

VIETNAM ATOMIC ENERGY COMMISSION



The  
**ANNUAL REPORT**  
for 2004

Hanoi, 10-2005

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**The**  
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The VAEC Annual Report for 2004 has been prepared as an account of works carried out at VAEC for the period 2004. Many results presented in the report have been obtained in collaboration with scientists from national and overseas universities and research institutions.

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## **Preface**

The research activities of the Vietnam Atomic Energy Commission (VAEC) during the period from 1 January to 31 December 2004 are presented in this Report. The research activities are focused on the following fields:

1. Nuclear Physics;
2. Reactor Physics and Nuclear Energy;
3. Nuclear Methods;
4. Nuclear Medicine and Radioisotope Production;
5. Radiation Protection and Radioactive Waste Management;
6. Ecology and Environment;
7. Biotechnology and Agriculture;
8. Radiation Technology;
9. Radiochemistry and Materials Sciences;
10. Computation and Other Related Topics.

The total number of permanent staff working at the VAEC as December 31, 2004 was 657 including the clerical service staff. The VAEC was funded from the Government with the amount to 43.244 billion VN Dong for FY 2004. The fund for the research contracts is 12.167 billion VN Dong in FY 2004. The international support for the VAEC activities is committed to 1,100,000 USD for the year including equipment, staff training and expert services.

Main results of fundamental and applied research implemented in the year were presented in 62 scientific articles, reports and contributions published in many journals, proceedings of conferences, etc. These results were obtained on the basis of the technical cooperation projects (14 TC projects), the research contracts with the IAEA (13 RCs), the research contracts with the Government, the Ministry of Science, Technology and Environment, Vietnam Atomic Energy Commission and the National Program for Fundamental Research (totally 65).

During the time of year 2004, in the VAEC there were 3 graduated in master courses and 1 graduated in Ph.D. courses; 197 people have been trained abroad in the fields of nuclear science and technology.

**Prof. Dr. Vuong Huu Tan**

Chairman, VAEC

# 1. Contributions

# 1.1 - Nuclear Physics

## ON A GENERAL APPROACH TO DETERMINING EXTERNAL SOURCES AS FUNCTIONALS OF ORDER PARAMETERS

**Tran Huu Phat**

*Vietnam Atomic Energy Commission (VAEC)*

**Abstract:** *Based on the DeWitt formula a general approach to determining external sources as functionals of order parameters is given. It provides with a powerful machinery to solve those physical problems which deal with the influence of external field.*

**1.** Due to the experimental observation of Bose-Einstein condensation, nowadays the study dealing with influence of external sources on quantum systems turns out to be one of the most important problems for both physics and technology.

It is known that a quantum system is given by a Lagrangian  $L$  of field operator  $O$ :

$$L = L[O]$$

The interaction of external field and the system is usually described by the interaction Lagrangian:

$$L_I = J(x)O^n(x), \quad n = 1, 2, 3, \dots$$

The total Lagrangian reads:

$$L_J = L[O] + J(x)O^n(x). \quad (1.1)$$

Corresponding (1.1) we define the generating functional of the connected Green functions

$$e^{iW[J]} = \int DO \exp i \left\{ \int dx \left[ L[O] + J(x)O^n(x) \right] \right\}. \quad (1.2)$$

From (1.2) it follows that

$$\frac{\delta W}{\delta J(x)} = \langle O^n(x) \rangle = \chi(x). \quad (1.3)$$

Then the effective action  $\Gamma[\chi]$  is defined as the Legendre transform of  $W[J]$ :

$$\Gamma[\chi] = W[J] - \int dx J(x)\chi(x). \quad (1.4)$$

(1.4) lead to the gap equation in favor of (1.3)

$$\frac{\delta \Gamma[\chi]}{\delta \chi(x)} = -J(x). \quad (1.5)$$

Based on (1.5) the expression for  $\Gamma$  is determined in term of  $J$  if  $J$  is known. However, for  $n \geq 2$ ,  $\Gamma$  the effective action for local composite operators, it is not easy

to calculate its explicit expression. In this respect, Fukuda [1] proposed the following method, this is the so-called inversion method. Instead of starting from equation (1.5) as the basic one for determining  $\chi$  in term of  $J$ , Fukuda solves equation (1.3), which gives

$$\chi = G[J] \quad (1.6)$$

Then  $J$  is exactly the inverse functional of  $\chi$

$$J = G^{-1}[\chi] = F[\chi]$$

Inserting the expression for  $J$  into the gap equation (1.5) we obtain

$$\Gamma[\chi] = \int D\chi F[\chi]$$

In reality (1.6) is a functional equation, therefore determining  $J$  as an inverse functional of  $\chi$  is not an easy problem. In general, several restrictions are imposed on  $J$  and the calculation can be done only in first approximations.

In this paper, taking into consideration the DeWitt formula [2] we establish a new approach to determining directly  $J$  as functional of order parameter.

**2.** For simplicity, let us begin with the real scalar field interacting with external field  $J$ , whose Lagrangian reads:

$$L_J = L[\phi] + K(x)\phi(x) + \frac{1}{2}J(x)\phi^2(x), \quad (2.1)$$

in which additional source  $K(x)$  is introduced and  $K$  tends to zero at the end. The classical action  $S$ , corresponding to (2.1), has the form

$$S_J = \int dx L_J = S[\phi] + \int dx \left[ K(x)\phi(x) + \frac{1}{2}J(x)\phi^2(x) \right], \quad (2.2)$$

where

$$S[\phi] = \int dx L[\phi]$$

is the classical action of the free field.

From the field equation  $\delta S_J = 0$  and (2.2) one deduces

$$\frac{\delta S}{\delta \phi(x)} = -K(x) - J(x)\phi(x). \quad (2.3)$$

Corresponding to (2.3) is the generating functional for connected Green functions  $W[J, K]$ , which is defined by

$$e^{iW[J,K]} = \int D\phi \exp i \left\{ S[\phi] + \int dx \left[ K\phi + \frac{1}{2}J\phi^2 \right] \right\}, \quad (2.4)$$

From (2.4) it follows that

$$\begin{aligned}\frac{\delta W}{\delta K(x)} &= \langle \phi(x) \rangle = \varphi(x). \\ \frac{\delta W}{\delta J(x)} &= \frac{1}{2} \langle \phi^2(x) \rangle = \frac{1}{2} \left( \varphi^2(x) + \Delta(x) \right).\end{aligned}$$

Then the effective action  $\Gamma[\varphi, \Delta]$  is defined as the double Legendre transform of  $W[K, J]$ :

$$\Gamma[\varphi, \Delta] = W[K, J] - \int dx \left[ K\varphi + \frac{1}{2}J(\varphi^2 + \Delta) \right]. \quad (2.5)$$

which provides the gap equations for order parameters  $\varphi$  and  $\Delta$ :

$$\begin{aligned}\frac{\delta \Gamma}{\delta \varphi(x)} &= -K(x) - J(x)\varphi(x). \\ \frac{\delta \Gamma}{\delta \Delta(x)} &= -\frac{1}{2}J(x).\end{aligned} \quad (2.6)$$

The physical configuration of system corresponds to  $K \rightarrow 0$ , of course. Equations (2.6) allow us to find  $\varphi$  and  $\Delta$  for given  $J$ . However, in our method, we will not calculate directly effective action  $\Gamma[\varphi, \Delta]$ . Instead, starting from (2.3) we try to determine  $J$  as functional of  $\varphi$  and  $\Delta$ . It is evident that this is an easier problem. Indeed, averaging both sides of (2.3) over vacuum state leads to

$$\left\langle \frac{\delta S}{\delta \phi(x)} \right\rangle = -K(x) - J(x)\varphi(x). \quad (2.7)$$

Next, in order to get second equation for two unknown  $J$  and  $K$ , both sides of (2.3) are multiplied by  $\phi$  and then averaged over vacuum state

$$\left\langle \phi(x) \frac{\delta S}{\delta \phi(x)} \right\rangle = -K(x)\varphi(x) - J(x) \left( \varphi^2(x) + \Delta(x) \right). \quad (2.8)$$

Solving the system of two equations (2.7) and (2.8) we arrive

$$J(x) = \Delta^{-1}(x) \left\{ \varphi(x) \left\langle \frac{\delta S}{\delta \phi(x)} \right\rangle - \left\langle \phi(x) \frac{\delta S}{\delta \phi(x)} \right\rangle \right\}. \quad (2.9)$$

We do not pay attention to  $K$  due to the fact that it is an artificial source. (2.9) shows that  $J$  is expressed in terms of vacuum expectation values of  $\frac{\delta S}{\delta \phi(x)}$  and  $\phi(x) \frac{\delta S}{\delta \phi(x)}$ , which can be calculated by means of the DeWitt formula [2]:

$$\langle A[\phi] \rangle =: \exp \left( i \sum_{n=2}^{\infty} \frac{(-i)^n}{n!} G^{i_1, i_2, \dots, i_n} \frac{\delta}{\delta \varphi^{i_1}} \dots \frac{\delta}{\delta \varphi^{i_n}} \right) : A[\varphi]$$

where  $: \dots :$  denotes the fact that propagators  $G^{i_1, i_2, \dots, i_n}$  are always standing in the left side of differential operators.

Similarly, the formalism presented above is easily extended to the complex scalar field. In this case, instead of (2.2), we have

$$S_J = \int dx L_J = S[\phi^*, \phi] + \int dx \left[ K^* \phi + \phi^* K + J \phi^* \phi \right]$$

which together  $\delta S_J = 0$  lead to the field equation

$$\frac{\delta S}{\delta \phi^*} = -K(x) - J(x)\phi(x). \quad (2.10)$$

Averaging both sides of (2.10) over vacuum state one has

$$\left\langle \frac{\delta S}{\delta \phi^*} \right\rangle = -K(x) - J(x)\varphi(x). \quad (2.11)$$

Next, multiplied both sides of (2.10) by  $\phi^*(x)$  and then averaged over vacuum state it is derived that

$$\begin{aligned} \left\langle \phi^*(x) \frac{\delta S}{\delta \phi^*} \right\rangle &= -K(x)\varphi^*(x) - J(x)\langle \phi^*(x)\phi(x) \rangle \\ &= -K(x)\varphi^*(x) - J(x)\left( \phi^*(x)\phi(x) + \Delta(x) \right). \end{aligned} \quad (2.12)$$

The expression for  $J$  is obtained as solution of the system of (2.11) and (2.12)

$$J(x) = \Delta^{-1}(x) \left\{ \varphi^*(x) \left\langle \frac{\delta S}{\delta \phi^*(x)} \right\rangle - \left\langle \phi^*(x) \frac{\delta S}{\delta \phi^*(x)} \right\rangle \right\}. \quad (2.13)$$

Finally, let us consider the spinor field under the influence of source, whose Lagrangian is given by

$$L_J = L[\bar{\psi}, \psi] + J(x)\bar{\psi}(x)\psi(x). \quad (2.14)$$

Corresponding to (2.14) is the classical action

$$S_J = S[\bar{\psi}, \psi] + \int dx J(x)\bar{\psi}(x)\psi(x). \quad (2.15)$$

From the field equation  $\delta S_J = 0$  follows that

$$\frac{\delta S}{\delta \bar{\psi}(x)} = -J(x)\psi(x). \quad (2.16)$$

Multiplying both sides of (2.16) by  $\bar{\psi}$  on the left and then averaging over vacuum state we get

$$\left\langle \bar{\psi}(x) \frac{\delta S}{\delta \bar{\psi}(x)} \right\rangle = -J(x)\langle \bar{\psi}(x)\psi(x) \rangle. \quad (2.17)$$

which provides immediately

$$J(x) = -G^{-1}(x) \left\langle \bar{\psi}(x) \frac{\delta S}{\delta \bar{\psi}(x)} \right\rangle, \quad (2.18)$$

where  $G^{-1}(x)$  is the inverse function of



$$G(x) = \langle \bar{\psi}(x)\psi(x) \rangle. \quad (2.19)$$

3. In the previous section a new approach to the inversion method of effective action is presented by means of classical action and the DeWitt formula. This is a very general formalism we can easily extend to those systems, which are more complicated than the ones considered here. However, it is necessary to mention that in the DeWitt formula there appear an infinite tower of propagators of the theory  $G^{i_1 \dots i_n}$ , defined by

$$G^{i_1 \dots i_n}(x_1, \dots, x_n) = \frac{\delta^n W[K]}{\delta K_{i_1}(x_1) \dots \delta K_{i_n}(x_n)},$$

which might be calculated in loop approximation if the following identity

$$\int dz \frac{\delta^2 W[J]}{\delta J(x) \delta J(z)} \frac{\delta^2 \Gamma[\varphi]}{\delta \varphi(z) \delta \varphi(y)} = -\delta(x - y).$$

is incorporated into consideration.

This is obviously a very complicated problem, which can be solved self-consistently only for every concrete system.

The financial support of the Vietnam Atomic Energy Commission under contract CS/04/04-06 is acknowledged with thanks.

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## 1.2 - Reactor Physics and Nuclear Energy

## MEASUREMENT OF NEUTRON CAPTURE CROSS SECTIONS ON FILTERED NEUTRON BEAMS OF 55keV AND 144keV

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**Abstract:** Under the fundamental research program on nuclear physics in the year 2004, the neutron capture cross sections of the  $^{109}\text{Ag}(n,\gamma)^{110m}\text{Ag}$ ,  $^{186}\text{W}(n,\gamma)^{187}\text{W}$  and  $^{158}\text{Gd}(n,\gamma)^{159}\text{Gd}$  have been measured at 55keV and 144keV by the activation method on filtered neutron beams of the nuclear research reactor, Dalat. The cross sections were determined relative to that of  $^{197}\text{Au}$  standard. In these experiments, the pure metallic foils of Ag, W, Gd and Au were used to prepare for targets. The specific activities of the irradiated samples were measured using a high efficient detector (HPGe), and the absolute efficiency calibration for detector was performed by using a set of standard radioisotope sources and a multinuclide standard solution. The present results were compared with the previous measurements from EXFOR-CINDA, and the evaluated values of ENDF/B-VI.

### I. Introduction

Average radioactive neutron capture cross sections in the keV energy region are important in the calculation and design of reactors as well as in the studies of nuclear physics, the s-process for nucleosynthesis in astrophysics and safety analysis. At present, the published experimental data is quite discrepant in different experiments, and it is still not satisfied in quality and quantity. That is the reason why new experimental data, theoretical predictions for more accurate parameters and improvement of theoretical description of neutron radioactive capture reaction are always necessary.

### II. Objective

The project have been implemented in order to push up the activities of fundamental research on nuclear physics, and to use effectively the research reactor and neutron facilities. In addition, these studies play an important role in process of education and development of human resource.

### III. Contents

The main contents of the project are as following: (i) Implementation of filtering and collimation for neutron beams, (ii) Implementation of measurement of average neutron capture cross section of  $^{109}\text{Ag}$ ,  $^{186}\text{W}$  and  $^{158}\text{Gd}$  at energies of 55keV and 144keV, (iii) Evaluation and discussion on present results in comparison with previous ones.

### IV. Method

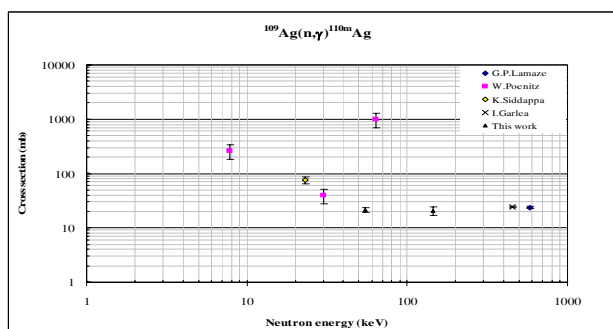
In the current study, the radioactive neutron capture cross section for the reactions of  $^{109}\text{Ag}(n,\gamma)^{110m}\text{Ag}$ ,  $^{186}\text{W}(n,\gamma)^{187}\text{W}$  and  $^{158}\text{Gd}(n,\gamma)^{159}\text{Gd}$  at energies of 55 keV and 144 keV have been measured by the activation method on the filtered neutron beams. The capture cross sections were obtained relative to the standard capture cross sections of  $^{197}\text{Au}$ . Specific activities of irradiated samples were measured by using a high quality gamma spectroscopy and HPGe detector with relative efficiency of 58%.

#### IV. Results and discussion

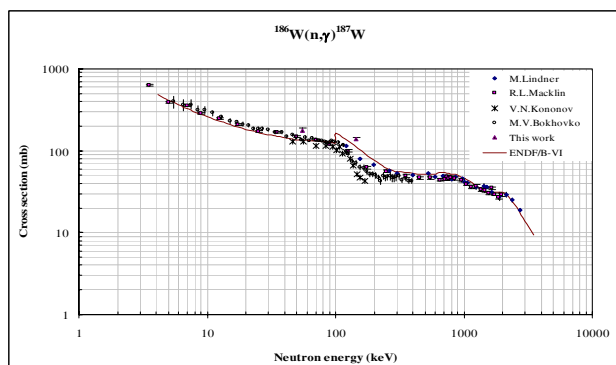
The experimental results in this work are given in Table 1. The previous measurements, EXFOR, and the evaluated data of ENDF/B-6, together with the current results, are plotted in Fig. 1, 2 and 3. In the energy regions of 55 keV and 144 keV, it can be seen from the figures that, in the case of  $^{109}\text{Ag}(n,\gamma)^{110\text{m}}\text{Ag}$  reaction, no experimental data of cross section have been reported before, and in the case of  $^{158}\text{Gd}(n,\gamma)^{159}\text{Gd}$  reaction, the current measurements are in good agreement with previous measurements and the evaluated data within the uncertainties, but in the case of  $^{186}\text{W}(n,\gamma)^{187}\text{W}$  reaction, the current measurements are higher by 8-30% than the previous measurements and the evaluated data. In addition, the experimental uncertainties of the current measurements are 5 to 10%, which are mainly due to the statistical errors (0.1-10%), the uncertainties of  $\gamma$ -ray detection efficiency (2.0%) and the reference cross section value (3.0%).

**Tab 1.** The radiative capture cross sections of  $^{109}\text{Ag}$ ,  $^{186}\text{W}$  and  $^{158}\text{Gd}$  measured in this work

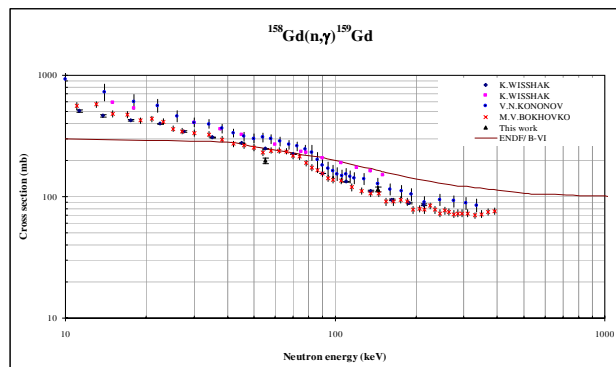
Neutron energies	$\langle\sigma_a\rangle^{\text{W}}$ (mb)	$\langle\sigma_a\rangle^{\text{Gd}}$ (mb)	$\langle\sigma_a\rangle^{\text{Ag}}$ (mb)
55 keV	$178.71 \pm 10.3$	$199.42 \pm 11.5$	$21.4 \pm 2.35$
144 keV	$139.78 \pm 5.3$	$114.85 \pm 5.26$	$20.7 \pm 3.47$



**Fig. 1.** Comparison of the previous experimental data with the present measurement for  $^{109}\text{Ag}(n,\gamma)^{110\text{m}}\text{Ag}$  reaction.



**Fig. 2.** Comparison of the previous experimental data and the evaluated cross sections with the present measurement for  $^{186}\text{W}(n,\gamma)^{187}\text{W}$  reaction.



**Fig. 3.** Comparison of the previous experimental data and the evaluated cross sections with the present measurement for  $^{158}\text{Gd}(n,\gamma)^{159}\text{Gd}$  reaction.

## **RENOVATION OF PROMPT GAMMA NEUTRON ACTIVATION ANALYSIS FACILITY AT THE DALAT REACTOR**

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Vuong Huu Tan<sup>2</sup> and Pham Dinh Khang<sup>3</sup>**

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**Abstract:** *The goal of the project is to design and construct a new PGNAA facility to replace the old one, which was installed at horizontal channel No.4 of the reactor in 1990. The parts of the facility consist of collimators, beam stopper, sample holder table, beam catcher, and biological shield. The design takes into account the basic parameters associated with it, such as adequate thermal neutron flux and cadmium ratio, good signal-to-background condition, small gamma-ray contamination in the beam and appropriately low dose-rate to the operating personnel. The design is patterned to the same PGNAA facilities in the world, with some modifications. The materials used in the construction are lead, lithium florin, cadmium, Teflon, and ion. The details of the study are:*

- a. Measurement of neutron spectrum in horizontal channel No. 4 of the reactor.*
- b. Design of the parts mentioned above with the aim of obtaining a clean homogenous thermal beam with low contamination by  $\gamma$ -radiation and thermal energy neutrons. The results on the neutron distribution is used as input for other programs to model the details of the experimental installations. For the design of the PGNAA facility, the code MCNP4C2 has been used to evaluate the behavior of filters, collimators, beam stopper, beam catcher, and shieldings.*
- c. Fabrication and installation of parts of the facility.*
- d. Determination of characterizations of PGNAA facility, such as neutron flux, gamma dose and cadmium ratio at sample position, sensitivity of Ti, absolute efficiency curve, background gamma-ray spectrum.*

### **Introduction**

The prompt gamma neutron activation analysis facility has been designed, constructed and installed at the radial beam port of Dalat Research Reactor (TRIGA MARK II). The facility consists of collimators, beam stopper, sample holder table, beam catcher, biological shield, which are being renovated from the old ones.

Utilization of the GEM sery HPGe-254 cc detector operated directly in measurements of thermal neutron capture gamma rays at the radial channel of the Dalat reactor with the objective of PGNAA has been carried out. The rather low thermal neutron flux at this channel and high gamma ray background did not allow to achieve the detection limits at sub-PPM concentration levels. The use of rubber LiF in lining of the collimator, sample box, beam trap, beam shuter could reduce gamma background, and then improve the sensitivity of the analysis

### **Neutron spectrum measurement**

Neutron spectrum at front and after filter were measured using activation foils of

Au, Co, Lu, Mn, Cu, In, Fe, Ti, U, Ni, Al, Np, Th. The gamma activity of the foils after irradiated in neutron fields was measured by HPGe detector. SANDPB code was used to process the collected data, and the results of measurement of thermal and fast neutron spectrum at channel No. 4 of Dalat reactor are shown in fig. 1

### Production of LiF rubber

LiF powder has fine characteristics in construction of PGNAA facility. LiF powder was produced from HF and LiOH and then was mixtured with natural rubber. The characteristics of the LiF rubber sheet were examined, and the results is shown in table 1.

