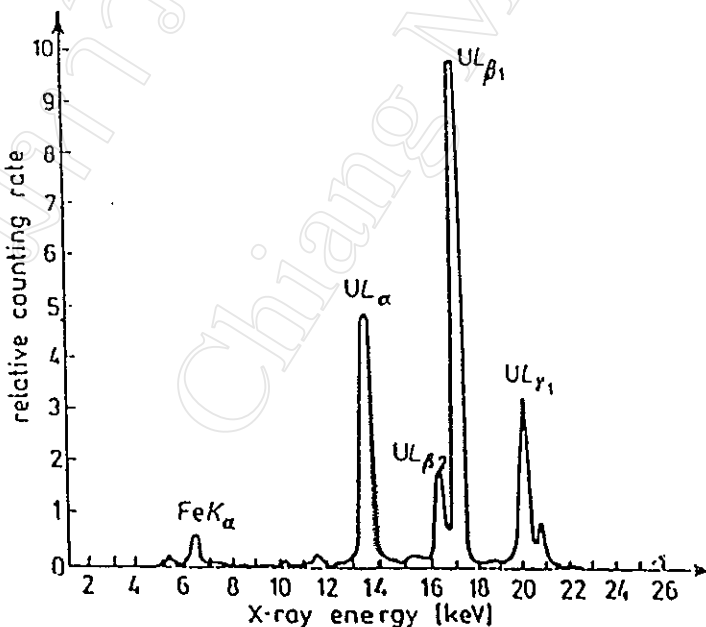


Fig B.1.4 X-ray spectrum from  $^{238}\text{Pu}$  source measured with Si(Li) detector

### B.1.2.2 Low power X-ray tube

X-ray tube composition is illustrated in Fig B.5

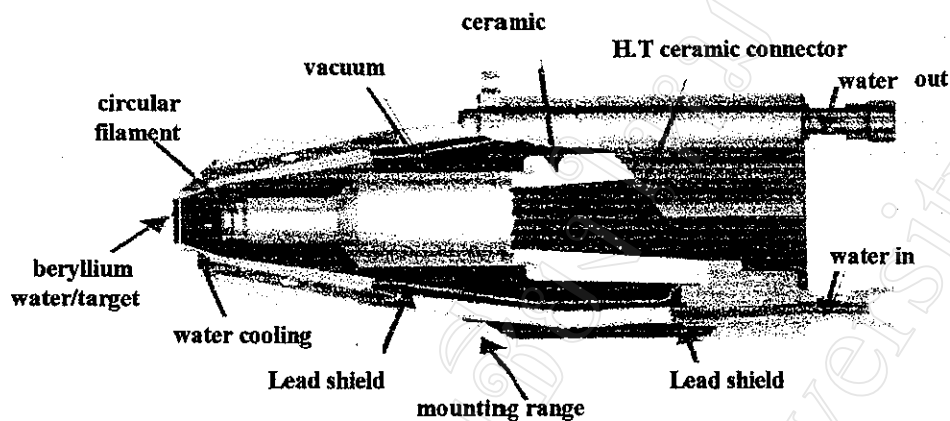


Fig B.1.5 X-ray composition

The X-ray tube consists of a vacuum enclosure containing source and target anode. The electron beam is generated using thermionic cathode and is accelerated toward the anode by electrostatic potential of typically 30-110 KeV. When the anode is bombarded by electron beam constitutes a source both of characteristic radiation of the anode element and of the Bremsstrahlung due to is several order of magnitudes lower than that of the electron induced Bremsstrahlung.

### B.1.3 Detector system

The instrumentation used to measure X-rays from analyte generally consists of a semiconductor detector, associated electronics, and a computer-based, multi-channel analyzer (MCA/computer). Many type of detectors are used in the EDXRF system such as Si(Li) detector or server type of HPGE detector. The types of detector in difference system are illustrated in Table B.1.1.