**Tab 1.** The absorbtion coefficient of LiF rubber sheets from ours and hungary

LiF rubber	Absorbtion coefficient (1/cm)
From Hungary	4,49 ± 0,52
Ours	3,99 ± 0,67

### Computer Simulations

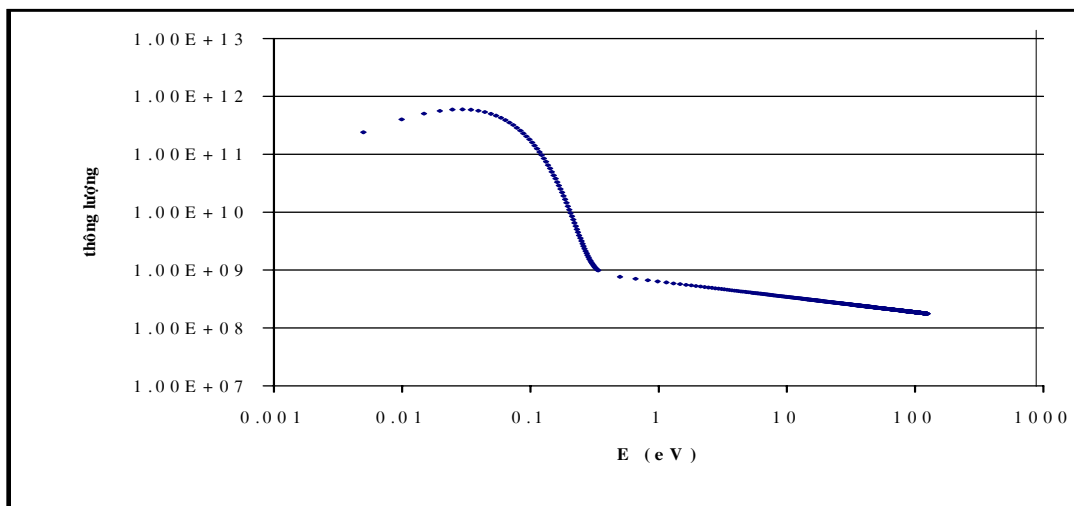
The installations between the source and the sample position have been designed with the aim of obtaining a clean homogenous thermal beam with low contamination by  $\gamma$ -radiation and high energy neutrons. The results on the source distribution obtained by those Monte-Carlo calculations can then be used as input for other programs to model the details of the experimental installations. For the design of the PGNAA facility, the code MCNP has been used to evaluate the behaviour of filters, shutters, apertures and shieldings.

### Experimental configuration

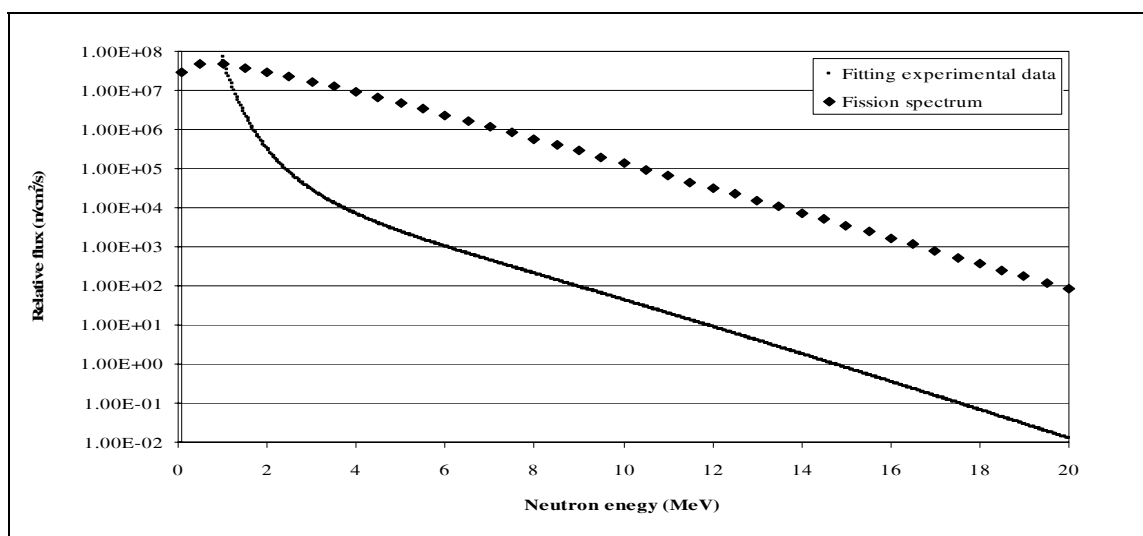
#### Neutron beam

The beam emerging from the reactor beam port consists mainly of fast and thermal neutrons and high-energy gamma rays. Peak to background ratio of the gamma-ray spectrum depends upon the background gamma radiation within the thermal neutron beam. Thermal neutrons are extracted from the beam port for PGNAA by slowing down the fast neutrons to thermal energy and filtering out the high-energy gamma rays. Radiation beam port No. 4 was selected for the installation of the PGNAA facility. The average neutron flux inside the reactor is of the order of  $10^{13}$  n.cm<sup>-2</sup>.s<sup>-1</sup> from which a neutron flux level of  $10^7$  n.cm<sup>-2</sup>.s<sup>-1</sup> is required at the base of the collimator for PGNAA. Single crystal silicon was selected as the moderator because of availability and the large diffusion length (40-cm thick, and placed 85 cm from the end side wall of the reactor). A 2-cm thick block of titanium is used as beam filter to minimize the high-energy gamma radiation at the sample position and to reduce the need for additional shielding outside the biological shield. The beam aperture consists of two boron carbide sheets (each 3-mm thick) to give an aperture diameter of 25 mm. A hollow graphite block 15-cm thick separates the aperture from the moderator block in order to obtain a uniform neutron beam, and the outer diameter of the divergent beam collimator is 30 mm. Streaming of the radiation is eliminated by using titanium and lead as beam stoppers that intercept all the radiation coming from the core of the reactor, gamma rays that arise from radiative capture of the neutrons, and scattered radiation from the sample and sample holder.

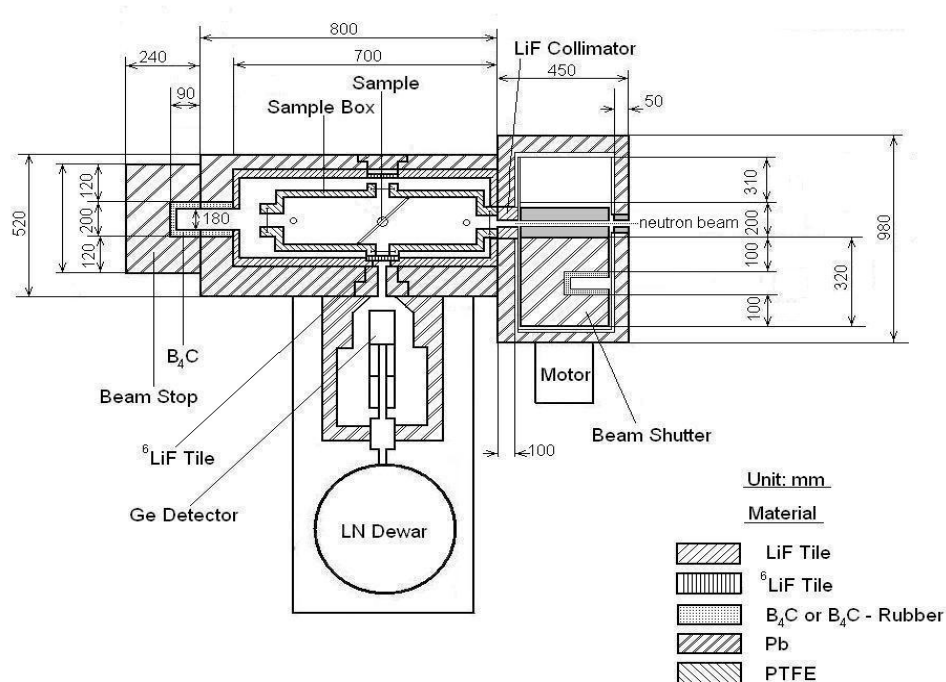
The beam shutter ensures the safe operation of the facility while positioning the sample. This shutter system consists of two parts: Beam shutter and trap. Beam shutter plays a key role to control the safe operation of the facility and to avoid radiation exposure to workers while positioning the samples, etc. Beam trap are used to intercept all the radiation coming from the core of the reactor, gamma radiation resulted through radiative capture of neutrons and scattered radiation from the object and the object holder etc. The shutter has two parts. The first part is made from borated paraffin and boron carbide and cadmium sheets, and it is lined by LiF rubber. It is enclosed in an aluminum casing. The slowed down and thermalized neutrons are attenuated and absorbed by borated paraffin, cadmium and boron carbide sheets. The second part of the shutter is 15 cm thick. It is made from lead bricks and boron carbide sheets and is enclosed in a steel casing. The shutter is mounted on a trolley and is operated manually. The beam trap is fabricated from borated paraffin, lead, boron carbide and steel. Additional shielding to scattered gamma and neutron radiation is provided by erecting a radiation enclosure of ordinary concrete blocks. The layout of the facility shown in Fig-2 describes the details of the beam port, single crystal silicon block, source aperture, titanium block and the collimator, etc.



**Fig. 1.** The thermal and fast neutron spectrum after neutron filter at channel No. 4







Sơ đồ mặt cắt ngang hệ PGNAA tại kênh số 4 lò phản ứng hạt nhân Đà Lạt

**Fig. 2.** The layout of the PGNAA facility at Dalat reactor

### ***Detector shield and sample arrangement***

The gain of the detection system was adjusted by covering the range of gamma-ray energy up to about 13 MeV. A 16k ADC was used to collect and sort the detector signal and the ORTEC Gamma-Vision was used for displaying and on-line analyses of the accumulating spectrum on the connected desktop PC. GEM series HPGe-254 cc detector manufactured by Ortec is used to count the prompt gamma rays (resolution of 1,9 keV at 1332 keV, relative efficiency of 58% at 1332 keV). The MCA has been calibrated from 0.121 to 8 MeV by means of the delayed gamma rays from <sup>152</sup>Eu and prompt gamma rays from <sup>35</sup>Cl(n,  $\gamma$ ) and <sup>14</sup>N(n,  $\gamma$ ), using the energies and intensities recommended by Revay and Molnar.

A PTFE sample box is placed behind the beam collimator. Samples are sealed in a film of 25- $\mu$ m thick fluorinated ethylenepropylene resin (FEP), and placed on the sample holder using 0.3-mm diameter PTFE string. In order to reduce the  $\gamma$ -ray background that originates from neutron scattered by construction materials and by the sample itself, all wall facing the of the neutron beam are covered with rubber LiF and  $\gamma$ -ray are shielded with 5 cm to 10 cm of Pb. The detector is shielded from the gamma background by a cylinder of 20- cm thick lead. The lead cylinder is lined by 3-mm thick of LiF rubber to reduce neutron absorption and scattering which would rather cause formation of background prompt gamma rays. The prompt gamma rays are detected through a window of rubber LiF (32-mm diameter) located in the upper lead layer.

### ***Characteristics of the system***

#### **Energy calibration**

For energy calibration, the prompt gamma-rays from the Fe(n,  $\gamma$ ) reaction was chosen because they are good precise and they cover essentially the entire range of

interest, which are from 122.3 keV to 9298.40 keV. Moreover, for most strong lines the intensities have been measured recently<sup>5</sup> with high precision with respect to the  $^{14}\text{N}(n,\gamma)$  capture lines, the primary standard for high energies<sup>6</sup>. The nitrogen data by Kennett et al.<sup>7</sup>, and by Journey et al.<sup>8</sup> are also available recommended for intensity standards.

A about 2.10 gram purity iron sample was irradiated for 6000 seconds and the capture gamma rays spectra was accumulated. The channel number in the measured spectrum, respect with the energies of prompt gamma-rays, and the uncertainties of these channel numbers from the analyzed spectrum. The second order polynomial in energy was used for energy calibration. Non-linearity over the above energy range was not significant.

### Neutron flux, cadmium ratio and gamma dose rate

The beam position was determined by neutron radiography, and the neutron flux and flux distribution were measured by means of activated Au foils. The cadmium ratio was also determined by the activation of Au foils with and without a cadmium cover. Neutron flux and cadmium ratio are  $2.1 \times 10^7 \text{ n.cm}^{-2}.\text{s}^{-1}$  and 110, respectively. Flux variations at the sample position during one reactor operation cycle of 100 hours were measured every 5 hours by means of 0.025-mm thick Au foils, and found to be 1.2%. The gamma dose rate at the sample position was determined by TLD to be 200 mR/h.

### Gamma-ray background

The position of the detector was determined by observing the total background counting rate for neutron beam on blank target, keeping the dead time of the ADC less than a few %. Hence the normal position of the detector is 25.5 cm distant from the target and the observed total background rate is about 3 keps.

The prompt gamma-ray background spectrum was collected in 60000 seconds and was processed. The capture gamma-ray table by Lone et al. was followed for identifying the prompt gamma-ray lines of different background elements. The sensitivity of gamma-ray lines of the background is shown in table 3.

**Tab 3.** Background peak count rate with beam incident on an empty Teflon bag

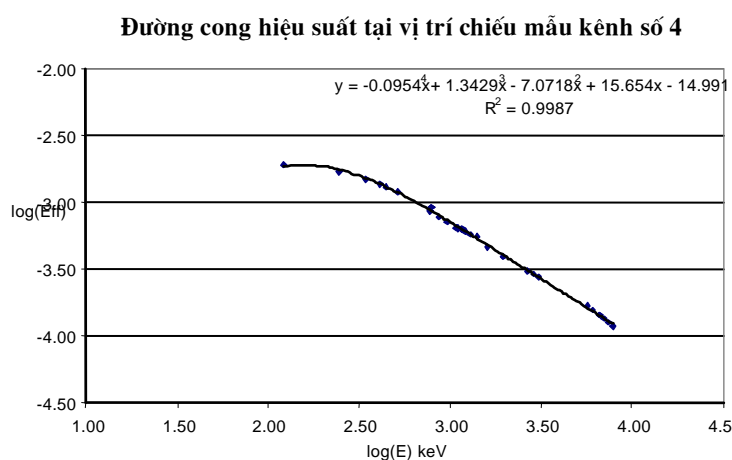
Energy [keV]	Element or Nuclide	Count rate [cps]
75	Pb $K_{\alpha}$	54.2
86	Pb $K_{\beta}$	17.8
112	Unknown	2.2
140	Unknown	17.9
159	$^{76}\text{Ge}$	24.1
175	$^{70}\text{Ge}$	4.9
198	Unknown	16.8
254	$^{74}\text{Ge}$	2.9
500	$^{72}\text{Ge}$ capture + $^{73}\text{Ge}$ inelastic	2.9
511	Annihilation	23.6
570	$^{207}\text{Bi}$ + $^{70}\text{Ge}$	0.05
596	$^{73}\text{Ge}$ capture + $^{74}\text{Ge}$ inelastic	10.6
708	$^{70}\text{Ge}$	1.22

870	Unknown	2.68
1063	$^{207}\text{Bi}$	0.06
1096	$^{70}\text{Ge}$	1.30
1294	Unknown	4.03
1460	$^{40}\text{K}$	1.31
1632	$^{70}\text{Ge}$ , $^{20}\text{F}$ , $^{207}\text{Bi}$	0.27
1779	$^{28}\text{Al}$	0.46
1885	N	0.41
2032	Li	0.09
2223	H	0.80
7368	Pb	0.36
10829	N	0.03

### Efficiency calibration

Energy calibration has been done each time of the measurement by using a simple linear relation for channel-energy. Identification of the peaks had little problem during the measurement of known samples and benchmark experiment since background peaks were identified in a series of separate long runs of upto 64,000 sec collection.

Efficiency calibration of the detector has been performed by using a set of radioisotope sources and (n, $\gamma$ ) reactions. In the present work,  $^{152}\text{Eu}$ , was used to generate the absolute efficiency curve in the lower energy range of 60 – 1408 keV by fixing the scale. The gamma emission probabilities except for  $^{152}\text{Eu}$  was taken from IAEA-TECDOC-619[6]. After the completion of the absolute efficiency curve with the standard radioisotope, the measurement of the prompt gamma-rays from the (n, $\gamma$ ) reactions of Cl and N was performed to extend the energy range to 10,829 keV. The  $\text{NH}_4\text{Cl}$  sample and the melamine sample were prepared and irradiated for the period to get the statistical uncertainty below 1% for the weakest peak from each set. The absolute gamma intensities for (n, $\gamma$ ) reactions of Cl and N were taken from the recently evaluated Budapest-LBNL dataset[8]. The measured datasets were combined with normalization determined through a fitting process by use of the 5<sup>th</sup> order polynomial form[9] in the whole energy range of 60 – 10,829 keV. In Fig. 4, the full energy peak efficiency of the PGNAA spectrometer is shown with the polynomial fitting line. The relative standard uncertainty is less than 3% for the lower energy range and less than 5% for the whole energy range.



**Fig. 4.** The absolute efficiency curve of PGNAA facility at Dalat reactor

### Examination of element sensitivities

The prompt gamma spectrum of NBS-1633a standard was irradiated and collected in 51000 seconds. The spectrum was processed using Gamma-Vision software, and the sensitivities of some elements in the standard is shown in table 3.

Element	Energy (keV)	Sensitivity at Dalat PGNAA facility (c/s/mg)	Sensitivity at JAERI PGNAA facility (c/s/mg)
K	771	0.017	0.058
Ca	1942	0.003	0.011
	4419	0.006	
Si	3539	0.001	0.0033
Al	1778	0.004	0.0121
Fe	352	0.012	0.0216
B	478	84.86	212
Cl	786+788	0.237	
	1165	0.159	0.442
H	2223	0.211	0.417
Ti	1381	0.084	0.191

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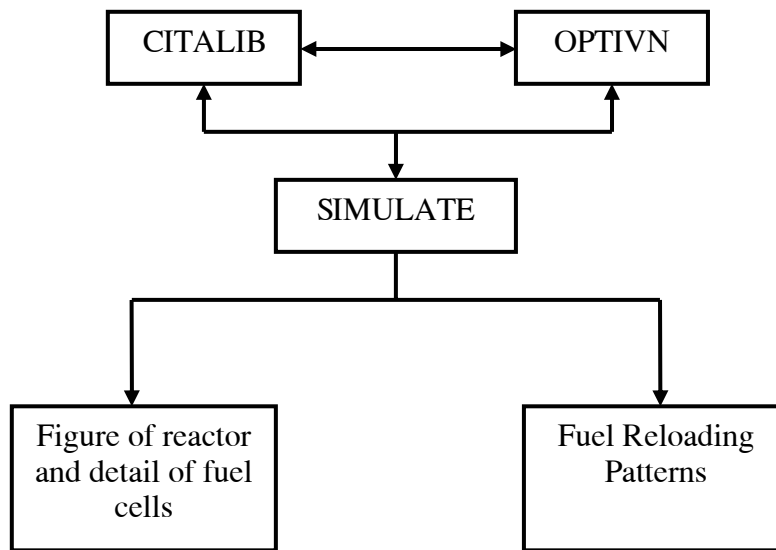
## DEVELOPMENT OF A COMPUTER CODE FOR REACTOR REFUELING OPTIMIZATION USING GENETIC ALGORITHMS

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**Abstract:** *This report represents the results of an institute project. The aim of this project is to develop a computer code solving the problem of multiobjective optimization of in-core fuel reloading patterns based on genetic algorithms combined with related techniques. An improved model of the in-core fuel loading optimization problem and a method for solving the problem using genetic algorithms based on a new coding procedure are also proposed. The code and the method are tested on a sample problem, which relies on the data of the Dalat research reactor. Illustrative results proves that the code and the new method can search optimal fuel reloading patterns that maximize the effective multiplication factor and minimize the power peaking factor within operational and safety constraints.*

The aim of this project is to develop a computer code solving the problem of multiobjective optimization of in-core fuel reloading patterns based on genetic algorithms combined with related techniques [1,2,3,4]. The code includes programmes written independently in languages Visual Fortran and Visual Basic, running on PCs. This version of the code can perform global reactor calculation, automatically searching fuel reloading patterns that maximize the effective multiplication factor and minimize the power peaking factor within rigorous constrains and graphical representation of reactor in two-dimensional geometry and optimal fuel loading patterns. The reactor calculation involves the finite difference diffusion theory representation of neutron transport theory [5], treating three space dimensions with arbitrary groups. The radial geometric mesh options in reactor calculation include slab, cylinder, hexagonal and triangular. The flowchart of the code, named REFUELOP, is showed in Fig. 1. The code includes three modules CITALIB, OPTIVN and SIMULATE. CITALIB is modified based on the CITATION reactor calculation code [6], module OPTIVN written in Visual Fortran is a genetic algorithm optimization programme, and SIMULATE written in Visual Basic is a graphical interface module.



**Fig. 1.** Flowchart of the REFUELOP computer code.

In addition, an improved model of the in-core fuel loading optimization problem and a method for solving the problem using genetic algorithms combined with a new coding procedure are proposed. The improved model includes a severe constraint resulting from reactor operational practice, which requires the reduction of the number of fuel shuffles. This helps to improve the reactor safety and economy because it reduces fuel handles and reduces shutdown period hence shutdown cost. The key feature of the solution approach is the way of coding to transfer a fuel loading pattern into chromosome and inversely. The type of chromosome that is suitable to this coding procedure is the one - dimensional chromosome with the number of genes in each chromosome equal to the maximum number of fuel shuffles and the order of a gene in chromosomes corresponding to a specific position in the reactor core.

The sample problem models the Dalat research reactor at the end of its first cycle. Illustrative calculations are applied to search optimal fuel loading patterns for both the conventional and improved models. Calculational results show that the searching process using genetic algorithms [7,8] in coordination with elitism strategy [9,10] can reach optimal fuel loading patterns for a limited number of generations. The optimal loading patterns are all low-leakage patterns, having advanced quality as compared with the practical solution.

The code might be used for training, research and improvement of fuel usage for some research reactors and PWR or BWR type power reactors.

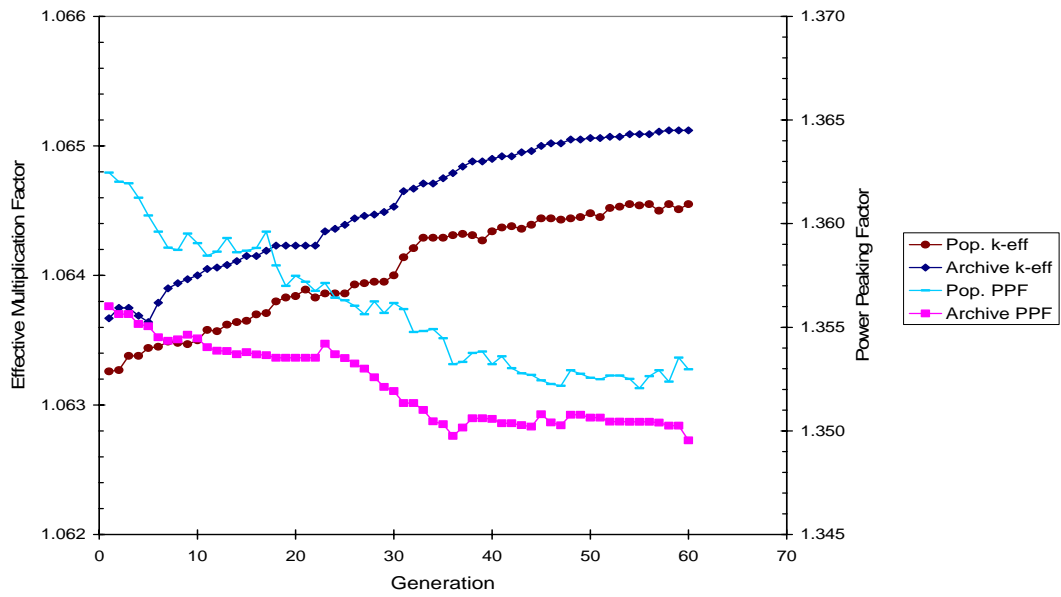


Fig. 2. Change in objectives in the optimal searching process.

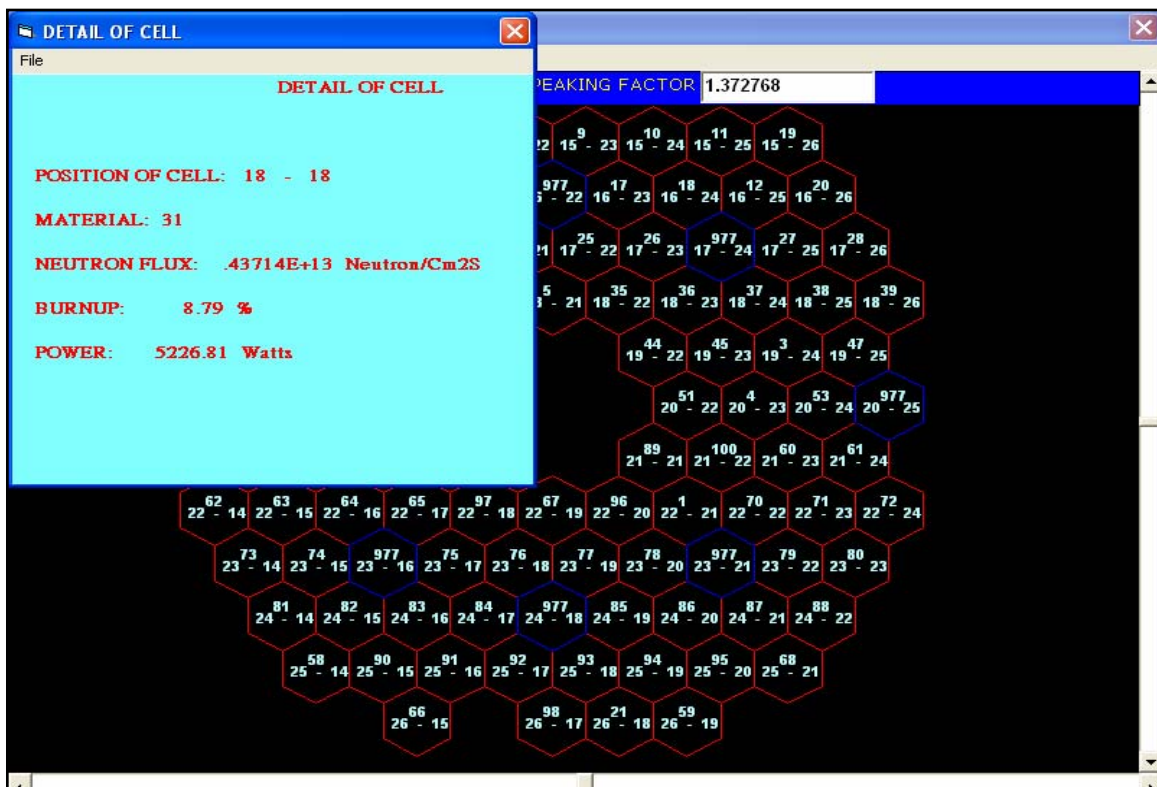


Fig. 3. Graphical representation of a loading pattern and the detail b characteristics of a fuel cell.

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## **USING BALANCE PROGRAM FOR ENERGY BALANCE ANALYSIS**

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**Abstract:** *Belong with development of the economy, the energy consumption will be increased very high in the future. Vietnam has a broad range of mineral resources. There is considerable energy potential on form of coal, oil and gas, hydropower and fuel wood. Recently, Vietnam is an exporter of energy. But in next two decades, the energy sources will be enough to meet requirement? The model BALANCE was used to solve energy planning problem. The objective of this model is analyzing energy system and built an energy development strategy in long term. After using model, the results are: total coal consumption will be 17.440 Mtoe in 2020 and 32 Mtoe in 2030. The biggest coal consumer is electricity sector. Total oil production consumption will be more than 30 Mtoe in 2020 and more than 50 Mtoe in 2030. If we have 4 refinery factories from now to 2030, total oil products import will be 11 Mtoe in 2020 and 25 Mtoe in 2030. The amount of gas supply in 2030 will be 20 billions m<sup>3</sup> (18 Mtoe). Vietnam needs to import 8.3 Mtoe more. Vietnam will become an energy importer in next 15 years.*

*In previous years, the economy of Vietnam was mainly based on agricultural production. But Viet Nam is moving rapidly from an agricultural to an industrial economy. Belong with the development of the economy, energy consumption increases very fast. So which energy sources should be used first and when it will be used...are questions need to be answered.*

*Vietnam has a broad range of mineral resources. There is considerable energy potential on form of coal, oil and gas, hydropower and fuel wood. Recently, Vietnam is energy exporter, but in near future Vietnam has enough energy to meet demand or we need to import form outside? It should be study carefully to answer.*

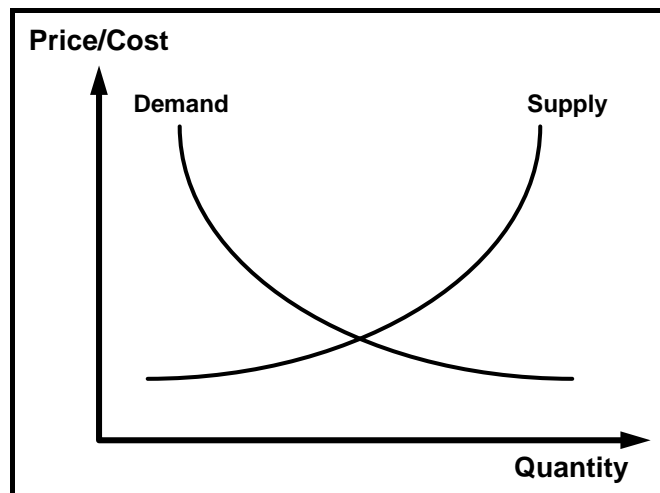
**In the frame of CS/04/04-14 project, BALANCE model was used to solve energy planning problem. The main target of this model is analyzing energy system and built an energy development strategy in long term. The objectives of this project are:**

1. Studying and using an international model for energy balance analysis.
2. Applying Balance for Vietnam energy system (planning period 2000-2030) to point out the supply capacity and demand of each energy source and give the recommendation about production, import and export energy to the decision maker.

The ENPEP for Windows model has its origins in the DOS version of the Energy and Power Evaluation Program (ENPEP). The objective of the ENPEP for Windows model is to simulate energy market and determine energy supply and demand balance over a long-term period of up to 75 years.

The central requirement of a comprehensive energy analysis is the evaluation of alternative configurations of the energy system that will balance energy supply and demand. The BALANCE Module of ENPEP is designed to provide the planner with this capability. BALANCE uses a non-linear, equilibrium approach to determine the energy

supply and demand balance. For its simulation, the Model uses an energy network that is designed to trace the flow of energy from primary resource (e.g., crude oil, coal) through to final energy demand (i.e., diesel, fuel oil) and/or useful energy demand (i.e., residential hot water, industrial process steam). Demand is sensitive to the prices of alternatives. Supply price is sensitive to the quantity demanded. BALANCE seeks to find the intersection of the supply and demand curves as illustrated followed.



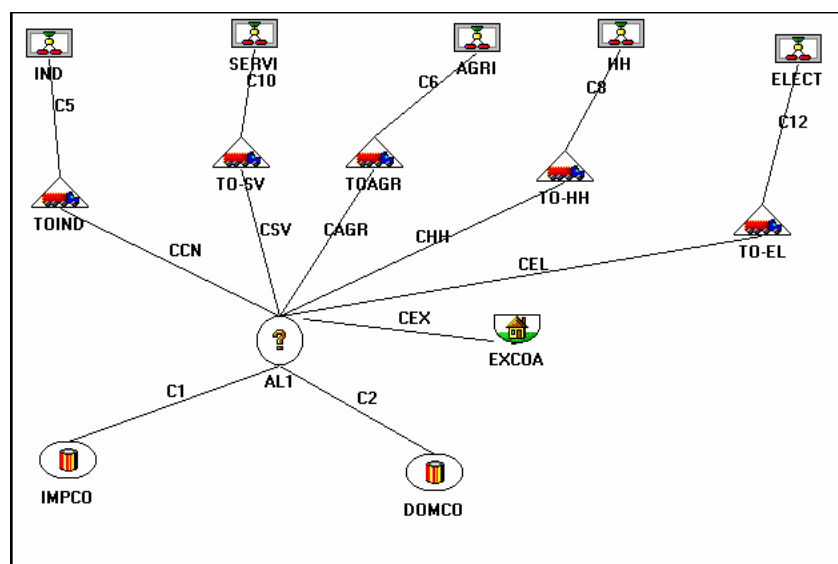
**Fig. 1. BALANCE Supply and Demand Curves**

ENPEP for Windows utilizes the full functionality of the Windows environment by allowing the users to build their energy networks within a graphical user interface right on the screen. The energy network represents all energy production, conversion, transport, distribution, and utilization activities in a country or region, as well as the flows of energy and fuels among those activities. The energy network is constructed with a set of submodels or building blocks, called *nodes*. The nodes of the network represent energy activities or processes, such as petroleum refining. The user connects the nodes with a set of *links*. The links represent energy and fuel flows and associated costs among the specific energy activities. Links convey this information (i.e., price and quantity) from one node to another. The energy network is developed by defining the energy flows among the different types of nodes for a given base year.

By convention the energy network is constructed such that demand nodes are located at the top of the network and energy supply resources are at the bottom of the network. Conversion process nodes are located in the middle. Once the network is constructed and historical energy flows are simulated, the module forecasts future energy demands and prices. Demands are simulated by computing energy flows from demand nodes through conversion processes down to the supply resource nodes. This process is referred to as the down pass node sequence. Energy prices are computed by estimating costs for energy extraction and conversion processes through to the demand nodes. This process is referred to as the up-pass sequence. In the down pass sequence, when the Model computes energy flows, price estimates from the previous up pass sequence are used to determine the market shares of competing energy alternatives (i.e., input links). The market share is estimated by a logit function where the market share of a commodity is a function of the commodity's price relative to the price of alternative commodities.

The up pass and down pass sequences are repeated until the difference in energy flows (i.e., quantities) on network links change very little from one iteration (i.e., down pass) to the next and the processes converge to within a user specified tolerance level.

In the project of “Using Balance program for energy balance analysis”, Vietnam energy system network was modeled in detail. From all primary energy sources in form of coal, oil, gas to energy conversion stages like electricity system, and energy consumers like industry, agriculture... Coal sector was modeled as the followed figure.



**Fig. 2. Vietnam coal sector**

And each sector will be disaggregated to sub-sectors and activities. After design Vietnam energy network, program was run. Based on the project officer point of view, the results are reasonable. The results are shown below:

- Coal resource: the coal consumption of whole energy system will increase from 4000 ktoe in 2000 to about 10000 ktoe in 2010, 17000 ktoe and 32000 ktoe in 2020 and 2030 respectively. So, we need to import 5000 ktoe in 2025. And we need to import 8890 ktoe in 2030 for domestic consumption.

- Gas resource: Total gas consumption will reach 15.6 Mtoe in 2020 and it will be 19.3 and 26.4 Mtoe in 2025 and 2030 respectively. So, if production capacity reaches 19 billions m<sup>3</sup> of gas in 2020 and 20 billions m<sup>3</sup> of gas in 2030, we will have to import 1.3 Mtoe in 2025 and 8.4 Mtoe in 2030.

- Oil products: Total oil products consumption will be 30463 ktoe in 2020 and up to 2030 it will reach 50568 ktoe. In which, domestic oil production are 19149 ktoe and 25532 ktoe in 2020 and 2030. Total oil products imported will be 11314 ktoe and 25032 ktoe in 2020 and 2030.

- Electricity production and consumption: Based on model's output, hydro power generation in 2020 will be 4907 ktoe (about 57 billions kwh) and it will reach 6667 ktoe (about 80 billions kwh). Gas electricity generation is 5100 ktoe and it will reach 10000 ktoe in 2030. Thermal power plants will produce 3188 ktoe in 2020 and it will reach 7661 ktoe in 2030. In 2030, nuclear power plant will produce 7961 ktoe,

contain of 23% total electricity production. Main consumer is industrial sector. In 2000, the share of electricity consumption of industry sector is only 41%, but up to 2030 the share is 57%. The share of electricity consumption of service and household sector are 38%. The rest part is transportation and agricultural sector.

In summary, the project was implemented successfully, reached the planning objectives with the limited of time and budget.

BALANCE program is a strong tool. It allows presenting whole energy network from production, transmission, distribution to consumption. It allows the user modeling fuel prices, policy and tax...On the other hand, the same as any other programs, BALANCE has some weak points. It is not an optimization program, so it can't give the minimum solution output for whole system. To model electricity system, BALANCE needs a result from other program...

The project's outputs are reasonable. Its can be used to help decision makers to make plan for Vietnam energy system development is the future. However, energy planning is a large area, it need to be researched more carefully and deeply in the future.

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## 1.3 - Nuclear Methods

## **EXPERIMENTAL RESEARCH ON SOIL EROSION AND SEDIMENTATION AT A SITE IN NORTHERN PART OF VIETNAM**

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Nguyen Quang Long<sup>2</sup>, Tran Duc Toan<sup>3</sup> and Nguyen Duy Phuong<sup>3</sup>**

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**Abstract:** *Research project was implemented on six run-off plots designed for monitoring soil erosion. The objectives of the project were to confirm the use of nuclear techniques in estimating soil erosion and redistribution; and to compare the results of these techniques with conventional techniques used by soil scientists.*

*Soil samples were analyzed for Cs-137 and Pb-210 contents and main soil properties. The Cs-137 and Pb-210 inventories at the plots were compared with the reference inventory, using conversion models to calculate soil erosion rates and soil redistribution. Results of soil erosion rates calculated by Cs-137 and Pb-210 are well matched with the results obtained from 11 years monitoring at run-off plots. Also, Cs-137 and Pb-210 inventories at the plots were compared with soil properties to find the correlation between Cs-137, Pb-210 and soil fertility.*

### **Introduction**

Soil erosion is one of the main reasons causing soil degradation in the hilly and mountainous areas. Soil erosion and sedimentation not only cause the degradation of arable land but also accelerate other natural processes such as bed sedimentation of rivers, reservoirs, and landslides.

To help farmers in restoring and maintaining the productivity of the lands, soil erosion rates are being estimated and soil conservation techniques have been implemented through the government agricultural projects (Ministry of Agriculture and Rural Development). Until now, most of the projects on soil erosion estimation have been carried out by conventional techniques at the National Institute for Soil and Fertilizer (NISF).

Advanced techniques such as Cs-137, Pb-210, and Be-7 techniques for assessing soil erosion have been used in developed countries for nearly 50 years, and have been reported in many scientific papers (for example, Ritchie and McHenry, 1990; Walling and He, 1999; Zapata and Garcia-Agudo, 2000; Zapata, 2002).

Recently, a joint FAO/IAEA research project from 1995 to 2000 has made standards of procedures in using nuclear techniques in soil erosion and sedimentation investigation. This led to the formation of other Technical Co-operation (TC) projects, one of them is RAS/5/039 part II (2003-2004): *Measuring soil Erosion and Sedimentation, and Associated Pesticide Contamination*.

In Vietnam, nuclear techniques have been tried in some areas with promising results (Hien et al., 2002; Nguyen Hao Quang, 2000; Nguyen Quang Long, 2003). Although nuclear scientists have been active in the use of these techniques for soil

erosion, and good laboratory facilities have been established for analyzing Cs-137 and Pb-210, our soil scientists still know very little about the techniques.

To validate and confirm the many advantages of Cs-137 and Pb-210 techniques in assessing soil erosion and redistribution, and to compare the results of these techniques with conventional techniques used by soil scientists, we have conducted a research project (under the Ministry of Science and Technology) for the year 2004 "*Experimental research on soil erosion and sedimentation at a site in northern part of Vietnam*" (code: B0/04/04-04). This project has also implemented a part of workplan as commitment of Vietnam in the project RAS/5/039 part II (2003-2004).

### **Materials and methods**

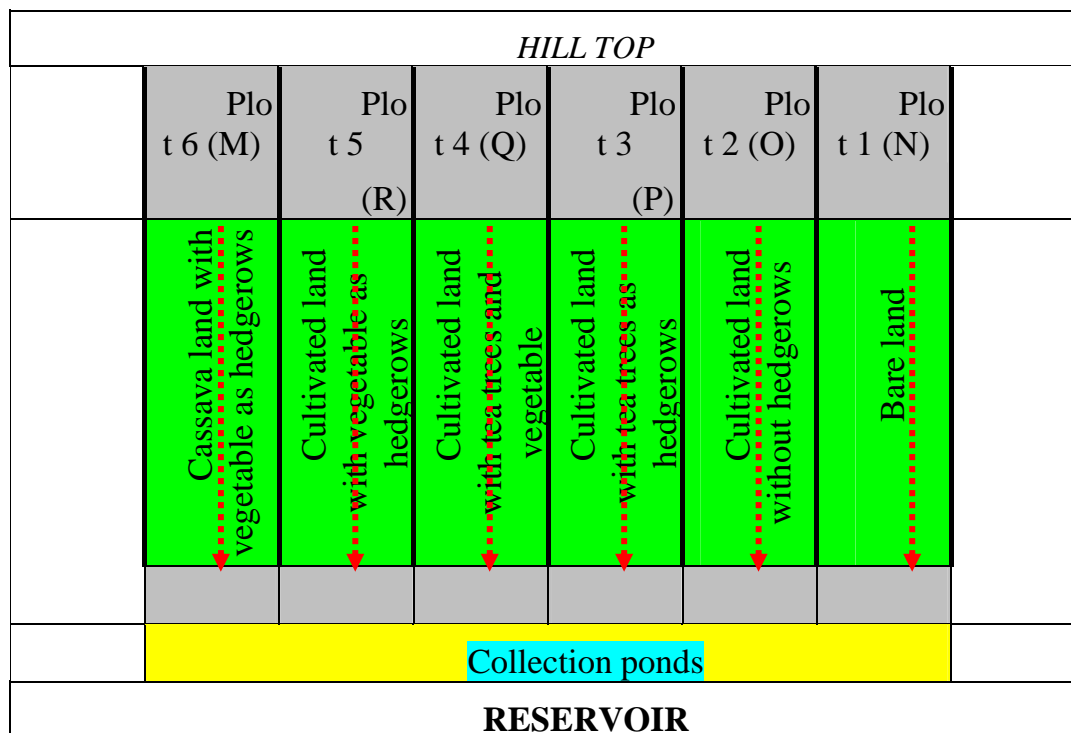
Research project has been implemented at Dong Quyt village, Hoa Son commune, Luong Son district, Hoa Binh Province, on six run-off plots designed for monitoring soil erosion by the National Institute for Soil and Fertilizer (NISF) since 1992. For the implementation of the project, a multidisciplinary team was formed with scientists from INST and NISF.

The Cs-137 reference inventory value were estimated first by the regression model based on the latitude and the annual rainfall data (Hien et al., 2002), and found to be around 850 Bq/m<sup>2</sup>. Research for the reference site was a very difficult task because of the dense population and unclear history of the cultivation practice in the area. After many interviews with local people we found two hilltops that have never been cultivated.

It was found that total Cs-137 inventory value from each point at one of the hills was around 205 Bq/m<sup>2</sup>, clearly lower than the estimated value of 850 Bq/m<sup>2</sup>. At the other site, the mean Cs-137 value for three points were 885 Bq/m<sup>2</sup> and were in good match with the estimated value. This hilltop, a place where the poles of the electric power transmit line is located, was considered a good choice for reference site. 44 samples for reference inventory were taken from 11 points of this site. At each point, four sample slides from depth interval of 0-10 cm, 10-20 cm, 20-30 cm, and 30-40 cm were taken for investigating depth distribution of Cs-137 and Pb-210.

Research plots are located on a hill slope, about 500 m from the reference site. Each plot has been designed from the top down the hill, with observation pond at the toe to collect run-off sediments. Every plot has dimension of 7.5 m wide and more than 30 m long (Figure 1). There are six plots for different types of erosion research: 1) bare land, 2) cultivated land without hedgerows, 3) cultivated land with tea trees as hedgerows, 4) cultivated land with tea trees and vegetable as hedgerows, 5) cultivated land with vegetable as hedgerows, and 6) cassava land with vegetable (replaced by vetiver grass in 2004) as hedgerows.

At each research plot, one transect was investigated with samples taken to the depth of 30 cm. Each transect goes along the length of the plot, in the middle, and consists of about 12 sample points, making total number of samples for Cs-137 and Pb-210 to be 72. At the same time, one soil sample from each point was taken to be analyzed for soil property and nutrition contents. In addition, two points were sampled by 4 slices of 10 cm interval to investigate depth distribution of Cs-137 and Pb-210, and mud samples at collection ponds were taken for analyses. Also, detailed topographic mapping of the sites was conducted for data interpretation.



**Fig. 1.** Research plots and sampling transects

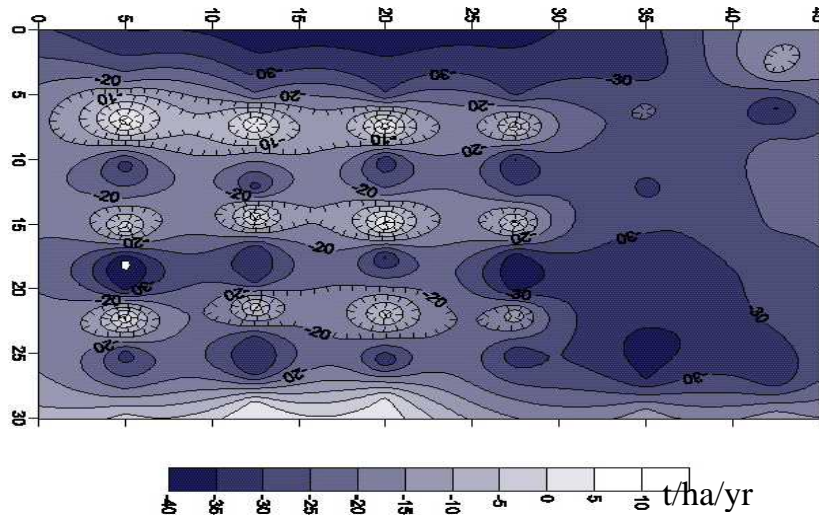
Soil samples were analyzed for Cs-137 and Pb-210 contents in the Environmental Radioactive Monitoring Laboratory of the INST by ORTEC HpGe detectors. Main soil properties such as OM, N, P<sub>2</sub>O<sub>5</sub>, K<sub>2</sub>O,... were analyzed at the NISF's laboratories.

Cs-137 and excess Pb-210 inventories at the plots were compared with the reference inventory, using conversion models (mainly, Proportional Model – PM and Mass-Balance Model – MBM) to calculate soil erosion rates and soil redistribution (Walling and He, 1999; Walling and He, 2001). Calculated soil erosion rates were compared with the results obtained by conventional technique conducted by soil scientists. Also, Cs-137 and Pb-210 inventories at the plots were compared with soil properties to find the correlation between Cs-137, Pb-210 and soil fertility.