Table B.1.1 Some type of detector

| type of detector          | Geometry            | Window thickness(mm) | Useful Energy |  | Material             | Standard Size       | Standard Energy Resolution                          |
|---------------------------|---------------------|----------------------|---------------|--|----------------------|---------------------|---|
|                           |                     |                      | Range         |  |                      |                     |   |
| HPGe Coaxial (GEM Series) | Closed-end Coaxial  | 600                  | 40 keV-10 MeV |  | P-Type HPGe          | 10%-100% Efficiency | 1.75-2.30 keV at 1.33 MeV                           |
| Gamma-X GMX Series        | Thin window Coaxial | 0.3<br>Ion implanted | 3 keV-10 MeV  |  | N-Type HPGe          | 10%-100% Efficiency | 1.80-2.40 keV at 1.33 MeV<br>665-1200keV at 5.9 keV |
| Si(Li) LEPS (GLP Series)  | Planar              | 0.1<br>Ion implanted | 1 keV-30 keV  |  | lithium drifted HPGe | 4-16 mm diameter    | 160-250 eV at 1.33 MeV                              |
| SLP Series)               |                     |                      |               |  | silicon              | diameter            | at 5.9 keV  |

### B.1.4 Quantitative analysis by EDXRF [42-43]

In quantitative analysis by EDXRF, quantify of interesting elements could be estimated from intensity of characteristic X-ray of interesting element. But X-ray fluorescence intensity of interesting elements may be alternated by matrix in sample. Matrix effect in EDXRF analysis cause by the influence of variation of the chemical composition of sample matrix on the fluorescence intensity of interested elements: The important matrix effects are absorption and enhancement effects. Absorption effect occurs when the variation in the matrix chemical compositions results in changes of the mean absorption coefficient of both the primary radiation of source and fluorescence radiation of the interesting element. A strong decrease of the fluorescence radiation of the interesting element will be observed if the concentration of disturbing element of slightly lower atomic number become large. Enhancement effect results from retransmission of the energy of the primary radiation of source in form of secondary fluorescence radiation is just slightly higher than the absorption edge of the interesting element, the latter will be excited more efficiency than by the primary radiation of source, whose energy is higher than that of secondary radiation and consequently further from the absorption edge. Therefore, the elimination of matrix effects is necessary for quantitative analysis is expected. Matrix correction must be performed in corresponding with the real sample. The matrix correction techniques were including emission-transmission, thin film method and stand addition techniques. In this research, emission-transmission was used to correct the matrix.

#### B.1.4.1 Emission-Transmission Method

The determination of absorption correction factor to eliminate matrix effect is necessary for quantitative analysis. Absorption correction factor is related to total mass absorption coefficient ( $\chi$ ) which varied with sample composition. In control sample,  $\chi$  is calculated by equation 1.1

$$\chi = \mu_m(E_o) / \sin \phi_1 + \mu_m(E_f) / \sin \phi_2 \quad (1.1)$$

where

$$\mu_m = \sum_{i=1}^n w_i \mu_i(E)$$

$\mu_i$  and  $w_i$  = individual mass absorption coefficients and weight fraction of interest element  $i$ , respectively and  $n$  is the number of components,

$\phi_1$  = the angle between excitation radiation from source and sample,

$\phi_2$  = the angle between characteristic x-ray of element  $i$  in sample and detector,

$E_o$  = incident radiation energy,

$E_i$  = energy of characteristic x-ray of element  $i$ .

However in unknown sample, total mass absorption coefficient could be estimated by using Emission-Transmission (E-T) method. Leroux and Mahmud as described in Fig B.1.6 suggested the principle of E-T method, in 1966.

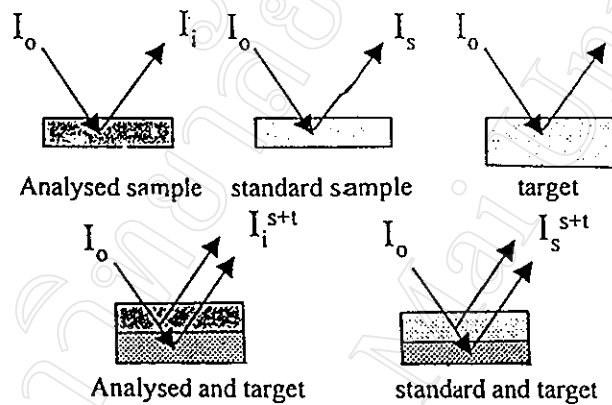


Fig B.1.6 Principle of Emission-Transmission (E-T) method

$I_i$  is the characteristic X-ray of element  $i$  from sample,  $I_i'$  is the characteristic X-ray of element  $i$  from target. Target is prepared in thick form with the same cross section area as the sample. It contains solely element  $i$  or its chemical compound to ensure that the concentration of element  $i$  is much greater than that in analyte and control sample.  $I_i^{s+t}$  is the characteristic X-ray of element  $i$  from sample and target.  $\chi_i$  is the mass absorption coefficient of X-ray measurement of element  $i$ ,  $\rho_m D$  is thickness of sample ( $\text{g/cm}^2$ ). These parameters are substituted in equation 1.2.

$$I_i^{s+t} - I_i = I_i' \exp(-\chi_i \rho_m D) \quad (1.2)$$

therefore

$$-\chi_i = \frac{\ln(R)}{\rho_m D} \quad (1.3)$$

where

$$R = \frac{(I_i^{s+t} - I_i)}{I_i'} \quad (1.4)$$

the quantify of element  $i$  in sample can be calculated by equation 1.5.

$$W_i = \frac{J_i F_i}{S_i} \quad (1.5)$$

when

$$F_i = \frac{\chi_i}{[1 - \exp(-\chi_i \rho_m D)]} \quad (1.6)$$

$F_i$  is the absorption correction factor.  $S_i$  is the sensitivity of element  $i$  analysis by using the same instrument which can be calculated by equation 1.5 when using standard sample.

## B.2 EXPERIMENTAL

### B 2.1 XRF apparatus

- 1) Pu-238 annular source, 8mCi
- 2) Detector system, consisted of
  - a) Si (Li) detector, 13mm<sup>2</sup> x 3mm, manufactured by Princeton Gamma-Tech
  - b) High voltage power supply, Canberra Model 3106 D
  - c) Preamplifier and amplifier, Ortec Model 472
  - d) Multichannel analyzer, Nuclear Data Model 65
  - e) Data system consisted of computer with the program QXAS-AXIL software.

Figures B.2.1-2.2 showed a diagram of XRF apparatus and detector system used.

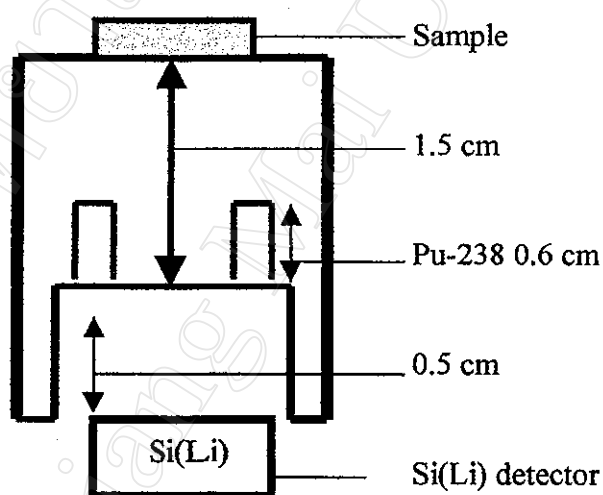


Fig B.2.1 XRF apparatus system [44]

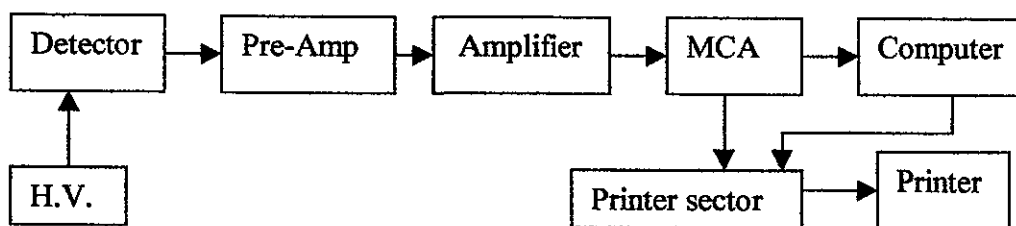


Fig B.2.2 Block diagram of detector system

- 3) Pellet hydraulic pressure, Car Laboratory Press Model M Max.0-5000  
Pound 0-22 Metric Ton