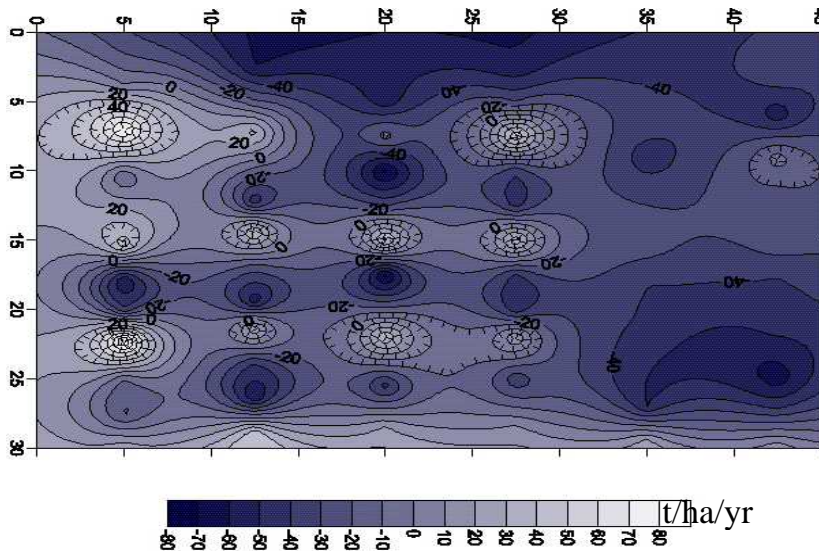
### Results

From results of erosion calculation we have constructed map of soil redistribution by Cs-137 as shown in Figure 2 and 3. It could be seen from these Figures that the hedge-rows areas are the places of sedimentation. The other areas are erosion ones with different degrees. Although the absolute values of erosion rates are still differ from Cs-137 to Pb-210 results, the pattern of soil redistribution is similar by both techniques.





**Fig. 2.** Soil redistribution pattern obtained by Cs-137. Negative values show erosion, positive values show sedimentation.

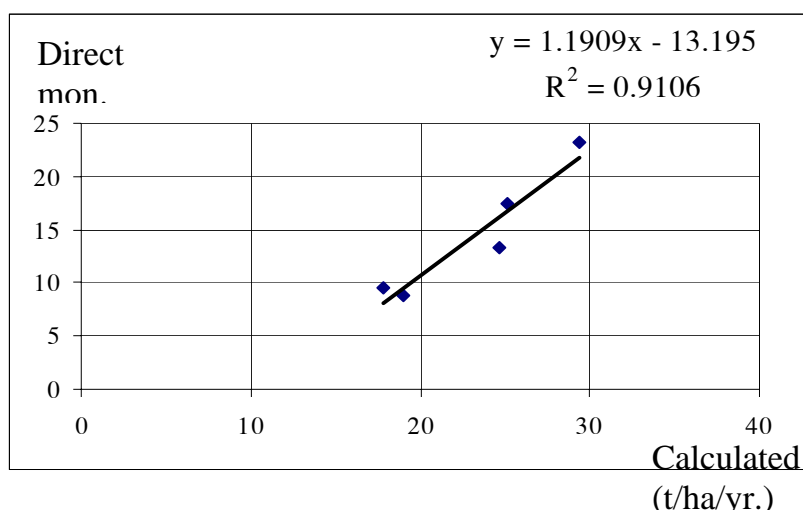


**Fig. 3.** Soil redistribution pattern obtained by Pb-210. Negative values show erosion, positive values show sedimentation.

For comparison with conventional technique, data of monitoring the amount of soil washed to the run-off tanks were collected. Results are put together in Table 1. From this Table we have calculated the correlation between the two types of results. Figure 4 shows one of the calculated linear correlation. Plot number 6 (M) has data of monitoring for only two year and has been excluded from comparison.

**Tab 4.** Synthesized results of soil erosion rates (t/ha/yr.) on research plots

Plot No	Direct Monitor.	Cs-137 PM Ref=985	Cs-137 PM Ref=824	Cs-137 MBM2 Ref=985	Cs-137 MBM2 Ref=824	Pb-210ex PM Ref=3443	Pb-210ex MBM2 Ref=3443
5 (R)	8.75	18.95	15.33	30.72	22.57	13.39	1112.36
4 (Q)	9.56	17.87	13.77	26.57	18.28	23.13	262.65
3 (P)	13.34	24.65	21.92	43.88	36.47	15.83	394.26
2 (O)	23.12	29.41	27.22	50.88	43.99	33.44	196.87
1 (N)	17.37	25.10	22.26	39.49	33.05	32.04	218.52

**Fig. 4.** Comparison of calculated erosion rates by Cs-137 (using PM, Reference value = 985 Bq/m<sup>2</sup>) with direct monitoring results.

We have also calculated the correlation between Cs-137, Pb-210 inventories and soil properties. It was noted that Cs-137 and Pb-210 were partly correlated with some soil properties such as: OM, total N, P, and exchanging capacities (Ca<sup>2+</sup>, Mg<sup>2+</sup>, CEC). However, the correlation need to be further investigated.

### Conclusion

Results of estimating soil erosion rates by Cs-137 are trustable and well matched with the results obtained by long time monitoring on run-off plots by conventional techniques. Both Cs-137 and excess Pb-210 techniques have the capability of showing soil redistribution pattern. It has a great mean for the application of these techniques, for only one site sampling could substitute long term, expensive monitoring at the run-off plots.

It is therefore recommended that the Cs-137 and Pb-210 techniques be used in the national research programs on evaluating soil erosion, sedimentation, and redistribution.

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## **DETERMINATION OF METAL CONCENTRATIONS IN GOLD ALLOYS BY X-RAY FLUORESCENCE METHOD**

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**Abstract:** *An XRF procedure is developed to analyze Ni, Cu, Zn, Pd, Ag and Au in jewellery gold alloys.*

*A standard calibration set including 14 gold alloys and 6 pure metals is made at Saigon Jewellery Enterprise. The Rousseau's Fundamental Algorithm is selected as matrix effect correction method for the case, with some extensions in formulas. Linear regressions between concentrations and corrected relative intensities show good effect of the correction for most of elements of interest.*

*Based on the method, an iterative correction algorithm is setup to calculate elemental concentrations in unknown samples. Analytical results of 6 test samples show a quick convergence of the algorithm and the agreement between XRF concentrations and nominal concentrations for most of test cases.*

### **I. Introduction**

Amongst analytical techniques widely used in fineness determination of gold products<sup>[1]</sup>, fire assay and ICP-AES/MS techniques are often employed for gold hallmarking<sup>2</sup> for their excellent accuracy (0.02% ã 0.1%). Compared to the above techniques, EDXRF has the advantage of being a non-destructive method, quick assay, cheaper instruments, but also has reduced accuracy (typically 0.1% ã 0.5%) and the disadvantage of analyzing on thin surface layer only. EDXRF is suitable for normal assaying requirements such as in-house quality control in manufacturing or for 'certifying' gold content in retail outlets. For markets where there isn't an independent system of hallmarking such as Vietnam, India, Thailand..., gold manufacturers may use EDXRF in marking<sup>3</sup> their products.

In Vietnam, XRF has been applied in gold assay since early 1990's. More than 10 EDXRF systems were installed by member institutes of VAEC. With simple algorithm of quantification, all of them can only determine gold concentration of binary Au-Ag alloys with best accuracy of 0.01%, suitable to the requirement of fineness determination of fine gold, which is widely used in commercial transactions. Up to now, there is no significant improvement to extend the ability of the XRF systems in analyzing more than 2 (3ã10) elements in carat gold, which takes more and more large amount and types in Vietnam jewellery market.

Based on the Rousseau's *Fundamental Algorithm*, the work is aimed at establishing an XRF procedure to analyze 6 elements in carat gold including Au, Ag, Cu, Ni, Zn, Pd, which are most commonly used in jewellery, coinage, electronics. The work includes some extensions in the algorithm for it to be more suitable to the case,

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\* Hallmark: the caratage (or fineness) stamped on a product by an independent third party (typically, an accredited Assay Office).

Mark: the caratage (or fineness) stamped on a product by the manufacturer.

preparation of standards and test samples, and setting up an iterative calculation loop for the quantitative analysis of unknown samples.

## II. Method

The *Fundamental Algorithm* of R. M. Rousseau published in detail in 1998 <sup>[i]</sup> is selected as basis of the procedure, owing to its explicitness and ease of manipulation. The use of relative intensities helps to reduce calculations on detector efficiencies and excitation geometry, which may lead to rough errors on analysis results. All physical parameters relative to photoelectric and fluorescence phenomena can be found in many published works <sup>[ii, iii, iv]</sup>. To make the algorithm more suitable to the considered case, its expressions are modified with more details in enhancement effect corrections, to take into account the *partial enhancement* of element pairs Cu-Ni, Zn-Cu, Ag-Pd, and the more complex enhancement effect on LX-ray generating elements (Au), which have 3 photo-absorption edges.

With the above correction in the *Fundamental Algorithm*, relation between concentration  $C_i$  and relative intensity of  $m^{\text{th}}$  fluorescence line  $R_i$  for element  $i$  will be expressed <sup>[v]</sup>:

$$C_i = R_{im} \frac{1 + \sum_j \alpha_{ij} C_j}{1 + \sum_j \varepsilon_{ij} C_j} \quad (1)$$

with

$$\alpha_{ij} = \frac{\sum_{E_v} \sum_k W_{ik}(E_v) \beta_{ij}(E_v)}{\sum_{E_v} \sum_k W_{ik}(E_v)} \quad (2)$$

$$\varepsilon_{ij} = \frac{\sum_{E_v} \sum_k W_{ik}(E_v) \delta_{ikm,j}(E_v)}{\sum_{E_v} \sum_k W_{ik}(E_v)} \quad (3)$$

$$\beta_{ij}(E_v) = \frac{\mu_j^*}{\mu_i^*} - 1 \quad (4)$$

$$\delta_{ikm,j} = \frac{1}{2} \cdot \frac{\tau_j(E_v)}{\tau_i(E_v)} \sum_{l=1}^{l_{\max,j}} D_{jl}(E_v) \frac{r_{jl} - 1}{r_{jl}} \omega_{jl} \sum_{n=1}^{n_{\max,j}} P_{jln} \cdot \tau_i(E_{jn}) D_{ik}(E_{jn}) P_{im,jn}(E_v) \quad (5)$$

$$W_{ik} = \frac{W'_{ik}(E_v)}{1 + \sum_j C_j \beta_{ij}(E_v)} \quad (6)$$

$$W'_{ik}(E_v) = \frac{\tau_i(E_v)}{\mu_i^*} f_{ikm} I_0(E_v) \Delta E_v \quad (7)$$

Detailed interpretations for formulas and notations can be found in the cited reference <sup>[v]</sup>.

In case of current experiments with monochromatic excitation, expressions of  $\alpha_{ij}$  và  $\varepsilon_{ij}$  are reduced to:

$$\alpha_{ij} = \frac{\sum_k f_{ikm} \beta_{ij}(E_0)}{\sum_k f_{ikm}} = \beta_{ij}(E_0) \quad (8)$$

$$\varepsilon_{ij} = \frac{\sum_k f_{ikm} \delta_{ikm,j}(E_0)}{\sum_k f_{ikm}} \quad (9)$$

### III. Experiments and Discussions

#### 1. Sample preparation:

Calibration standards and test samples, which are prepared at Saigon Jewellery Enterprise, consist of:

- One calibration set including 14 alloy samples and 6 pure metal samples,
- 6 test alloys.

Raw material for element Au is Swiss fine gold 999.9‰. For the other elements, raw materials are fine metals of pA type.

Nominal values for elemental concentrations of standards and test samples (Tab 1) are provided referring to raw material weights prepared for each sample, and analytical results of Cu and Zn provided independently by AAS and TXRF techniques at NRI.

**Tab 1.** Nominal elemental concentrations for standards and test samples.

N <sup>o</sup>	Sample name	Elemental Concentration <sup>vi</sup> , w%					
		Ni	Cu	Zn	Pd	Ag	Au
<b>Calibration standards:</b>							
01	Au-1					66.91	33.09
02	Au-2		19.14 ± 0.12			46.62	34.24
03	Au-3		19.31 ± 0.11		32.28	11.12	37.29
04	Au-5	9.83	18.95 ± 0.20	3.67 ± 0.12		27.24	40.31
05	Au-6		8.44 ± 0.18		26.13	13.08	52.35
06	Au-7				13.98	28.04	57.98
07	Au-8	16.00	11.86 ± 0.15	1.99 ± 0.12		8.48	61.68
08	Au-9	17.23	13.85 ± 0.28	10.18 ± 0.10			58.73

N <sup>o</sup>	Sample name	Elemental Concentration <sup>vi</sup> , w%					
		Ni	Cu	Zn	Pd	Ag	Au
09	Au-10	13.13	9.12 ± 0.26	2.13 ± 0.07			75.62
10	Au-11	15.01			10.01		74.99
11	Au-12	25.01					74.99
12	Au-13		4.71 ± 0.26			3.00	92.29
13	Au-14		3.62 ± 0.19				96.38
14	Au-15		1.47 ± 0.08				98.53
<b>Test samples:</b>							
01	T-22		4.85 ± 0.18			3.24	91.92
02	T-18A		10.37 ± 0.07		0.89	12.72	76.02
03	T-18B	0.70	9.06 ± 0.42		12.49	3.02	74.74
04	T-18C	10.04			15.00		74.96
05	T-14A	17.49	11.70 ± 0.10	9.59 ± 0.11			61.23
06	T-14B	14.36	26.44 ± 0.95				59.20

## 2. Regressions of elemental concentrations vs relative intensities

From the XRF measurement results of standards, relation between concentration and relative intensity for each element are made by linear regression with *non-corrected* form:

$$C_i = A_i^0 \times R_i + B_i^0 \quad (10)$$

and *corrected* form:

$$C_i = A_i \times (R_i \cdot F_i) + B_i \quad (11)$$

where the intensity correction factor  $F_i$  is derived from the Rousseau's

*Fundamental Algorithm:*

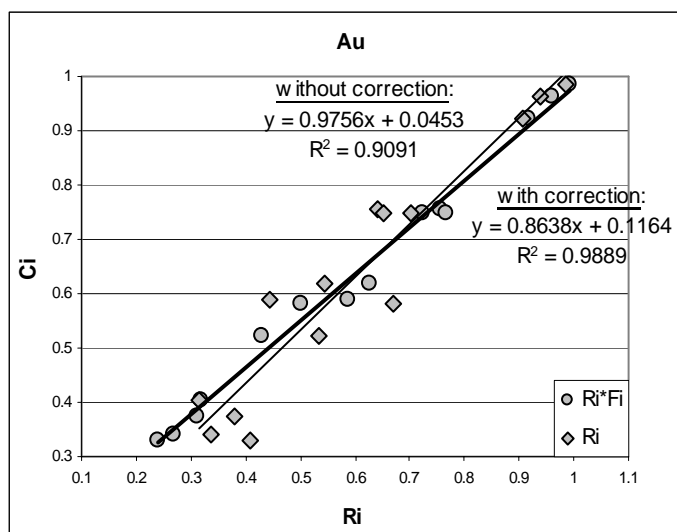
$$F_i = \frac{1 + \sum_j \alpha_{ij} C_j}{1 + \sum_j \varepsilon_{ij} C_j} \quad (12)$$

<sup>1</sup> Values accompanied by errors are analytical results.



Regression results (tab 2) show good affect of matrix effect correction for cases of Ni, Zn, Au. Both correlation factor and interpolation error are improved significantly, especially for Au, maximum interpolation error is reduced from 1.85% (non-corrected) down to 0.65% (corrected).

For the case of Cu, Pd and Ag, the corrections don't show clear affect of improving the precision. This may be caused by large errors in nominal elemental concentrations and spectrum analysis for these elements.



**Fig. 1.** Correlation between Au concentration and Au-L $\alpha_1$  line intensity, with and without correction.

**Tab 2.** Regression of  $C_i$  vs  $R_i$  for elements

El.	Number of observ.'s	Conc. range, w%	without correction			with correction		
			R <sup>2</sup>	SE	Interpol. error, w%.	R <sup>2</sup>	SE	Interpol. error, w%.
Ni	6	9.00 ÷ 25.00	0.869	0.021	0.36 ÷ 1.62	0.929	0.015	0.26 ÷ 1.19
Cu	10	1.50 ÷ 24.00	0.933	0.018	0.20 ÷ 0.95	0.902	0.022	0.24 ÷ 1.15
Zn	4	2.00 ÷ 10.00	0.959	0.010	0.26 ÷ 0.50	0.993	0.004	0.10 ÷ 0.20
Pd	4	10.00 ÷ 32.00	0.988	0.014	0.35 ÷ 0.91	0.994	0.010	0.25 ÷ 0.66
Ag	7	3.00 ÷ 45.00	0.992	0.014	0.23 ÷ 0.88	0.995	0.012	0.19 ÷ 0.73
Au	14	30.00 ÷ 99.00	0.909	0.071	0.51 ÷ 1.85	0.989	0.025	0.18 ÷ 0.65

The regression lines are considered as calibrations for a procedure of analyzing unknown samples. The above quality parameters of regression lines will affect on *precision* of analytical results. Affect of the procedure (which includes the correction algorithm) on *accuracy* will be evaluated by analyzing test samples.

### 3. Iterative calculation of unknown concentrations

In practice of analysis of an unknown sample, calculation of the correction coefficients  $\alpha_{ij}$ ,  $\varepsilon_{ij}$  and consequently the matrix correction factor  $F_i$  for each element

requires to know concentrations of all elements and compounds in the sample, which are things the analysis must provide. This difficulty is solved by an iterative correction algorithm consisting of following operations:

1. *Step (0)*: Calculate first estimations  $C_i^{(0)}$  for all elements in the sample using the non-corrected calibrations (10);
2. *Start step (n)*: using concentrations estimated in step  $(n-1)$ , calculate correction coefficients of step  $(n)$ :  $\alpha_{ij}^{(n)}$ ,  $\varepsilon_{ij}^{(n)}$  and correction factor  $F_i^{(n)}$ ;
3. Calculate concentration estimations of step  $(n)$   $C_i^{(n)}$  using corrected calibrations (11);
4. Check the convergence: compare the relative difference  $\delta_i^{(n)} = (C_i^{(n)} - C_i^{(n-1)}) / C_i^{(n-1)}$  to a predefined convergence criterion  $\lambda$  for all elements of interest. If  $|\delta_i^{(n)}| > \lambda$ , repeat the calculation from the operation 2); if  $|\delta_i^{(n)}| \leq \lambda$ , finish calculation, assign  $C_i = C_i^{(n)}$ .

#### 4. Application of the procedure for test samples

The analyses of test samples show the quick and stable convergence of the iterative algorithm. With predefined convergence criterion  $\lambda = 0.001$ , analytical results all converge after 3÷6 iterations.

**Tab 3.** Analytical results of test sample.

A – Non-corrected;

B – Corrected.

Sample	Concentration, w%											
	Ni		Cu		Zn		Pd		Ag		Au	
	A	B	A	B	A	B	A	B	A	B	A	B
T22			4.49	5.70 ± 0.45					3.32	3.37 ± 0.40	92.20	91.94 ± 0.60
T18A			9.75	11.13 ± 0.26					12.05	11.96 ± 0.23	78.20	76.91 ± 0.40
T18B			7.74	8.84 ± 0.27			12.18	12.54 ± 0.46	3.10	3.19 ± 0.41	76.98	75.43 ± 0.39
T18C	9.96	10.94 ± 0.58					14.42	14.74 ± 0.36			75.62	74.32 ± 0.38
T14A	22.17	18.08 ± 0.34	13.99	12.60 ± 0.26	9.51	8.70 ± 0.18					54.33	60.62 ± 0.32
T14B	17.44	14.18 ± 0.34	29.80	27.41 ± 1.71							52.76	58.42 ± 0.34

**Tab 4.** Differences between analytical results and nominal values (in Tab 1)

A Non-corrected.

B – Corrected.

Sample	Difference, w%											
	Ni		Cu		Zn		Pd		Ag		Au	
	A	B	A	B	A	B	A	B	A	B	A	B
T22			-0.36	-0.15					0.08	0.13	0.28	0.02
T18A			-0.62	0.76			-0.89	-0.89	-0.67	-0.76	2.18	0.89
T18B	-0.70	-0.70	-1.32	-0.22			-0.31	0.05	0.08	0.17	2.24	0.69
T18C	-0.07	0.90					-0.58	-0.26			0.65	-0.64
T14A	4.68	0.59	2.30	0.91	-0.08	-0.89					-6.90	-0.61
T14B	3.08	-0.18	3.36	0.96							-6.44	-0.78

Analytical results collected in Tab 3 and

**Tab 4** show:

- For Au, most of corrected results are closer to nominal values than non-corrected ones. The lower the Au concentration, the more significant correction is. In the two 14ct samples (T14A, T14B), differences are reduced for about 10 times when corrected.
- For elements Ni and Cu, the correction makes clear effects on 14ct samples, since the matrix effect is very complex with strong enhancement amongst Zn, Cu, Ni, and the enhancement of Au on these elements.
- For Pd and Ag, the correction doesn't make a clear effect compared to non-correlated case. This result agrees with calculations on enhancement factor  $1 + \sum_j C_j \varepsilon_{ij}$  for these elements; values of enhancement factors are always equal 1 for Ag and  $1 \div 1.01$  for Pd on all samples. One cannot distinguish the correlated result from non-correlated result if the error of nominal concentration or measurement error are so high.

The appearance of an element at a concentration level lower or close to the system detection limit, for instance, Pd (0.89%) in T18A and Ni (0.7%) in T18B, is a source of error for the other elements. Therefore, the procedure is applicable only for samples which consist of 6 elements of current work in calibrated concentration range (Tab 2).

#### IV. Conclusions

The above experimental results show a good effect of the correction method, especially for the case of element Au. The established analytical procedure is good enough to be applied to determine the Au fineness of most carat gold with the accuracy less than 1%. However, to aim at improving the accuracy of the procedure and

expanding the application of the method for other alloy objects, the experiments of the work should be proceed again with more detailed evaluations on error contribution of experiment phases such as the accuracy of the nominal elemental concentrations, the stability of the XRF system, uncertainty of X-ray intensity determination.

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# DESIGN AND THE CONSTRUCTION OF A 16K MULTICHANNEL DATA PROCESSING UNIT INTERFACING TO A PRINTER PORT

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**Abstract:** *Fast growth of the computer technology and its implementation in nuclear instruments has strong influence on the multichannel analyser. In several years, normally PC-based functional Units through I/O channel mode or RS232 port were designed and constructed. Now, there are a number of attractive alternative available: separate MCDs as NIM modules with external memory, linked to the computer seems to be more economic choice. These units, converting personal computer into the MCA, can be found on the market.*

*In the past, a design of an interfacing card through an I/O channel port was a popular type. It is so far not a well-known one. Although the accessing clock runs fast enough, it is not compatible with the new type of the computer, and not convenient to replace as having malfunctioning. To respond to the current needs of radiation detection and measurements, a MCD unit interfacing to PC through a parallel port (LPT1 or LPT2) or USB is mentioned. In the method, a way for Read/Write cycles, decoding address is simpler. Therefore, few new interfacing techniques are studied in the sub-project. Results are used in the design of the MCD which can make a combination between an ADC unit and the host computer through a parallel port for Gamma spectrometry system.*

## I. Introduction

In the reality, accompany with the growth of Science and technology, nuclear techniques has also been strongly developed in Vietnam. Obviously, the demand of instruments about quality and quantity is increasing much more. However, all of import instruments are hard to meet the current demand. Therefore, study on, development of instruments, and making domestic ones are significant.