### **B.2.2 Chemical and Material**

- 1) Certified reference material, SRM 2710 (Motana soil)certified value of arsenic in Motana =  $626 \pm 38 \text{ mg Kg}^{-1}$ , manufactured by the Nation Institute of Standard and Technology (NIST), U.S.A
- 2) Arsenic trioxide,  $\text{As}_2\text{O}_3$ , MW 197.84, AR Grade, Merck, Germany
- 3) Stick cassava flour ( starch binder)

### **B.2.3 Sample material**

About 10 kg of five natural agricultural soil samples were collected from both unpollutant, non-residential areas and presumably polluted mining industrial areas in Ronpibul distric. The samples were dried in air, quartered, ground and powdered in an agate mortar, passed through 325 mesh sieves and stored in polyethylene bags.

### **B.2.4 E-T method and the absorption correction factor**

The emission-transmission (E-T method) was applied to determine As (concentration ) in soil sample in order to compare the mass absorption coefficient obtained by E-T method with the theoretical estimated value by equation 1.1 as mention in section B.1.4.1.

#### **B.2.4.1 Pellet preparation**

Sticky cassava flour was selected as a matrix binder. The standard pellets were prepared by solid dilution technique. Sticky cassava flour and arsenic oxide were blended in agate motar to homogenize the sample. The targets of arsenic were prepared by the same procedure as that of standard.

Soil sample: Sticky cassava flour and soil sample were blended in agate motar to homogenize the sarnple in a 50:50 weight ratio. Sample of intermediate thickness (approx.  $\rho_m D = 0.161 \text{ g/cm}^2$ ) were prepared in the form of pellets with a diameter of 2.76 cm, by hydraulic pressing them at 20,000 pound/in<sup>2</sup>. For standard preparation, sticky cassava flours and arsenic oxide were blended in

agate mortar to homogenize in a 1:100 weight ratio and prepared in the form of pellets in the same way of sample. The target of arsenic was prepared by the same procedure as that of standard sample, but arsenic oxide and sticky cassava flour were mixed in a 1:20 by weight ratio.

#### B 2.4.2 Analysis of soil samples

Pellet excitation was done with Pu-238 annular source (8mCi). The photopeak area of 10.543 keV characteristic X-ray of As was detected and counted on Si(Li) detector. The weights of soil sample and starch binder in the sample pellets and  $As_2O_3$  and starch binder in the standard pellets are shown in Table B.2.1. The measuring times used in the experiment are shown Table B.2.2.

**Table B 2.1** The weights of soil sample, starch binder and  $As_2O_3$  in pellets

| Sample No | Soil (g)         | Starch Binder(g) | Soil (%)          | Pellet weight (g) |
|-----------|------------------|------------------|-------------------|-------------------|
| S1        | 0.5649           | 1.2620           | 44.76             | 0.8617            |
| S2        | 0.4986           | 1.0089           | 49.42             | 0.8056            |
| S3        | 0.5036           | 1.0076           | 49.98             | 0.7083            |
| S4        | 0.5841           | 1.4385           | 40.60             | 0.9723            |
| S5        | 0.6280           | 1.3339           | 47.08             | 0.9598            |
| Standard  |                  |                  |                   |                   |
| $As_2O_3$ | Starch Binder(g) | $As_2O_3$ (%)    | Pellet weight (g) |                   |
| 0.0198    | 1.8126           | 1.09             | 0.7473            |                   |

**Table B.2.2** Measuring time in this experiment.

| Sample                      | Measuring time (s) |
|-----------------------------|--------------------|
| Target pellet               | 600                |
| Standard pellet             | 1500               |
| Soil sample pellet          | 2000               |
| Target + soil sample pellet | 1000               |
| Target + standard pellet    | 600                |

### B.3 RESULTS AND DISCUSSIONS

The aim of this experiment was to confirm and compare the values obtained from INAA with those obtained from XRFA method. The XRFA are non-destructive, no pretreatment necessary as INAA method. The other advantage is that XRFA can be used as effective analytical technique for widely different concentration ranges. V.Cercasov *et al.* examined the suitability of the applied INAA and XRFA techniques to determine the element concentration in difference matrix at the realistically concentration ranges, and found that arsenic could be analyzed by both INAA and XRFA.

X-ray spectra of soil sample show a number of characteristic X-ray peaks which correspond to the trace elements present in the sample.

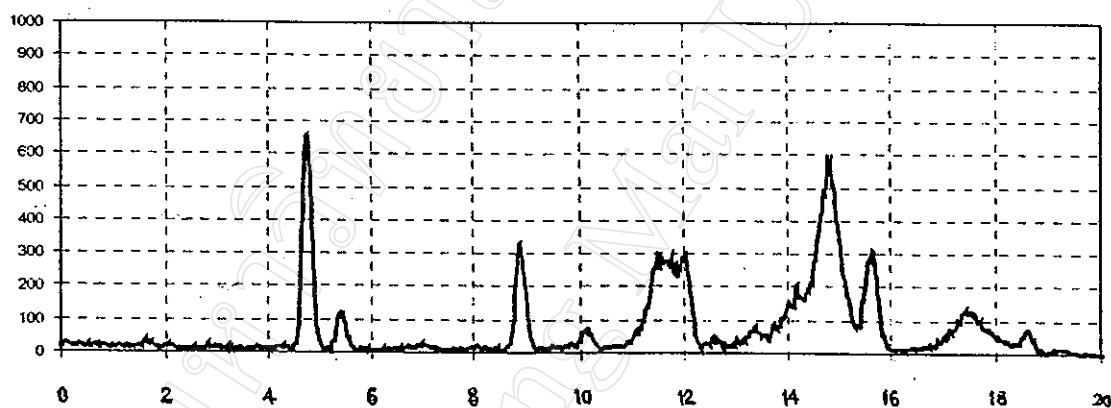


Fig B.3.1 X-ray fluorescence spectrum of soil sample No 1

The results from XRFA calculation of As in difference soil samples are shown in Table B.3.1 and the arsenic concentrations by XRF (E-T method) compared with INAA method are shown Table B.3.2.

It was found from the results that the arsenic obtained from XRFA agreed with those obtained from INAA technique with in 10%.



**Table B.3.1** Results from XRFA calculation of As in difference soil samples ( when %W(As) = 0.8273 and It = 302.31 cps)