On this occasion, development of nuclear electronics instruments for Physics research is a necessary part in NRI, Dalat. Thanks to the support of VAEC and NRI, the sub-project of “Design and the construction of a 16k multichannel data processing unit interfacing to a printer port” had been performed in the year of 2004. The gathered results are satisfied for experiments, and has been accepted by end-users. The main contents include: (i) Study on and design of the hardware through a parallel port for an MCD modular, (ii) Development of the application software compatible with the modular.

## II. Objective

To admit information of gamma emission intensity, and of branch ratio, the performance of a measurement system of good quality is significant. The main task of the sub-project is to design and fabricate a 16k-multichannel data processing unit for nuclear structure in the research reactor, Dalat.

## III. Contents

1. Design and the construction of a 16k Multichannel data processing unit
2. Development of an application software for read/write data
3. Writing a basic programme for spectra process.

#### **IV. Method**

1. Using data tranceiver method through a parallel port
2. Interfacing to an ADC due to pulse synchronization
3. Using direct and indirect decoding methods for control

#### **V. Results, specification**

- The unit tested technical characteristics that compatible with standard ones
- Multichannel data processing for 16k spectrum
- Interfacing to PC through a parallel port
- External memory, maximum intensity:  $2^{23}-1$
- Time for measurement: preset(1s...99999s) or non-stop
- Acquisition mode: PHA
- Development of application software by VC++ under Windows (9x or later)
- Low power supply: +5VDC, 220mA; NIM-2M standard

#### **VI. Conclusion**

Study on, design and the construction of the aforementioned modular satisfied the current needs for implement of radiation detection and measurements; the modular has been using and improving. When all of functional electronic moduls are combined together, a Multi channel analyser will be performed to serve for research and obtaining information from radiation events. The unit is fabricated from contemporary electronics devices, therefore, maintenance and repair of its malfunctioning is easy; it is also convenient to interface to PC since the hand-shaking mode through a parallel port. In addition, the software has been developed by Visual C++. The software has responded to the following functions: control of hardware, data acquisition and gamma peak analysis. The unit is also able to combine with other functional electronics modular to perform a gamma coincidence spectrometry system at the Dalat reactor.

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## **APPROACH TO DETERMINATION OF RESIDUAL OIL SATURATION IN BACH HO SANDSTONE RESERVOIR BY SINGLE WELL TRACER TEST-SWTT**

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**Abstract:** *In the tertiary oil recovery, Residual Oil Saturation (Sor) means the oil percentage remaining in formation may be recovered by improved method. Thus, Sor is very important information in making tertiary recovery project feasible. The Single Well Tracer Test is reliable method amongst other methods for determination of Sor. In SWTT tracer in form of ester of alcohol and fat acid, which is able to participate in oil and water is injected with water into water flooded production well to create an annulus surrounding well bore. After a sufficient well shutin time, a part of ester will be hydrolyzed into secondary tracer, alcohol, which is able to participate in water phase only. When re-open of the well both tracers ester and alcohol will move backward to the well with different velocity due to chromatographic retardation effect. The retardation depends on oil/water partitioning coefficient of the ester and certainly on the percentage of oil in the rock pore which contacts with moving water (Sor). Therefore, Sor is determined basing on the retardation of ester in re-produced water in comparison with alcohol in tracer concentration curves by means of water analysis and partitioning coefficient determined in the Lab test.*

*The Project implemented in two years 2003-2004 aims at development of the method in the laboratory in regard with Vietnam reservoir condition, firstly in Sandstone which is popular, rather familiar in application. The results obtained shall be the base to further application in field.*

*The results were establishment of methodology of SWTT, study of hydrolysis, partition of 10 distinguished esters in order to select 4 tracer candidates such as Ethyl Acetate, Ethyl Propionate, Ethyl Lactate và Ethyl 2 Hydroxy Isobutyrate which have low thermal sensitivity and can work well in high temperature reservoir as well as other technical requirement. The results of Core Tests in Bach ho and Brea Sandstone rock gave good agreement with referenced Sor. And lastly the technical procedure was designed for the further application in the field.*

### **Introduction**

In the tertiary oil recovery, Residual Oil Saturation (Sor) means the oil percentage remaining in formation may be recovered by improved method. Thus, Sor is very important information in making tertiary recovery project feasible. The Single Well Tracer Test is reliable method amongst other methods for determination of Sor. In SWTT tracer in form of ester of alcohol and fat acid, which is able to participate in oil and water is injected with water into water flooded production well to create an annulus surrounding well bore. After a sufficient well shutin time, a part of ester will be hydrolyzed into secondary tracer, alcohol, which is able to participate in water phase only. When re-open of the well both tracers ester and alcohol will move backward to the well with different velocity due to chromatographic retardation effect. The retardation

depends on oil/water partitioning coefficient of the ester and certainly on the percentage of oil in the rock pore which contacts with moving water ( $S_{or}$ ). Therefore,  $S_{or}$  is determined basing on the retardation of ester in re-produced water in comparison with alcohol in tracer concentration curves by means of water analysis and partitioning coefficient determined in the Lab test.

The Project implemented in two years 2003-2004 aims at development of the method in the laboratory in regard with Vietnam reservoir condition, firstly in Sandstone which is popular, rather familiar in application. The results obtained shall be the base to further application in field.

#### Project Element Tasks

- Study of methodology of SWTT in high temperature ( $>100^{\circ}\text{C}$ ) and large range varying temperature due to high thickness of oil bearing intervals.
- Study of characteristics of hydrolysis, partitioning, water solubility of the esters in reservoir condition to select the tracer candidates.
- Outline the schedule of SWTT.

#### Results

**1. Study of characteristics of hydrolysis, partitioning, water solubility of 10 distinguished esters in reservoir condition at different temperature to select the tracer candidates.**

##### Hydrolysis

Ester solution in produced water prepared at 500-1000ppm was heated in 50, 100, 130 and  $150^{\circ}\text{C}$  by using quartz ampoule of 20cc volume with septum. Periodically after 8 to 10h of heating the solution was analyzed by gaschromatograph. The hydrolysis rate versus heating time  $K_H$  ( $\text{h}^{-1}$ ) was determined by the formula:

$$K_H(T^0) = \frac{1}{t} \text{Ln}\left(\frac{C_0}{C(t)}\right)$$

The results showed that, hydrolytic time ranging from 10h to 77h and from 25h to 140h in the case of  $150^{\circ}\text{C}$  and  $100^{\circ}\text{C}$  respectively is appropriate to remain ester of 10% up. In fact the remains of ester may be higher than those number because a part of ester dissolved into oil phase, which could not be hydrolyzed.

**Tab 1.** Results of determination of hydrolysis rate of esters

Ester	$K_H$ -50°C	$K_H$ -100°C	$K_H$ -130°C	$K_H$ -150°C
Ethyl Lactate			0.10±0.01	
Ethyl 2 Hydroxy Isobutyrate			0.037±0.006	
Ethyl Propionate	0.003±0.0006	0.047±0.01		0.260±0.002
Propyl Acetate	0.005±0.0008	0.043±0.008		0.240±0.002
Ethyl Butyrate	0.008±0.001	0.048±0.008		0.10±0.01
Ethyl Valerate	0.020±0.005	0.06±0.01		0.100±0.006



Ethyl Heptanoate	0.025±0.005	0.06±0.009		0.095±0.002
Ethyl Isobutyrate		0.024±0.005	0.040±0.003	0.07±0.02
Ethyl Trimethyl Acetate		0.023±0.001	0.050±0.004	0.05±0.004
Ethyl Isovalerate		0.024±0.004	0.040±0.005	0.070±0.005
Ethyl Acetate		0.050±0.002	0.085±0.001	

### *Determination of Partitioning Coefficient Kd*

Kd is determined by the ratio of ester concentration in oil phase and water phase. Ester solution of 2000-3000ppm concentration in produced water was heated at different temperature and analyzed periodically after 15 minutes of heating. The results are listed in table 2.

**Tab 2.** Partitioning coefficient of esters at different temperature.

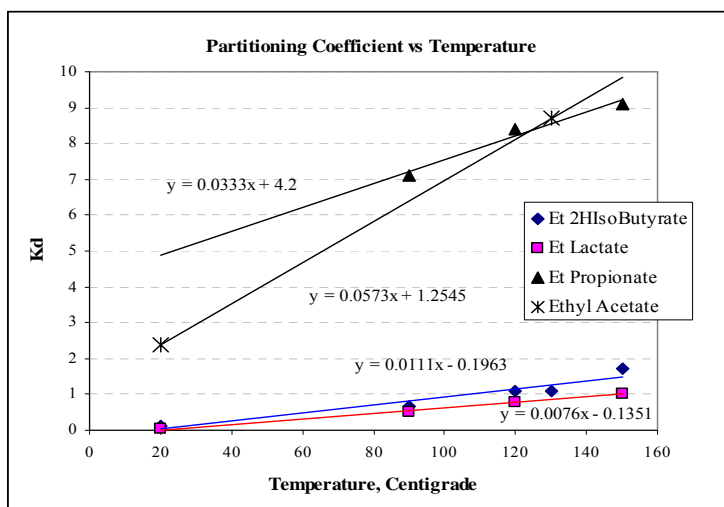
Partitioning Coefficient Kd						
No	Ester	20°C	90°C	120°C	130°C	150°C
1	Ethyl Acetate	2.4			8.7	
2	Ethyl Propionate		7.1	8.4		9.1
3	Ethyl Butyrate	50			67	
4	Ethyl Isobutyrate	17.3				
5	Ethyl Trimethyl Acetate	87				
6	Ethyl Isovalerate	78				
7	Ethyl Lactate	0.03	0.5	0.8		1.0
8	Ethyl 2 Hydroxy Isobutyrate	0.12	0.7	1.1	1.1	1.7

### *2. Selection of appropriate esters*

**Tab 3.** The esters selected as suitable tracer in regard of hydrolysis and partition in high temperature.

No	Ester	Solub 20°C	Kd 20°C	K <sub>H</sub> 50°C	Kd 90°C	K <sub>H</sub> 100°C	Kd 120°C	K <sub>H</sub> 130°C	Kd 130°C	K <sub>H</sub> 150°C	Kd 150°C
1	Ethyl Acetate	8%	2.4			0.050 ±0.002		0.085 ±0.001	8.7		
2	Ethyl Propionate	3%		0.003 ±0.0006	7.1	0.047 ±0.01	8.4			0.260 ±0.002	9.1
3	Ethyl Lactate	2%	0.03		0.5		0.8	0.10 ±0.01			1.0
4	Ethyl 2 H-Isobutyrate	7%	0.12		0.7		1.1	0.037 ±0.006	1.1		1.7

The relation of Partitioning Coefficient to temperature was expressed in graphic of Fig. 1.



**Fig. 1.** The increase of Kd vs. temperature

**3. The Sensitivity of Sor determined value vs. temperature**

The sensitivity of determination of Sor vs. temperature was evaluated by the following equation:

$$Sor = \frac{\left(\frac{V_r}{V_0} - 1\right)}{\left(Kd + \frac{V_r}{V_0} - 1\right)} \times 100$$

$V_r$  and  $V_0$  - porous volume in terms of residence time for partitioning and non-partitioning tracer were determined based on the response curves of tracer. The accuracy of those values depend on the flow meter, therefore the determined Sor accuracy depend on Kd in turn. Kd is determined in the Lab test basing on the average formation temperature. In the case of oil bearing thickness higher than 100m, the temperature can vary up to 4°C/100m which influences the accuracy of determination of Sor.

Thus, the relation  $Sor = f[Kd(T^{\circ}C)]$  was established in order to calculate the sensitivity  $\Delta(Sor)/\Delta T$  for step of  $\Delta T=10^{\circ}C$  (Table 4 and Fig.2).

**Tab 4.** The sensitivity of determination of Sor vs. temperature

Temperature Sensitivity of Sor								
	EA	( $V_r/V_0=4$ )	EP	( $V_r/V_0=8$ )	EL	( $V_r/V_0=1.05$ )	Et2HIBT	( $V_r/V_0=1.5$ )
T,°C	Kd	Sor,%	Kd	Sor,%	Kd	Sor,%	Kd	Sor,%
20	2.4	55.7		59.0	0.03	297.0	0.12	100.0
90		32.0	7.1	49.4	0.5	47.4	0.67	30.0
120		27.1	8.4	46.2	0.8	34.8	1.1	23.1

130	8.7	25.7		45.2		32.0	1.1	21.4
150		23.4	9.1	43.3	1	27.5	1.7	18.8
	$K_d = 0.057T + 1.3$		$K_d = 0.03T + 4.2$		$K_d = 0.008T - 0.14$		$K_d = 0.01T - 0.2$	
	$\Delta Sor \leq 1.5\%/10oC$		$\Delta Sor \leq 1.0\%/10oC$		$\Delta Sor \leq 4.0\%/10oC$		$\Delta Sor \leq 2.0\%/10oC$	

When below 90<sup>0</sup>C, gradient  $\Delta Sor$  is rather high, about 4% in range of 10<sup>0</sup>C, while above 90<sup>0</sup>C, gradient  $\Delta Sor$  decreases under 4%, even smaller than 1.5% in the case of Ethyl Acetate. It means the accuracy of determination of  $Sor$  may achieve as low as 1.5% over the oil bearing thickness of few hundred meter. The published works of [12, 26] reported the accuracy of 10% of  $K_d$  makes the error of 5% and of  $Sor$  in pore volume. The 10% error of retardation ratio  $V_r/V_o$  can cause 10% error for  $Sor$ .

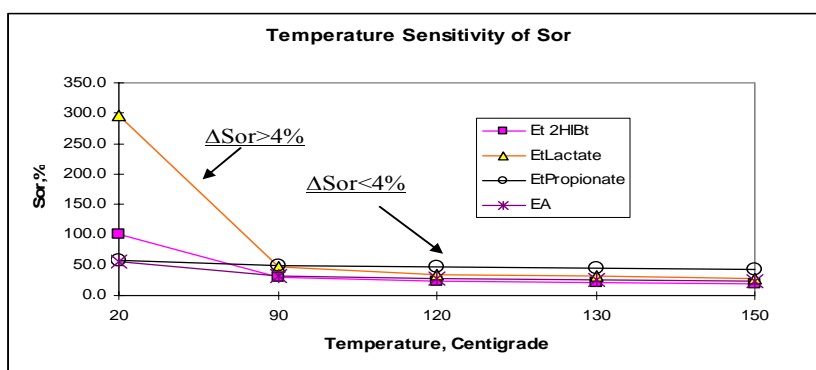


Fig. 2. The change of determined  $Sor$  vs. varying temperature.

4. Core Test

The core tests were implemented in the Lab of Vietsovpetro and also in the Tracer Lab of NRI. The scheme of equipment for core test is shown in Fig.3.

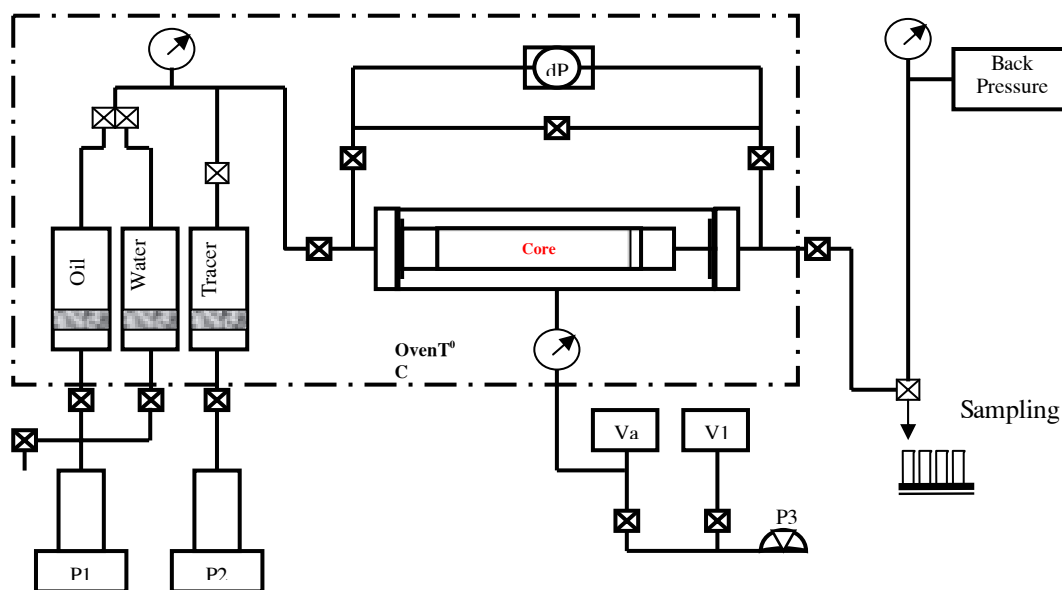
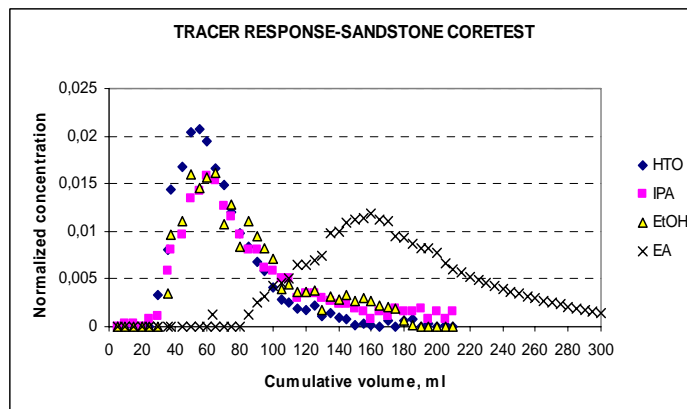


Fig. 3. Scheme of equipment for core test

After being saturated by oil the core then was flushed by water until residual oil saturation status. The tracers were injected as pulse with water. The samples were collected by fractional collector and analyzed by gaschromatograph Shimadzu GC-14B, SRI 8610C and Packard LSC 2900TR.

*Bach ho Core:*

In the Bach ho core the ester Ethyl Acetate (EA) and Isopropanol used as partitioning tracers, Ethanol (EtOH) and HTO are non-partitioning tracers. The results in Fig. 4 showed the large clearance between the response curves of EA and EtOH, HTO ( $V_r/V_o=2.9$ ), while little one in the case of Isopropanol ( $V_r/V_o=1.44$ ).



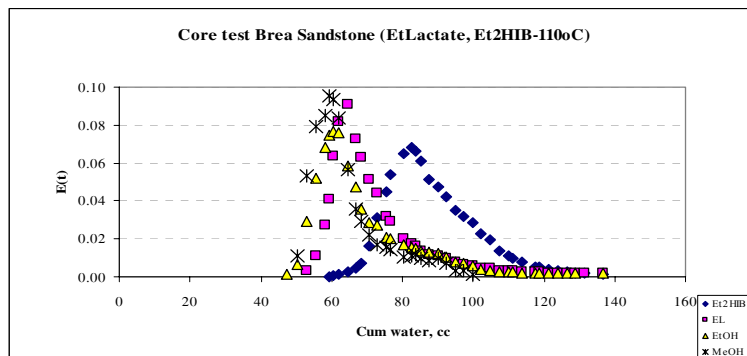
**Fig. 4.** Tracer response curves, Bach ho core.

**Tab 5.** Sor determined in the core of Bach ho, 130<sup>0</sup>C

Ethyl Acetate			Isopropanol			Reference Sor %	
Kd	$V_r/V_o$	Sor %	Kd	$V_r/V_o$	Sor %	Vietsovpetro	RTD
3.4	2.9	30	0.39	1.44	24	35.8	32

*Brea Core:*

In the Brea core, Ethyl 2 Hydroxy Isobutyrate (E2HIB) and Ethyl Lactate (EL) are partitioning tracers and Ethanol, Methanol are non-partitioning. The curve of E2HIB stands clear from EtOH and MeOH ( $V_r/V_o=1.4$ ), while EL curve is closer ( $V_r/V_o=1.08$ ).



**Fig. 5.** Tracer response cures of Brea Core.

Fig. 6. Sor determined in Brea Core, 110°C

Ethyl 2 Hydroxy Isobutyrate			Ethyl Lactate			Reference (RTD) Sor %
Kd	V <sub>r</sub> /V <sub>o</sub>	Sor %	Kd	V <sub>r</sub> /V <sub>o</sub>	Sor %	
1.21	1.4	23	0.6	1.08	16	26
1.14		24	0.8		13	
1.16		24	0.7		14	

### 5. Schedule of SWTT

#### 1. Well assignment

- a- Production well of Water Cut >80%, or Oil Cut <5%.
- b- Production method can be gaslift, merged pump...
- c- Adequacy of current logging data.

#### 2. Test design

- a) Integration of data of temperature log, production, geology and well bore structure.
- b) Sampling produced water and oil at the well head for Lab test.
- c) 4 tracers decided as below:
  - First Ester, K<sub>d</sub> (1)
  - Second Ester, K<sub>d</sub> (2); K<sub>d</sub>(1)/K<sub>d</sub>(2) >> 1
  - Balancing tracer (Methanol C-14)
  - Injection indicator (HTO)
- d) Determination of K<sub>d</sub> and K<sub>H</sub> of 4 Esters in the range of logged temperature.
- e) From determined K<sub>d</sub> and K<sub>H</sub> values select 2 esters as above criteria.
- f) Calculation of tracer amount, well shut in time, tested zone size, injection and sucking flow.
- g) Built of detailed schedule.

#### 3. Field works

- a) Field survey
- b) Preparation of equipment and facility used in field (Fig.6).
- c) Preparation of Tracer chemicals.
- d) Installation, operation test.
- e) If the well has been shut in long time (longer than 1 month), it is needed to re-produce few weeks until steady flow of water and oil. Repeat step b of 2.

- f) Storage of produced water up to 100m<sup>3</sup>.
- g) Conducting schedule.

#### 4. Sampling and analysis

- a) Procedures.
- b) Sampling and analysis on the site.

#### 5. Data process

Use of Noldor, DTS Pro for data processing.

Drift correction.

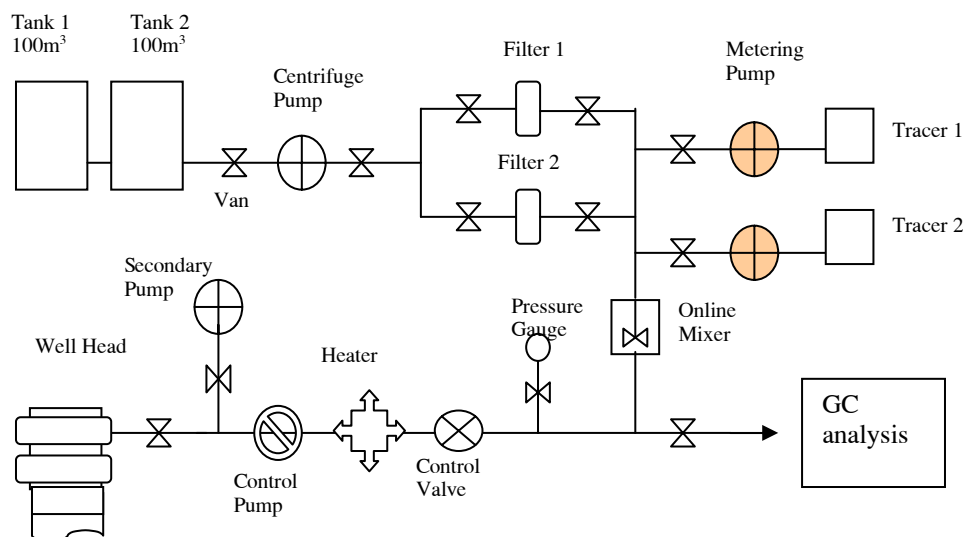
Calculation of Sor by using methods Lanmark, Mass Balance [13].

#### 6. Interpretation

Comparison of determined Sor with those of other methods.

Evaluation of accuracy.

#### 7. Report



**Fig. 6.** Instrumentation of SWTT

### Conclusions

The results of Project implementation were establishment of methodology of SWTT, study of hydrolysis, partition of 10 distinguished esters in order to select 4 tracer candidates such as Ethyl Acetate, Ethyl Propionate, Ethyl Lactate và Ethyl 2 Hydroxy Isobutyrate which have low thermal sensitivity and can work well in high temperature reservoir as well as other technical requirement. The results of Core Tests in Bach ho and Brea Sandstone rock gave good agreement with referenced Sor. And lastly the technical procedure was designed for the further application in the field.

Through implementation of the project the facility of research in SWTT was improved so that further studies of Sor and tracer chemicals will be able to carry out in the Tracer Laboratory.

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## DESIGN AND CONSTRUCTION OF MULTI-CHANNEL DATA LOGGER SYSTEM USING THE SCINTILLATION DETECTOR, INTERFACING WITH PC VIA USB PORT

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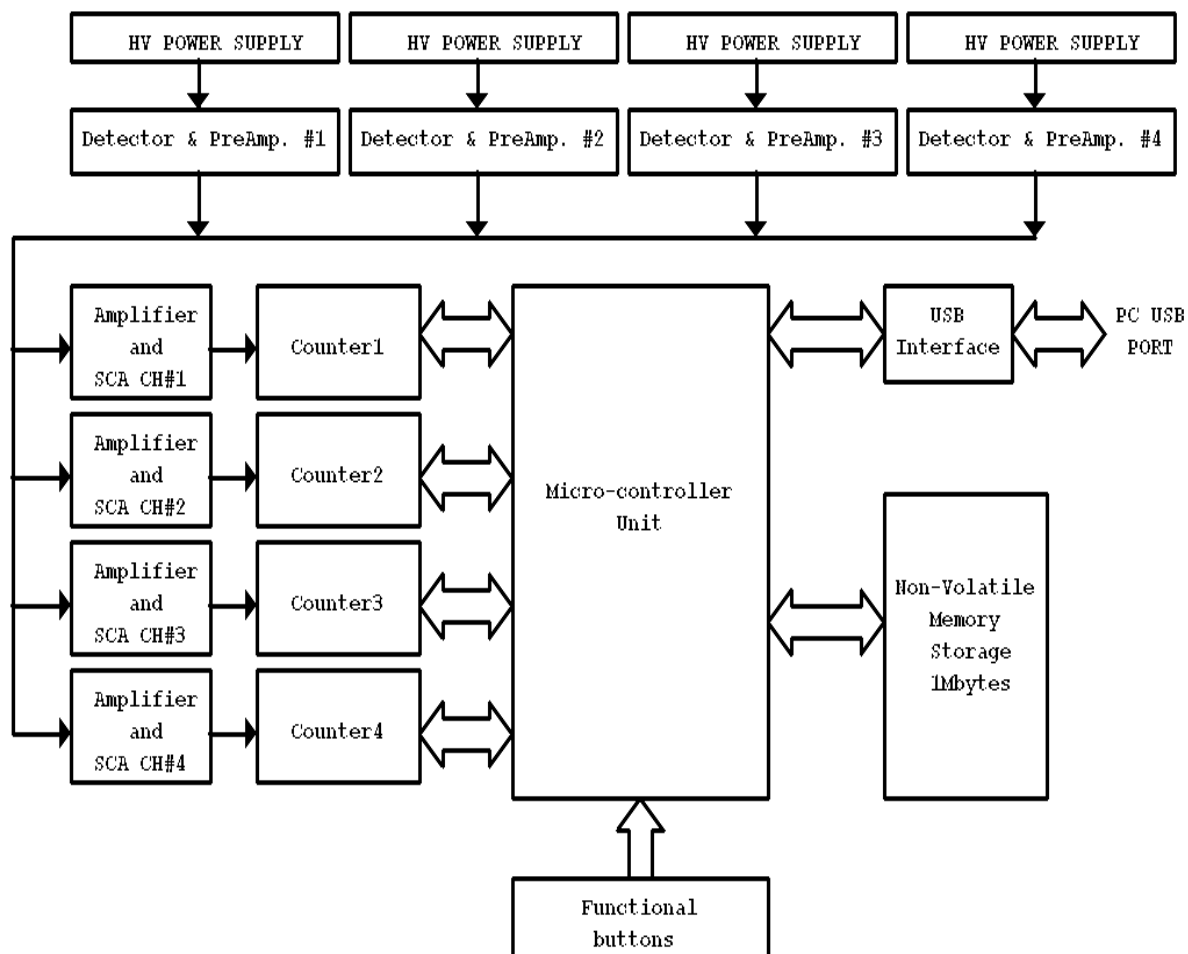
**Abstract:** *The radiation multi-channel data loggers system that includes a built-in USB interfacing controller has been developed by NRI. This system is designed around AT89C52 Micro-controller and consists of High voltage power supplies, amplifiers, single channel analyzers, counters/Timers and multi-channel data loggers. This system has also built-in 1Mbytes non-volatile memory. Communication between the system and PC implements via USB bus. This system has 4 separable channels and can be recorded the count rate of radiation pulses on four channels simultaneously for long period.*

### Introduction

Multi-channel Data Logger System used to measure and record the events continuously in long period. The Data record getting from this system during measurement process can be used for manage, monitoring, evaluating the interested events.

Universal Serial Bus, a new interface communication standard, has been developed recently. The application of USB port to communication between Peripheral interface devices and PC becomes convenient and popular nowadays. The Demand of interfacing and communication between the peripheral Electronic Devices and personal computer is big. Almost of them communicated with PC via the classical I/O port such as Parallel or Serial ports. The limitation of the old I/O ports is the lack of a bidirectional peripheral bus, which can be run at high speed, and do not have the attributes of plug-and-play.

The USB is the answer to connectivity for the PC architecture. It is a fast, bi-directional, isochronous, low-cost, dynamically attachable serial interface that is consistent with the requirements of the PC platform of today and tomorrow.



**Fig. 1.** Block diagram

The block diagram of radiation multi-channel data loggers system is shown in fig.1.

According to the block diagram, the system consists of some main modules as follow:

- High voltage power supply: There are four HVPS modules which are exactly the same can be biased for four separated Scintillation detectors. The output voltage can be adjusted in the range from 0 to 2KV and shown on the display panel.

- Amplifiers and Timing single channel Analyzers also divided into four identical modules. Amplifiers take the radiation pulses from pre-amplifier and gain them to get suitable pulse for operating the discriminators stage. The discriminator has two threshold stages for low level and window level setting. This threshold level can be changed between from 0 to 5V. The TTL output pulses on discriminator will appear if there is suitable pulse coming to discriminator input, of which the amplitude are between two threshold level setting. The TTL output pulses from TSCA stage will be counted by Counter/Timer.

- Counter/Timer: there are four high capacity counter channels for counting the count rate. Preset time can be set by application software. The results keep in non-volatile memory (off-line mode) or send to PC (on-line mode).

- All HVPS and AMP. & Discriminator modules have been designed and assembled in standard 1M Eurocard frame, the other parts are built in reduced Eurocard case.

### **Purposes of the project**

Research on design and construction of four channel data logger system interfaced with PC via USB bus. This System four separated channel for measurement and recording the count rate of radiation pulses. One of four channels consists of the High voltage power supply, Amplifier, single channel analyzer and counter/timer. This system can operate in online or off line mode. Record of data collected during measurement process can be kept in the memory for downloading or sent to PC directly through USB bus. High voltage power supply designed to bias for Scintillation detector.

The application software need developing to control the USB bus, to get data record from or to send control command to multi-channel data logger system.

### **Research activities**

Design and construction the four channel Data logger system using scintillation detectors which has some main modules and application software as follow:

- High voltage power supply 0÷2KV: They are 4 separated module in standard Eurocard case.
- Aplifier, shapping time stage and SCA: They are 4 separated module in standard Eurocard case.
- Multi channel Data logger device. This device has 4 counter channel, Timer, buit-in USB controller. All of them have been controller by AT89C52 controller under the firmware. This device was design to operate in OFF-LINE or ONN-LINE mode.
  - ON-LINE mode: Communication and control from PC via USB bus and USB driver software writen in visual basic.
  - OFF-LINE mode: Manual operation.
  - Capacity of one counter is the  $2^{32}-1$  count per channel.
  - In OFF-LINE mode: Data record can be kept in memory maximum for 60000 data record of four channel count rates.
  - Preset time can be set in the range from 0.1 to 9999 second with the step 0.1second increment by software.
- The firmware was developed in the C language.
- The application software is written in VB language for running in win 9X or winXP.

### Method used for research

- Design and construction of some suitable electronic circuit with the mentioned-above specification.
- Research on the field of application of USB bus of standard version 1.1.
- The firmware was developed in the C language and the application software is written in VB language for running in Win 9X or WinXP.

### Results

One four channel data logger system has been constructed, its specifications are as follows.

#### Amplifier specifications

- Output pulse polarity: plus
- Output amplitude: 0V ÷ 10V
- Selected shaping time: 0.5; 1; 2  $\mu$ S
- Input impedance: 1000 $\Omega$
- Output impedance: 50  $\Omega$
- Gain: 5 ÷ 75
- Maximum pulse rate input: 400KHz
- Non-linearity error: 0.2%
- Bias:  $\pm$  15V, 35mA

#### Single channel analyzer specification

- Low level and window thresholds can be adjusted in the range from 0V to 5V with the 50mV increment step. Input pulses are unipolar plus pulses of which the amplitude is between 0V to 10V.
- Output pulses are TTL square wave, of which the period is about 5 $\mu$ S
- High voltage power supply specifications
- High voltage output bias: Changes from 0V to 2KV by potentiometer.
- Load current: 1.5mA/1500V, suitable for Scintillation detector.
- Display high output voltage on digital meter.
- Counter/Timer specifications
- Four separated counter channels with the capacity of  $2^{32}$  -1 counts/channel.
- Preset time can be set by the software application in two ranges:
  - From 1 to 9999 seconds, 1second step if Selected Time Base set to value 1s
  - From 1 to 999.9 seconds, 0.1second step if Selected Time Base set to value 0.1s

#### Multi-channel data logger device specifications

- Operating mode: this device can operate in two mode, they are Off line mode ( manual operation mode) and online mode ( PC control mode).
- Data and control command transfer between device and PC via USB bus at the speed of 16kb/s
- In Offline mode, Use function keys to start/stop the measurement process or to erase contents of the RAM. The built-in non volatile RAM can save about 60000 records of four channel count rate. All data records kept in RAM can load into the PC.
- In Online mode, operation is followed the instructions from application software

#### Bias output specifications for Eurocard case

- Bias and current output:  
+5V/2A, ±15V/1A, ±12V/500mA. Stable regulable voltage output: 0.05% with standard current load. AC input: 220÷240V.

#### Bias output specifications for Multi-channel Data logger device

- + 5V/1.5A, Stable regulable voltage output: 0.05% with standard current load. AC input: 220÷240V.

### Conclusions

Based on the technical standard and specifications specified in the contract, we carried out to design and construct the electronic system named Multi-channel data loggers. After checking and testing, the results shown that this system operates well and meet fully specifications above-mentioned.

To apply and test the version 1.1 of USB bus in the field of communication and I/O interfacing between PC and peripheral devices is the considerable advance in the Nuclear Research Institute. However, to develop this interface application better in advance, we need to study and apply the USB bus version 2.0 for high speed (maximum transfer speed can be 480Mbits/s)

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## **PORTABLE X-RAY FLUORESCENCE SPECTROMETER USING XR-100CR DETECTOR**

**Vu Quoc Trong, Thai My Phe, Chau Le Ha, Huynh Long  
Pham Thi My Anh, Bui Phi Khanh and Huynh Dong Phuong**

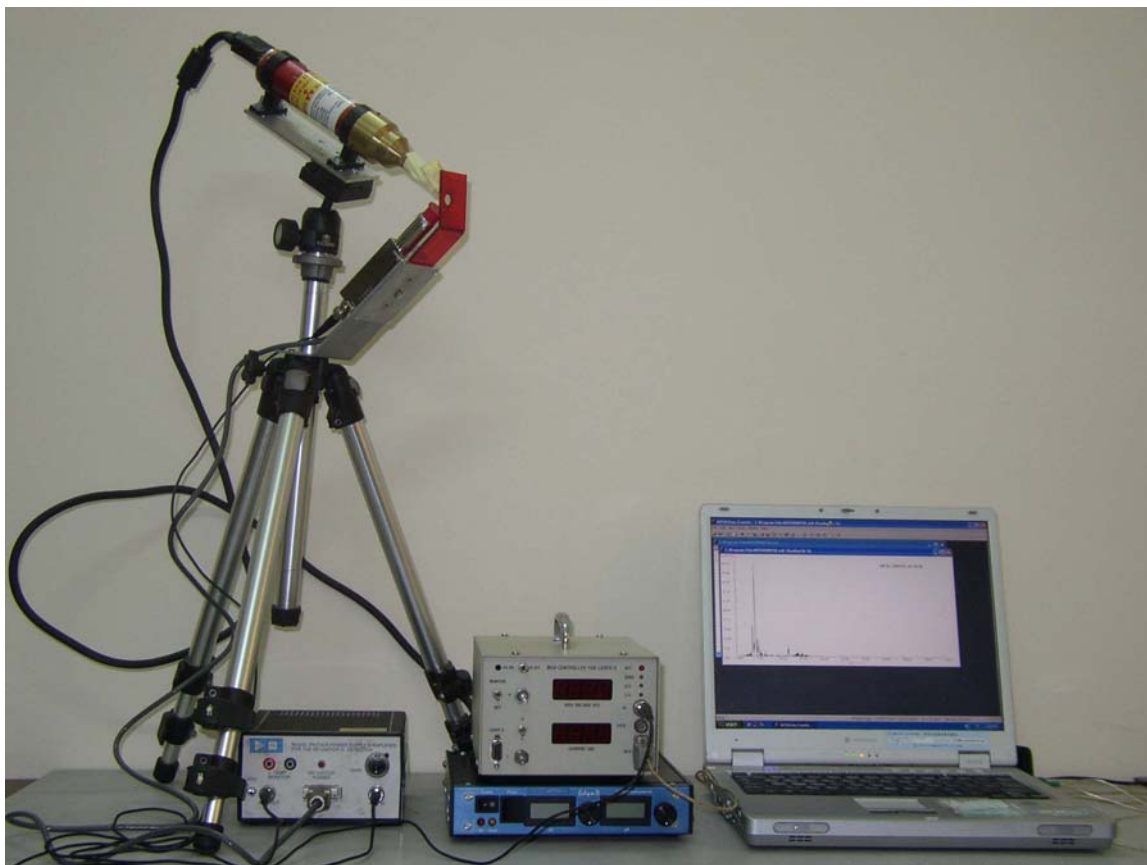
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**Abstract:** *Si-PIN photodiode has been being used as radiation detection probe since not long ago. But with obvious advantages as high energy resolution, needless liquid nitrogen and stable operation, this type of probe has been using more and more. The XR100-CR detector including a thermoelectricity cooled Si-PIN photodiode as an X-ray detector, a charge sensitive preamplifier and a novel  $-30^{\circ}\text{C}$  temperature regulation electronic circuit is enclosed in a single miniature package. It has small enclosure size ( $9.5 \times 4.4 \times 2.9$  cm), light weight (125g), high energy resolution (the 5.9 keV peak of  $^{55}\text{Fe}$  is 186 eV FWHM with 20ns shaping time) and low power consumption (<1Watt). With these facilities, this detector is able to use for in-site and outdoor X-ray Fluorescence analysis applications. Nowadays, compact X-ray spectrometers using XR100-CR are installed in factories produce cement, steel, paper, glass and ceramic, etc. to monitor interested chemical elements. Portable X-ray spectrometers are also promoted for outdoor non-destructive analysis of various objects, that we want to know some chemical elements in their composition, such as steel pipes, minerals, antiques and containers, etc. Moreover, electronic devices are more better and specialization with every passing day. The preeminence of XR100-CR detector and modern electronics have been bringing XRF analysis techniques to existence human activities. The portable XRF equipment described in this report is a multifunctional instrument for in-situ, non-destructive and real-time analysis of alloys, minerals, chemicals, papers, and glasses, etc. It was designed by Nuclear Electronics Department (NED) and the XRF group of Radiation Safety and Environment Department, Center for Nuclear Techniques, HCMC.*

The report includes two main parts:

- Developing a portable spectrometer to be used with XR100-CR detector. The designation of the device must be satisfied outdoor conditions such small size, stable operation and low power consumption.

Establishing procedures of XRF analyzing methods for some alloys in laboratory. Base on the developed equipment and analysis results gathered in laboratory, outdoor XRF analyzing procedures will be accomplished.



**Fig. 1.** The XRF Spectrometer

### **I. The XRF Analysis Device**

The portable XRF equipment described in this annual report is a multifunctional instrument for in-situ, non-destructive and real-time analysis of alloys, minerals, chemicals, papers, and glasses, etc. It was designed by Nuclear Electronics Department (NED) and the XRF group of Radiation Safety and Environment Department, Center for Nuclear Techniques, HCMC, under a project of the Minister of Science and Technology.

Major components, which include a radiation x-ray detection probe, an excitation laser-X device and a spectroscopy shaping amplifier/power supply, were ordered from Amptek, an American Famous Nuclear Instrument Company. Others such as mechanics, multi-channel analyzer, DC power supply and software were developed by the XRF group and Nuclear Electronics Department.

The XR-100CR is a new high tech x-ray detector comprised preamplifier and cooler system using a thermoelectrically cooled Si-PIN photodiode as an x-ray detector. Also mounted on the cooler are the input FET and a novel feedback circuit. These components are kept at approximately  $-30^{\circ}\text{C}$ , and can be monitored by an internal temperature sensor. The hermetic package of the detector has a light tight, vacuum tight Beryllium window. The very thin 25  $\mu\text{m}$  Beryllium window is enable for soft x-ray detection.

Power to the XR-100CR is provided by the PX2CR Power Supply. The PX2CR is AC powered and also includes a spectroscopy shaping amplifier. The XR-

100CR/PX2CR system ensures stable operation in less than one minute from power turn-on.

The Multi Channel Analyzer (MCA) based on the Linear low power 12-bit ADC LTC1277 and a micro-controller AT89C52 acquires multi-channel spectrum. A real time keeper MT48T59Y with 8 Kbytes of battery back-up SRAM and an EEPROM AT29C040 with 512Kbytes of non-volatile memory are also combined into the MCA circuit for spectroscopy storage and real time maintenance. The RS232 serial interface allows the MCA link with computer via comm. Ports.

The radiation source  $^{241}\text{Am}$  is used as an excitation device for X-Ray Fluorescence (XRF) analysis. The complete XRF system used the radiation source  $^{241}\text{Am}$  as excitation device is shown in Figure 1. This configuration is very useful for laboratory conditions.

The Laser X is a self-contained miniature X-ray tube system, which includes the X-ray tube, the power supply and the control electronics in a single compact enclosure. It is designed to replace radioisotopes in X-ray fluorescence analysis applications. It features a 35 kV/100  $\mu\text{A}$  power supply with a solid silver target. A special CONTROLLER provided both Voltage and Current control to the LASER-X has been developed. The voltage is displayed from 0 to 35kV, and the current is displayed from 0 to 100  $\mu\text{A}$ . The Laser X is compatible with in-situ and outdoor environment.

Specifications	
Number of channels	1024
Energy Resolution @ 5.9 keV ( $^{55}\text{Fe}$ )	200eV
Differential Error	0,5 %
Integral Error	1%
Channel drift	1 channel/24 hours
Dead time	45 $\mu\text{s}$
Temperature stable	$\sim 10^{-1}$ channel/ $^{\circ}\text{C}$
Power consumption	400mA
Weight of the electronic device	5,5 Kg

## II. The Software Win-EDXRF (*Energy Dispersive X-ray Fluorescence*)

The software WIN-EDXRF developed in Visual Basic version 6.0 runs with window 95, 98 and XP versions. Besides main functions of a normal MCA software, the WIN-EDXRF has the following special functions for XRF analysis:

- Real time X-ray spectroscopy acquisition.
- Analyzing XRF spectrum by the non-linear least squares fitting method with XRF background spectrum is seventh-class linear polynomial as function of energy.
- Determining the amount of elements by the fundamental parameter method.



The main display of the WIN-EDXRF program is shown in Figure 2. The program communicates with users via very friendly tools of the visual basic such as pop-up driven menu and dialog boxes. Major facilities of the program are listed below:

- XRF spectroscopy acquisition
- Acquisition time settings
- Energy calibration
- Selecting interested analysis elements from table of elements for XRF
- Analyzing XRF Spectrum by the non-linear least squares fitting method.
- Determining the amount of a chemical element by using the fundamental parameter method.
- Saving, loading and printing out results.