| Sample No.                                  | wt(sheet) g.  | pD            | Ii(cps)      | Ist(cps)      | It(cps)       | R             | X              | Fi             | %As             | dil.fac.       | net As(g)       | mg/kg(1)       | %SD         |
|---|---------------|---------------|--------------|---------------|---------------|---------------|----------------|----------------|-----------------|----------------|-----------------|----------------|-------------|
| <b>Standard As<sub>2</sub>O<sub>3</sub></b> | <b>0.7473</b> | <b>0.1213</b> | <b>45.37</b> | <b>186.91</b> | <b>302.31</b> | <b>0.4682</b> | <b>6.2554</b>  | <b>11.7625</b> | <b>8.27E-01</b> |                |                 |                |             |
| Sample1(1)                                  | 0.8617        | 0.1399        | 3.61         | 39.80         | 302.31        | 0.1197        | 15.1740        | 17.2376        | 9.64E-02        | 2.23402        | 2.15E-01        | 2154.12        |             |
| Sample1(2)                                  | 0.8617        | 0.1399        | 3.75         | 41.00         | 302.31        | 0.1232        | 14.9670        | 17.0706        | 9.91E-02        | 2.23402        | 2.21E-01        | 2214.05        |             |
| <b>Average</b>                              | <b>0.8617</b> | <b>0.1399</b> | <b>3.68</b>  | <b>40.40</b>  | <b>302.31</b> | <b>0.1215</b> | <b>15.0705</b> | <b>17.1541</b> | <b>0.0978</b>   | <b>2.23402</b> | <b>0.2184</b>   | <b>2184.09</b> | <b>1.94</b> |
| Sample2(1)                                  | 0.8056        | 0.1308        | 2.90         | 36.86         | 302.31        | 0.1123        | 16.7167        | 18.8324        | 8.47E-02        | 2.02347        | 1.71E-01        | 1713.16        |             |
| Sample2(2)                                  | 0.8056        | 0.1308        | 2.91         | 37.95         | 302.31        | 0.1159        | 16.4772        | 18.6376        | 8.41E-02        | 2.02347        | 1.70E-01        | 1701.29        |             |
| <b>Average</b>                              | <b>0.8056</b> | <b>0.1308</b> | <b>2.91</b>  | <b>37.41</b>  | <b>302.31</b> | <b>0.1141</b> | <b>16.5970</b> | <b>18.7350</b> | <b>0.0844</b>   | <b>2.02347</b> | <b>1.71E-01</b> | <b>1707.23</b> | <b>0.49</b> |
| Sample3(1)                                  | 0.7083        | 0.1150        | 0.27         | 108.62        | 302.31        | 0.3584        | 8.9244         | 13.9092        | 5.89E-03        | 2.00079        | 1.18E-02        | 117.78         |             |
| Sample3(2)                                  | 0.7083        | 0.1150        | 0.28         | 105.96        | 302.31        | 0.3496        | 9.1408         | 14.0535        | 5.99E-03        | 2.00079        | 1.20E-02        | 119.87         |             |
| <b>erage</b>                                | <b>0.7083</b> | <b>0.1150</b> | <b>0.27</b>  | <b>107.29</b> | <b>302.31</b> | <b>0.3540</b> | <b>9.0326</b>  | <b>13.9814</b> | <b>0.0059</b>   | <b>2.00079</b> | <b>1.19E-02</b> | <b>118.83</b>  | <b>1.25</b> |
| Sample4(1)                                  | 0.9723        | 0.1578        | 0.48         | 27.98         | 302.31        | 0.0910        | 15.1871        | 16.7071        | 1.24E-02        | 2.46276        | 3.05E-02        | 305.11         |             |
| Sample4(2)                                  | 0.9723        | 0.1578        | 0.52         | 29.55         | 302.31        | 0.0960        | 14.8449        | 16.4218        | 1.32E-02        | 2.46276        | 3.24E-02        | 323.93         |             |
| <b>Average</b>                              | <b>0.9723</b> | <b>0.1578</b> | <b>0.50</b>  | <b>28.76</b>  | <b>302.31</b> | <b>0.0935</b> | <b>15.0160</b> | <b>16.5645</b> | <b>0.0128</b>   | <b>2.46276</b> | <b>3.15E-02</b> | <b>314.52</b>  | <b>4.23</b> |
| Sample5(1)                                  | 0.9598        | 0.1558        | 1.03         | 24.64         | 302.31        | 0.0781        | 16.3650        | 17.7512        | 2.83E-02        | 2.12404        | 6.00E-02        | 600.10         |             |
| Sample5(2)                                  | 0.9598        | 0.1558        | 1.09         | 24.35         | 302.31        | 0.0769        | 16.4611        | 17.8330        | 3.02E-02        | 2.12404        | 6.42E-02        | 641.52         |             |
| <b>Average</b>                              | <b>0.9598</b> | <b>0.1558</b> | <b>1.06</b>  | <b>24.49</b>  | <b>302.31</b> | <b>0.0775</b> | <b>16.4130</b> | <b>17.7921</b> | <b>0.0292</b>   | <b>2.12404</b> | <b>6.21E-02</b> | <b>620.81</b>  | <b>4.72</b> |

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**Paper Presented** S. Putaraporn, O. Arquero, S. Liawriangrat, S. Kaweerat and S. Pimjun, **Determination of Arsenic in Contaminated Soil Samples by NAA**, 8<sup>th</sup>, Congress of Science and Nuclear Technology, Thailand, 2001  
S. Putaraporn, O. Arquero, S. Liawriangrat, S. Kaweerat and S. Pimjun, **Determination of Arsenic in Contaminated Soil Samples from Amphur Ronpibul using NAA and X-ray Fluorescence Techniques**, 27<sup>th</sup>, Congress of Science and Technology of Thailand, 2001