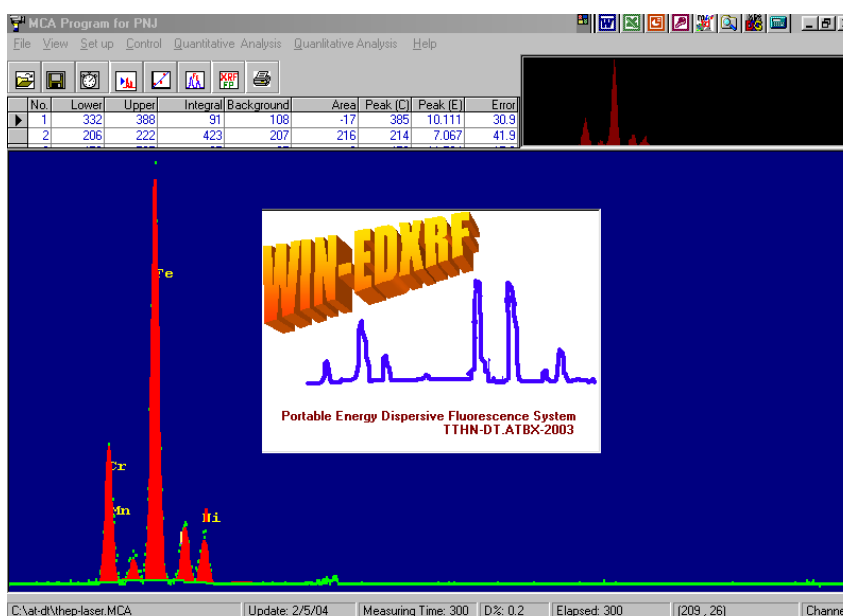


Fig. 2. The main display of the WIN-EDXRF program

### III. Experimental Results

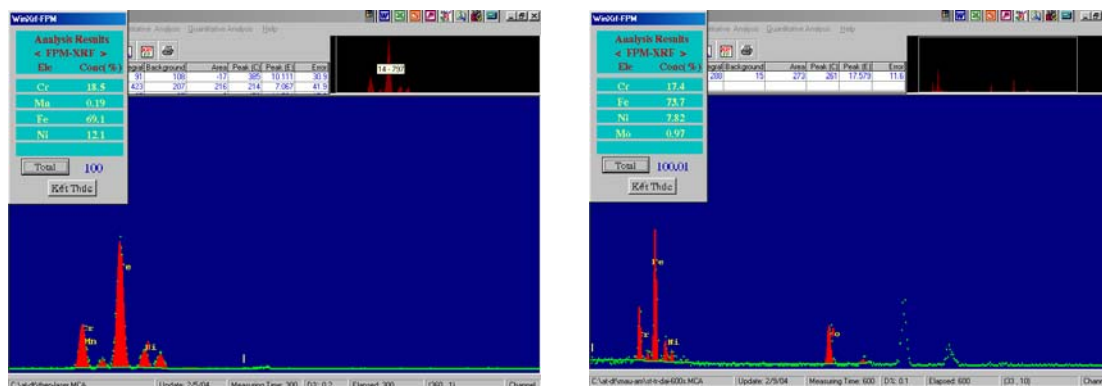


Fig. 3. The stainless steel XRF From Laser-X and radiation source  $^{241}\text{Am}$

With the XRF analysis method , procedure of sample preparation is not very complicated as other analysis methods. The equipment is able to obtain reliable results after some minutes analysis . After many measurements have been carried out, the analysis abilities of the equipment are mentioned in some preliminary conclusions below:

- Analyzing amount of macro-elements in stainless steel alloys (Cr, Mn, Fe, Ni, Mo) with more than 1% sensitivity and less than 10% error.
- Analyzing amount of macro-elements in precious alloys in jewelry industry (Cu, Zn, Ti, Ni, Au, Pt, Pd and Ag).
- Analyzing composition of steel alloys (Fe, Pb, W, Zn ).
- Fast qualitative analysis of interested chemical elements.

However, macro-element analysis abilities of the equipment will be improved for analyzing from Silicon to Uranium, if X-ray excitation devices are X-ray generators or various radio isotopes as  $^{55}\text{Fe}$ ,  $^{109}\text{Cd}$  and  $^{241}\text{Am}$ , etc.

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12. <http://www.amptek.com>, <http://www.altera.com>, <http://www.atmel.com>

## **HIGH RESOLUTION TIME OF POSITRON ANNIHILATION PECTROSCOPY**

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**Abstract:** *The ORTEC conventional positron lifetime spectrometer (PLS) with 12,9 cm<sup>3</sup> plastic scintillation detector (BC-148), mounted with photo-multiplier (8850PMT), CFD discriminator (583) has been installed at the laboratory of physics of Center for Nuclear Techniques (Vietnam Atomic Energy Commission). The technical features of this system were investigated. The results show that the resolution time is better than 195 ps, and peak to background ratio in the spectrum measured with 10  $\mu$ Ci Na-22 is greater than 4000 of this conventional positron lifetime spectroscopy. The results of research using this spectrometer to study the porosity of materials are presented. The positronium formation in the medium of meso- and macro-pores, the correlation of macro pore size, porosity and positron lifetime characteristics will be discussed. The application of the PLS for the purpose of research and training are also proposed.*

### **Introduction**

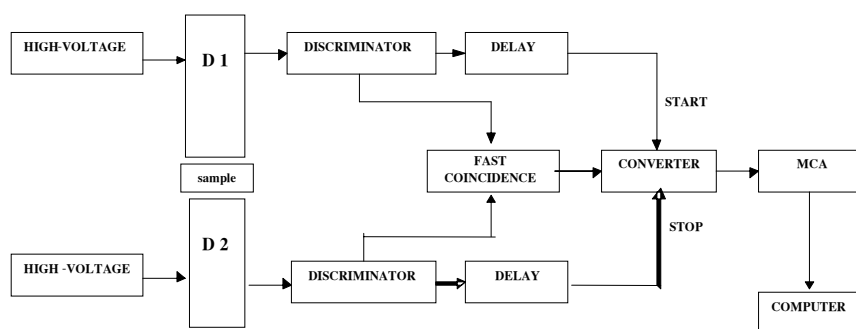
Conventional Positron Lifetime Spectrometer (PLS) is a powerful tool to analyze the vacancy-type defects in materials [1-4]. The formation of positronium at the surface and in the porous medium, the long lifetime components caused by the pick-off o-Ps annihilation, provide the tool to determine the porosity of the materials. One can find the requirements of measurements of porosity in many fields such as: materials, geology, and medicine membrane. Recently, there has been a growing interest in PAS application to investigate the porosity of materials and the macro-porosity of rocks, whose composition may cause strong effect to the positron annihilation characteristics. The relationship of positron annihilation characteristics with porosity of rocks has found. The development of Positron Lifetime Spectroscopy is also intensive investigation for the time [5-9]. In this report the new installation of Positron Lifetime Spectrometer at Center for Nuclear Techniques (Ho Chi Mink City), VAEC and its applications are introduced

### **Experiments**

#### ***1. Setting up the Positron Lifetime Spectroscopy***

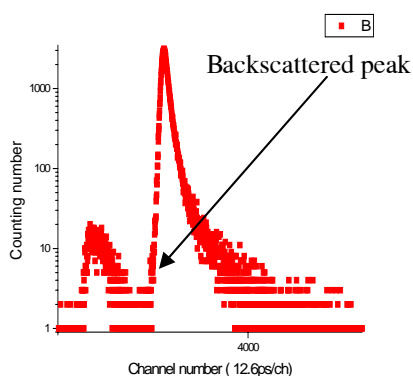
The conventional Positron Lifetime Spectroscopy includes: two plastic (12.9 cm<sup>3</sup> BS-148) detectors, these detectors were mounted with photomultiplier (8850PMT); two fast discriminators (ORTEC 583); two delayed blocks; fast coincidence block; the Time to Amplitude Converter; the MCA with MAESTO software

The principle scheme of the Positron Lifetime Spectrometry can be seen in figure 1. There are two photomultipliers: “start and stop”, which are supplied by HV of 1.99 kV for start and 2.29 kV for stop.

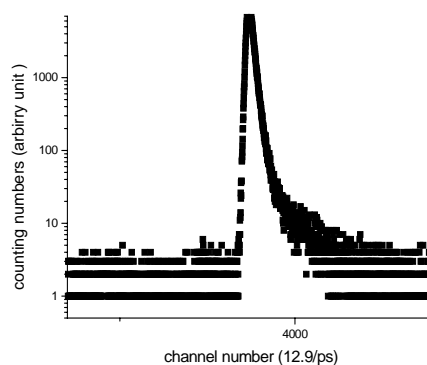


**Fig. 1.** Technical Scheme of the Positron Lifetime Spectrometry

The reason for the setting of different HVs will be described in the below discussion. The regime of the fast constant discriminators (CFD) was chosen so that the 1278 keV signals from the start and 511 keV signals from the stop PLS were the best selection. The signals from CFD then delayed to the linear region of TAC to convert to the amplitude signals. The amplitude signals then were proceed by MCA. The SCA output signals of the CFD were not only fed to the fast coincidence but also kicked up the start and stop inputs of coincidence block. When putting up the HV of two photomultipliers at the same value of 2.29 kV, the time resolution obtained from decomposition of measured spectra using RESEDIT of PATFIT was 195 ps. Because of existence of a strange peak in the spectrum as shown in the Figure 2, the backscatter influence was supposed . To treat this effect, the start HV to 1.99 kV reduced, the backscatter peak then disappeared as shown in figure 3.



**Fig. 2.** The backscatter effect



**Fig. 3.** Spectrum without backscattered peak

## 2. Experiment with porous samples

The positron lifetime spectra were measured with porous samples. The positron source is 10  $\mu$ Ci Na-22. The samples are polymer membranes with different pore-sizes, ranged between 0.2 and 0.5  $\mu$ m. The positron lifetime spectra obtained from different pore-size samples are shown in figure 4.

## Discussion

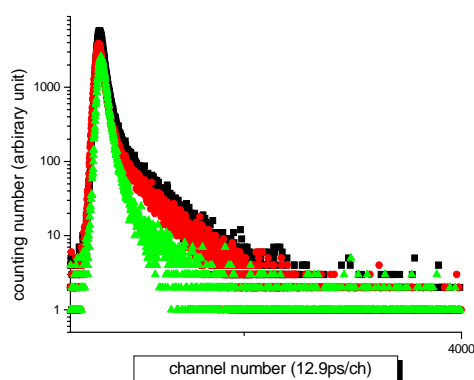
Lifetime resolution of spectrometer depends strongly on the pulse leading edge and “CFD walk”. These parameters were fixed by the ORTEC manufacture. The important parameter of spectrometer is the ratio of peak to background. This ratio depends on activity of the Na-22 source as well as the adjustments of SCA and coincidence block. By our adjustment, the achieved ratio is better than 4000 with 10  $\mu$ Ci Na-22 positron source. The backscattered peak in the spectrum as shown in figure 2 not only affects to the de-convolution analysis but also increases the time resolution of spectrometer as well. By eliminating the backscattered peak the resolution then achieved to 163 ps.

In porous materials, positrons migrate and be trapped at pores, then positronium (Ps) is formed there. O-Ps in vacuum decays into  $3\gamma$ -rays with lifetime of 142 ns. When o-Ps localized in closed pore, the lifetime of o-Ps reduced because of  $2\gamma$  annihilation, which occurs upon collision with pore wall. When the pore sizes reduced, the positronium lifetime then decreased. So that the pore size can be quantified by the positron lifetime spectroscopy [10-11]. The lifetime induced pick-off annihilation of o-Ps then relates to the pore size. In polymers and molecular solids, the correlation between the ortho-Ps lifetime ( $\tau_3$ ) and pore radius (R) is empirically described as [12]:

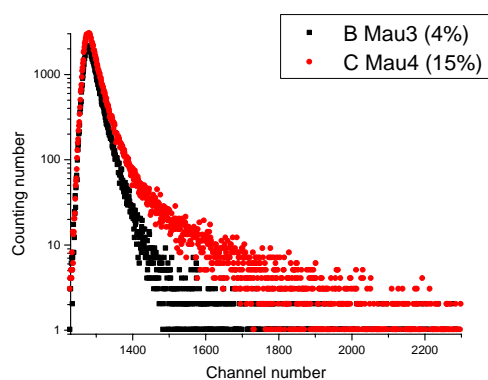
$$\tau_3 = \frac{1}{\lambda_0} \left[ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin\left(2\pi \frac{R}{R_0}\right) \right]^{-1} \quad (1)$$

Where  $R_0=R+\Delta R$  and  $\Delta R=1.656\text{\AA}$  was proposed for both liquids and molecular solids,  $\lambda_0=\pi r_0 c \rho_0$  stands for decay rate in the virtual electron layer [13],  $r_0$  is classical electron radius and  $\rho_0$  is the density of electron at the site of positron. The formula is assumed to be adequate for the micro-pore materials.

In the range of macro-pore materials the investigation are now increasing to be interested. The difference porous samples and with difference size of pores have been being studied.



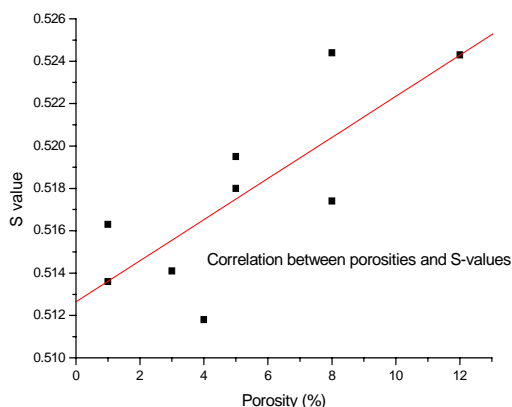
**Fig. 4.** The effect of pore-size on the lifetime of positronium



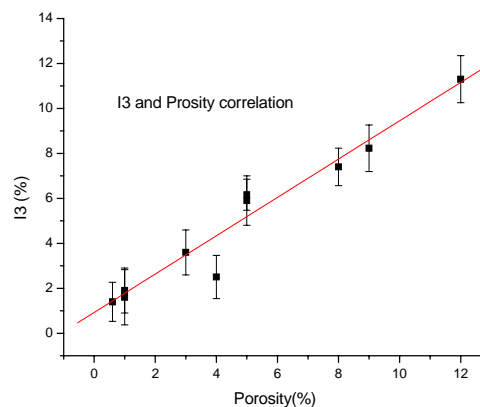
**Fig. 5.** The effect of porosity on the lifetime of positronium

The correlation between porosity of sandstone and positron annihilation characteristics were also exhibited in the previous research [14] and presented in figures 6, 7.

The results show that there is a relationship between positron annihilation characteristics and porosity as well as pore-size of materials in the range of micro pore. However, the correlation between the pore-size and positron lifetime in the experiments did not suit formula (1).



**Fig. 6.** Correlation between Doppler broadening and porosity



**Fig. 7.** Correlation between Positron lifetime and porosity

### Conclusion

The positron spectroscopy has recently been set-up at Center for Nuclear Techniques in Ho Chi Minh City, VAEC . The resolution time of the system is found to be 163 ps. The backscatter influence in the spectra has been overcome. The correlation between the porosity of materials and positron annihilation characteristics has been being investigated. Some of the experimental results show that the traditional formula for describing the correlation between the ortho-Ps lifetime and pore radius does not satisfy for all cases. The research is on the progress, however the effect of pick-off annihilation of o-Ps and porosity was found to be indicated. This instrument can be applied to the research not only in the field of materials but also for the training purpose in Vietnam as well.

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# APPLICATION OF THE PILE ECHO TEST AND SINGLE HOLE SONIC LOGGING TO EVALUATE THE DEPTH AND INTEGRITY OF STRUCTURAL FOUNDATIONS

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**Abstract:** *Solid foundations are integral important part of any structures. Obtaining accurate and timely information on the integrity of structural foundations is essential for project progress and success. Recently, under the framework of the basic VAEC projects and project VIE/8/013, a system of the advanced non-destructive methods to diagnose the quality of structural foundation have been promoted in Center for Nuclear Techniques Hochiminh City. In this report, the Pile Echo Test (PET) and Single Hole Sonic Logging (SSL) were evaluated. Background information on principle and general description of the methods as it is typically applied in the evaluation of foundations are also summarized. A suitable experimental model of the shaft foundations was prepared, where the artificial defects can be controlled for PET and SSL were conducted. Some suitable test sites were also selected, where the foundation depths can be controlled for the PET tests were conducted by impacting the driven piles.*

*The primary objective of the test program, with PET technique is to evaluate the accuracy of methods in determining the pile lengths, to evaluate the capabilities and limitation of the method and the equipped system PET, to define the quality of foundation piles from the estimated wave velocities. The test program with SSL technique is to evaluate the ability of the SSL method to identify the defects present in the experimental model, to evaluate the capabilities of the method and the equipped system Cs-97, to improve the presentation of test results to meet requirements for interpreting the quality of drilled shafts by the cross-hole sonic method.*

*The testing program with PET and SSL techniques were described and results are presented. The results shown that PET tests, as conventionally practiced, can be used to define the pile lengths with the accuracy of the evaluated depths can be obtained about  $\pm 10\%$  and depended on the assumed wave velocity. The estimate wave velocities from the PET test can be used to identify the quality of pile material. The PET tests successfully identified the location and extent of the built-in defects on experimental model shaft with 30% changes of pile cross sections, PET can be used to detect major and serious variations of quality and size, large defects, changes in pile diameter as well as approximate pile length. The results of testing program also demonstrated the SSL is a valuable non-destructive method to supplement in assessing the integrity of deep foundations, especial in small diameter piles where is difficult to arrange assess tubes and in the pile defects oriented horizontal direction.*

*The acquired capabilities are valuable asset to apply the Pile Echo Test (PET) and Single Hole Sonic Logging (SSL) - advanced non-destructive testing (NDT) techniques for testing the integrity and the pile length of the concrete foundations.*

## **Introduction**

Solid foundations are integral important part of any structures and therefore their continual use under acceptable conditions of safety is vital for the overall economic and



social development of the community. Obtaining accurate and timely information on the integrity of concrete structures, especial in the foundations is essential for project progress and success. Non-destructive evaluation methods (NDE) are good quality control tools and contribute to the development of more efficient and reliable constructed systems.

Up to date, the modern non-destructive methods for testing the integrity of structural foundations can be classified in two groups: first, tests performed in pre-placed access tubes or drilled holes with the most common methods include the cross-hole sonic method and the parallel seismic test and second, tests which are applied to the shaft head after construction with named surface reflection methods include the sonic echo tests, pile integrity tests, impulse response tests ..... Recently, a modification of cross-hole sonic logging is single hole sonic tests has been studying to check the quality of small diameter piles.

Recently, under the framework of the basic VAEC projects and project VIE/8/013, a system of the advanced non-destructive methods to diagnose the quality of structural foundations have been promoted in Center for Nuclear Techniques, Hochiminh City. An experimental program was carried out to analyze the applicability of NDT the Pile Echo Test (PET) and Single Hole Sonic Logging (SSL) to evaluate the integrity and depth of fecundated piles. The purposes of the test program, with PET technique is to evaluate the accuracy of measurements in determining the pile lengths, to evaluate the capabilities and limitation of the method and the equipped system PET, to define the quality of foundation piles from the estimated wave velocities. The test program with SSL technique is to evaluate the ability of the SSL method to identify the defects present in the experimental model, to evaluate the capabilities of the method and the equipped system Cs-97, to improve the presentation of test results to meet requirements for interpreting the quality of drilled shafts by the cross-hole sonic method.

## **Experimental Program**

### ***Experimental sites***

In the co-operation with Construction Company No. 5, suitable field-testing was done on 04 construction sites (fig. 1):

- The An Loc high building project: using the driven piles with sizes are (250x250x5000) mm, (250x250x12000) mm, and (250x250x9000) mm. There are a group of piles are ready to drive and some piles driven in the soil will be used to evaluate the accuracy of the PET tests in determining the pile lengths.
- The Nam Long building project: using the driven piles with sizes are (100x100x2000) mm, (250x250x9000) mm, (3000x600x1000) mm. The piles prepared to drive in this site will be selected to study the effects of measuring positions (impact and receiver) in the PET test.
- The Cuu Long high building project: using the driven piles with sizes are (250x250x5000) mm, (250x250x12000) mm, and (250x250x9000) mm. There are group of piles are ready to drive, some piles driven in the soil and groups of piles with poor quality are unacceptable to drive in this site. These piles will be used to evaluate the pile lengths in soil, quality of the piles in the PET tests.

- The high building project of DANH hotel: using the drilled shafts with diameters are 600mm, 1000mm and 45m of length. In this project, there is one drilled shaft which was detected the defects in the 37-39m of depth by the Cross Hole Sonic Logging. This drilled shaft will be used to evaluate the ability of PET test in checking this defect.

With conditional sites, to meet the requirements of experimental program, a suitable experimental model of the shaft foundations was prepared, where the artificial defects can be controlled for the SSL and PET was conducted. There are 04 concrete blocks in the experimental model with the ducts (plastic and steel) were cast into each block during construction. The details of defect characters are described in figure 2.

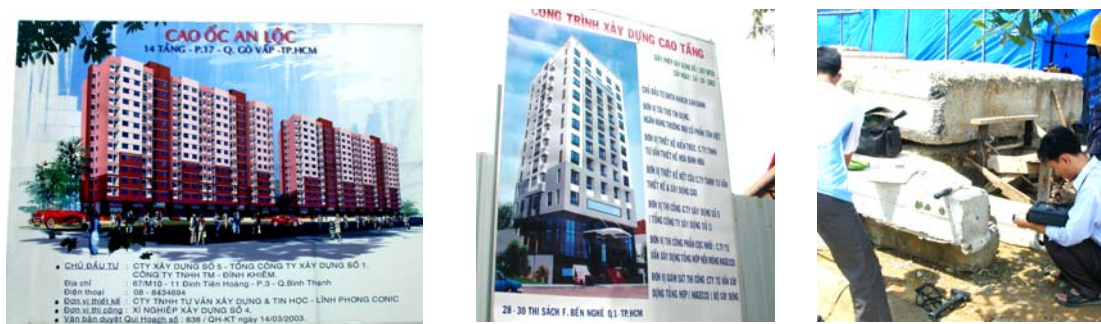


Fig. 1. Experimental sites

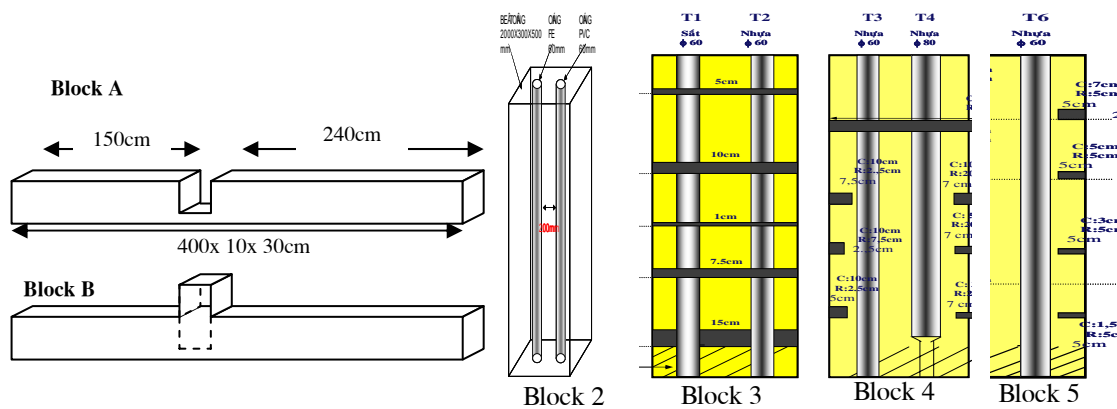
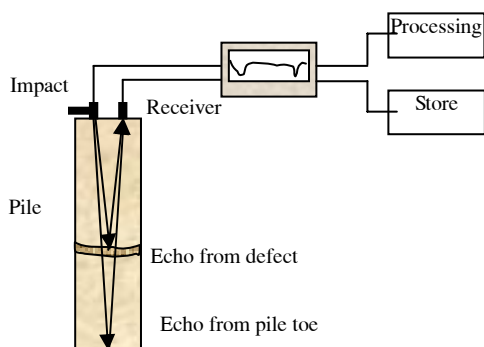


Fig. 2. The details of defect characters in the experimental model

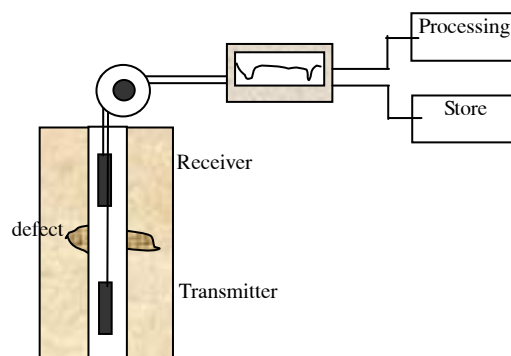
**Procedures of tests**

The equipment utilized in the experiment program for the pile echo tests is PET-Piletest.com Ltd-ISRAEL. The basic technical principle of the PET is shown in Figure 3. Each pile of the driven pile groups was tested. For each test series, the impacts of the hammer generates a compressive stress wave in the pile, and the motion associated with this wave is monitored by an accelerometer placed on the top of pile. The stress wave propagate down the pile and is reflected when it encounters either the pile toe or a non uniformity of the pile. These reflections cause a change in the acceleration signal measured on the top pile.

The equipment utilized in the experiment program for the single-hole sonic tests is Cs-97-CEBTP-FRANCE. The basic technical principle of the SSL is shown in Figure 4. For each test, the transmitter and receiver probes are placed in the same access ducts. The signal travels in a vertical direction. The probes were placed in the bottom of the ducts and lifted usually in unison in the water-filled duct to test the full shaft length from bottom to top, to create the graphs of received signals.



**Fig. 3.** Technical principle of the PET



**Fig. 4.** Technical principle of the SSL

## Test results

### 1. The PET tests

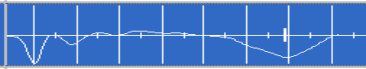
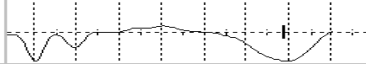
#### - Pile length of foundation

The group of driven piles in the stock was carried out the PET tests at the Anloc project. The results of the tests are shown in Table 1. The Difference of these evaluated pile lengths can be obtained less than  $\pm 10\%$  with estimated waves velocity is 3500m/s.

**Table 1.** The results of the PET tests for the pile group at An Loc Project

Pile	Actual pile length (m)	Evaluated lengths L (m)	$\Delta L$ (m)	Difference (%)
12. HUNG	5.5	5.4	0.1	2.0%
13. HUNG1	12.0	12.6	0.6	5.0%
15. H01	12.0	12.2	0.2	1.7%
16. NAGECC	9.6	9.2	0.4	4.2%
17. PHUONG	5.5	5.6	0.1	2.0%
18. SCQC	12.0	12.1	0.1	0.8%
19. SCQC1	9.6	9.4	0.2	2.1%
20. TUTIEN	12.0	12.5	0.5	4.2%
21. X	12.0	12.2	0.2	1.7%
22. X0	8.6	9.0	0.4	4.7%
23. X1	5.5	5.3	0.2	4.0%

The pile lengths were also evaluated on the piles which were driven in the soil. The results of PET test for the pile length with 12m is shown in Fig. 5

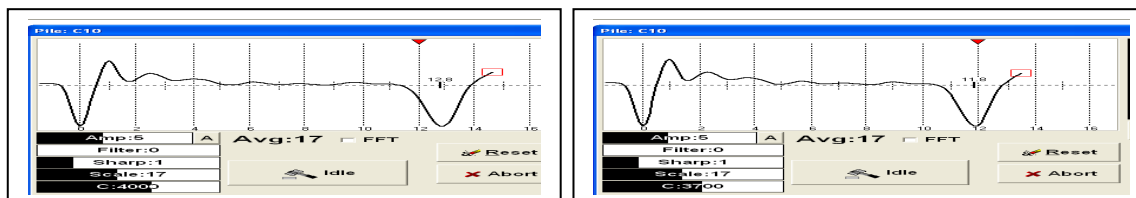
8	<b>N4</b>	<b>11.9</b>	Date:22/10/2003 c =3500 Amp =38	
9	<b>N4-1</b>	<b>11.8</b>	Date:22/10/2003 c =3500 Amp =36	

Pile	Actual pile length (m)	Evaluated lengths L (m)	$\Delta L$	Difference (%)
N4 / test 1	12.0	11.9	0.1	<1.0%
N4-1/test 2	12.0	11.8	0.2	1.7%

**Fig. 5.** Pile with 12m length was driven in soil

*- Effect of the assumed wave velocity in the estimated pile length*

Effect of the assumed wave velocity was studied in the group of driven piles of the Cuu Long project. The differences in the estimated pile lengths of the PET tests with the assumed wave velocity 4000m/s was supplied from PET equipment and wave velocity were determined by the Pulse velocity measurement equipment PUNDIT at pile heads are shown in fig. 6 in which SS is the difference of the assumed velocity and SSBC is the difference of determined velocity at site with the actual pile lengths.



**Fig. 6.** Effect of the assumed wave velocity in the estimated pile length.

Pile C10:V(PUNDIT): = 4.623Km/s; VPET(EVA): 3.698Km/s; VPET(ASSUMED): 4000m/s; Actual pile length = 11M; SS=16.4%(12.8m); SSBC=7.3%(11.8m)

*- Detected the discontinuities/ defects*

Ability of the PET tests in detecting the discontinuity was carried out on the bock A and B of the experiment model. Results of tests in changing the cross section 60% of pile are shown in fig. 7 with concrete ages of 3 days. To detect the defects in changing the cross section of pile less than 30% must use the impacts with higher frequencies (fig. 8).

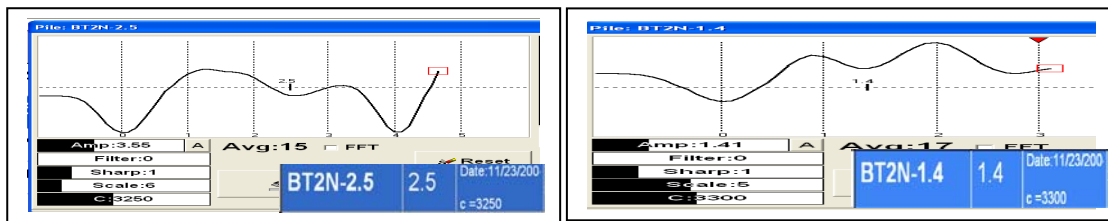


Fig. 7. PET tests on experiment model with concrete ages of 3 days.

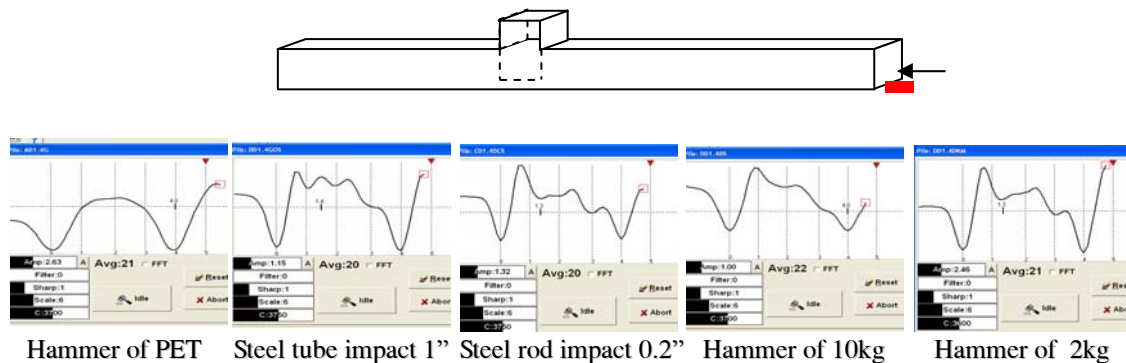


Fig. 8. Effects of difference frequencies from impacts in PET tests (block B)

Results of the PET tests re-examined on the drilled shafts CT2 at the DANH project is given fig. 9, the results shown the suitability of the detectable defects at 38-39m of depth by the PET test with Cross Hole Sonic Logging method.

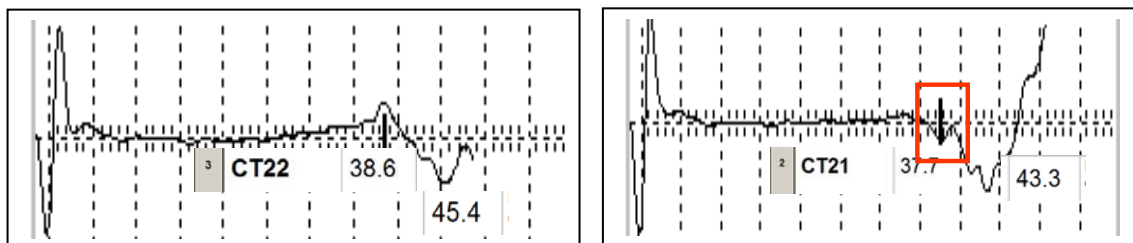


Fig. 9. PET test of drilled shafts CT2

*- The measuring positions (impact and receiver) in the PET test.*

The driven piles with sizes are (100x100x2000)mm, (250x250x9000)mm, (3000x600x1000)mm at the Nam Long building project were selected to study the effects of measuring positions (impact and receiver) in the PET test. Results of test are given in fig. 10, 11, 12, 13 shown that importance of the measuring positions for the abilities of PET tests in testing the pile length and detectable defects.

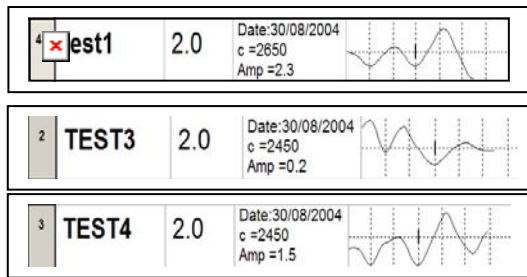


Fig. 10. PET tests on pile length 2m

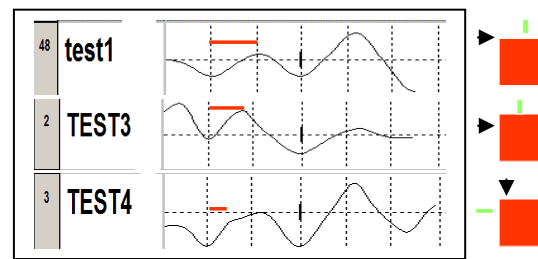


Fig. 11. Effect of wave lengths

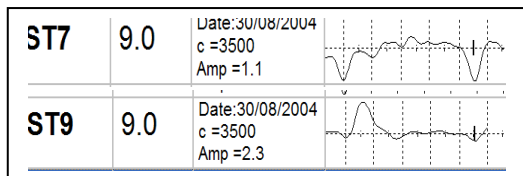


Fig. 12. PET tests on pile length 9m

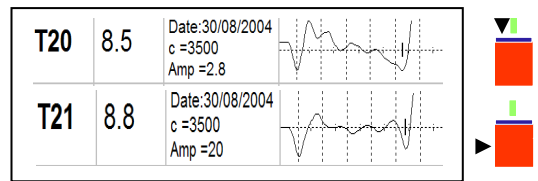


Fig. 13. PET on pile covering steel plate

**The SSL tests**

**- The effective zone of the sonic wave field**

To investigate the effective zone of sonic wave field in SSL test of the equipment Cs-97, an experiment as showing in fig. 14 was carried out. SSL system was moved to steel block and monitoring the first arrival time (FAT) of sonic wave by receiver. Results of FAT measurements were also given in fig. 14 with the probe separation 300mm.

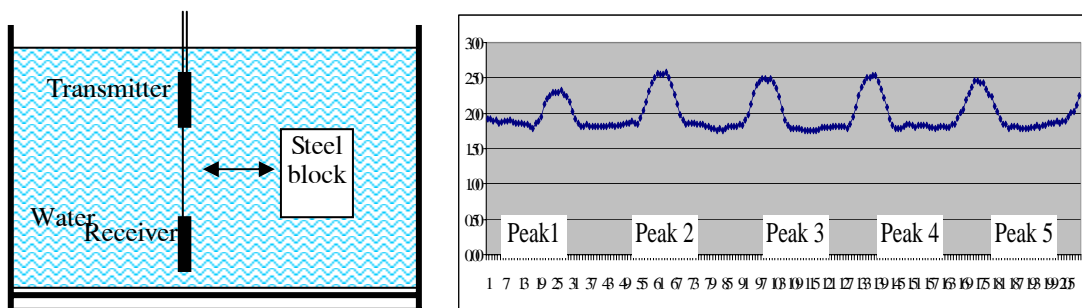
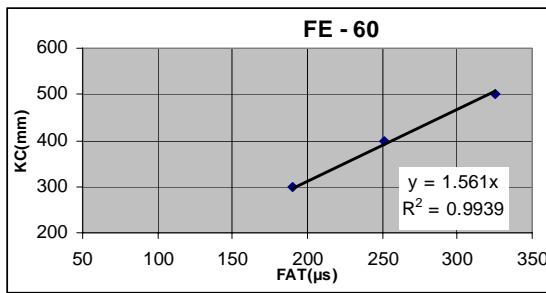


Fig. 14: Arrangement of experiment and results of FAT measurements

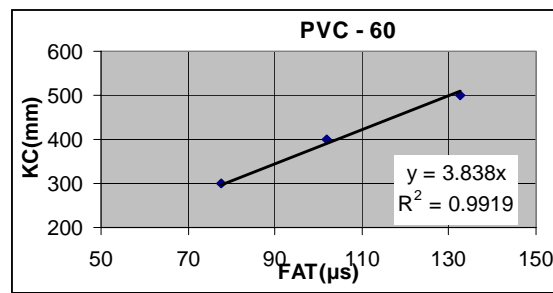
According to the results of the experiment, the effective size of sonic wave field in SSL test was 12cm radius in the steel - water media then was 8cm radius in the concrete - water media.

**- The suitable tube material for SSL tests**

To study the influence of tube material, the SSL tests were carried out on the block 2. The obtained results of SSL tests from PVC and steel tube were compared (fig. 15, 16). In each of the tubes, the SSL tests were repeated with probe spacing of 300, 400, 500mm. The results were given in fig 15, 16 shown clearly the steel tube prevented the wave coming to receiver from concrete.



**Fig. 15.** FAT of the steel tube

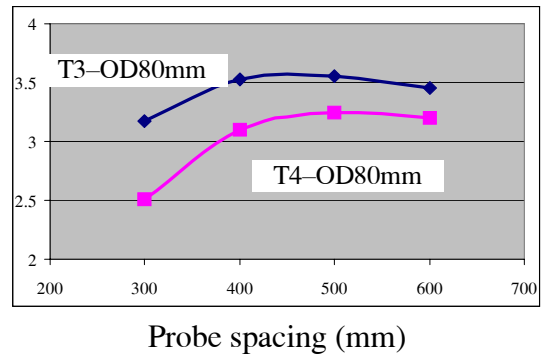


**Fig. 16.** FAT of the PVC tube

**- Optimal probe spacing**

There are four separations of transmitter and receive were selected in the experiment are 300, 400, 500, 600mm. The SSL tests were carried out on the tubes T3 and T4 of block 3. The obtained results in fig 17 shown the optimal probe spacing should be selected about 500mm.

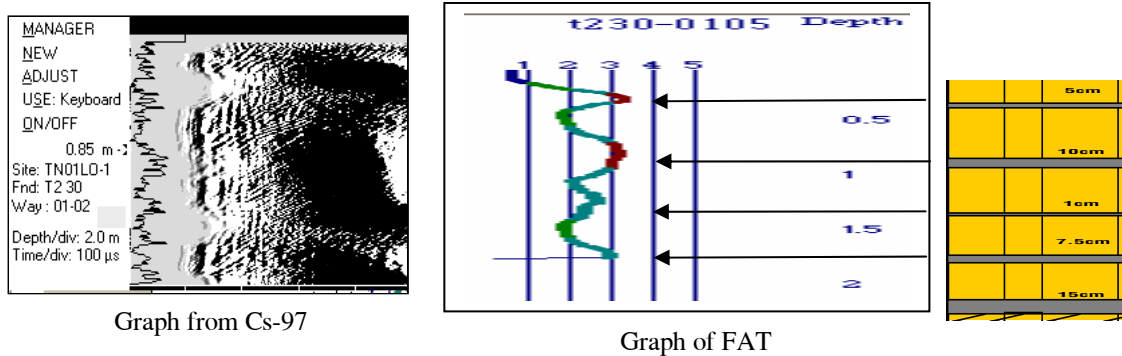
Probe spacing (mm)	SSL tests in T3		SSL tests in T4	
	FAT (μs)	Velocity (Km/s)	FAT (μs)	Velocity (Km/s)
300	213.79	3.45	187.8	3.20
400	149.91	3.56	154.5	3.24
500	113.62	3.53	129.4	3.10
600	94.73	3.18	120.1	2.51



**Fig. 17.** SSL tests in the T3, T4 of blocks 3

**- The ability of the SSL with Cs-97 for testing the defects**

In the SSL tests, the detectable defects in the piles will depend on their positions and sizes and directions. To investigate the detection range and threshold defect size of SSL test using the Cs-97 equipment, experiments of SSL were carried out on the blocks 2, 3, 4 of experimental model. In each of experiments, the SSL tests used 300, 400, 500, 600mm probe spacing.



**Fig. 18.** The SSL tests of blocks 2

The results of these experiments are shown in fig. 18, 19 demonstrated clearly detectable defects. The manufactured defects located horizontal direction will be identify easy (fig. 18). However, the defects located adjacent to the tube (not contact) or in spacing between the tubes can not be identified (fig. 19).

The SSL tests of bolck 3 – tube T3

The SSL tests of bolck 3 – tube T4

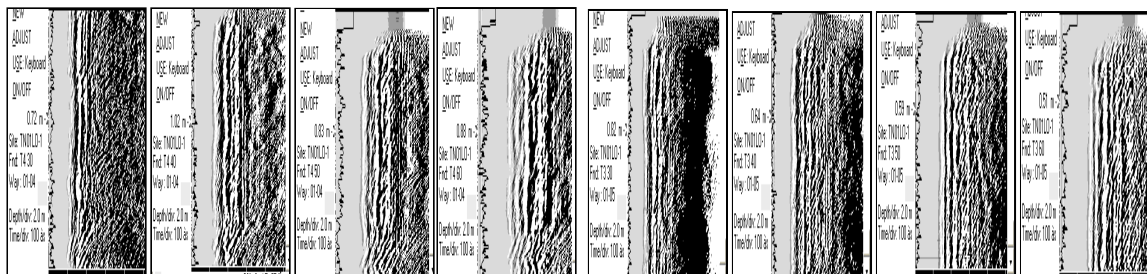


Fig. 19. The SSL tests of blocks 3, 4

### Conclusion

Based on the obtained results of experimental program for Pile Echo Testing (PET) and Single Hole Sonic testing (SSL) performed, the following conclusion can be drawn:

- PET is a Quick, minimal pile preparation and economic tests to check the integrity and the length of installed foundation piles. This method can be used to detect major and serious variations of quality and in pile diameter as well as approximate pile length. The accuracy in testing the length is less than  $\pm 10\%$ ; depend on the estimated wave velocity. To detect the defects in changing the cross section of pile less than 30% must use the impacts with higher frequencies.

- In the PET tests, the length of the foundation to test is limited. This limit depends on ground characteristics. Soil friction and poor concrete quality are often the greatest obstacles for successful PET tests. In many case, the selection of some positions for the PET test can improve the abilities of PET tests to detect the defects. For PET, it is recommended that approximate pile length and soil conditions at site, if available, must also be provide as they will aid in the interpretation of data.

- Single Hole sonic logging (SSL) is a variation of the Cross Hole Sonic Logging method (CSL) using the transmitter and receiver are placed in the same tube and the wave travels in a vertical direction. SSL tests with Cs-97 equipment demonstrated that it has provided to be a viable to assess the integrity of concrete piles in the surrounded zones of tube about 8cm, special to supplement for CSL in detecting the thin defects with horizontal direction. The SSL tests can not detect the defects without preventing the propagation of the first arrival waves from the transmitter to receiver.

- In the SSL tests, the use of plastic access tubes is mandatory. The probe spacing should be selected about 400-500mm using Cs-97 equipment.

The results of this works show the potential of SSL and PET can be applied to a wider range of complex site condition. The acquired capabilities are a valuable asset that can clearly be utilized as a part of an effort to apply the advanced NDT techniques for testing the quality of structures.



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## **STUDY ON THE DETERMINATION OF V, Cr, Fe, Ti, Zr IN ILMENITE MINERAL BY USING X-RAY FLUORESCENCE**

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**Abstract:** *The content of some elements such as V, Cr, Fe, Ti, Zr in ilmenite mineral was determined directly and quantitatively by using X-ray fluorescence spectrometry.*

*The important parameters, which influenced with the analytical results such as Cu, Mo secondary fluorescence target, excited high voltage, tube current of X-ray generator, and sample preparation procedure for ilmenite mineral samples was investigated and setting optimized. The data acquisition and processing were done by a Energy Dispersive Spectrometer (ED-XRF) Compact generator CK-5 with Molipden anode, Cu secondary target, the GENIE-2000 and Win Axil software. Base on the measurement of standard samples using fundamental parameter mode in Win Axil software, the content of V, Cr, Ti, Fe, Zr in samples was calculated accurately.*

*The precision and accuracy of quantitative analysis was tested by references material standard and comparative analysis with different chemical analytical methods.*

*The analytical procedures were set-up and applied for the determination of V, Cr, Fe, Ti, Zr in Vietnam exporting ilmenite mineral with high precision and accuracy.*

**Keyword:** *X-ray fluorescence, V, Cr, Ti, Fe, Zr elements, ilmenite mineral.*

### **Introduction**

Vietnam with hundreds of kilometer of coastal regions has a large amount of deposited mineral. The main and useful minerals are ilmenite, zircon, and rutile. These are valuable minerals for our economy because they could be exported.

The quantitative determination of the elements mentioned above is usually performed by some classical chemical analytical methods. However, these analytical procedures are rather complicated. The X-ray Fluorescence Analysis was selected due to the following advantages: rapid and simultaneous determination of the above mentioned elements in ilmenite mineral.

### **Experimental**

#### *1. Equipment*

The X-ray fluorescence spectrometry system includes:

The excitation source: X-ray tube: Compact generator 3K5 with Mo anode and Mo secondary target;

Si (Li) SL 30165 detector of 30 mm<sup>2</sup> and 25μm Be window with energy resolution of 180eV (at 5.9 keV) of <sup>55</sup>Fe;

Pre-amplifier Canberra Model 2008B. Canberra AFT Research Amplifier Model 2025;

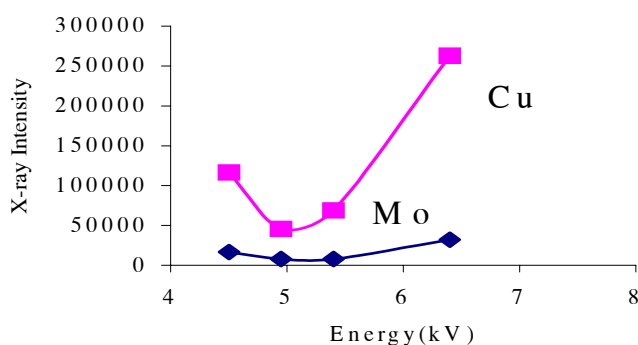
Canberra Multiport II Multichannel analyser;

Data acquisition software GENIE-2000, spectrum processing: Win Axil;

2. Study on the using Cu and Mo secondary target to excite Xray fluorescence of Cr, Ti, V, Fe and Zr

The purpose of this study is to compare the difference of fluorescence yield when using Cu secondary target with energy 8.05keV or Mo secondary target with energy 17.48keV for the excitation of Ti, Fe, Cr, V, and Zr in ilmenite mineral.

In the table 2, the samples were measured in a secondary target system, the X tube was operated at 30kV and 15mA, the spectra were collected for 200 seconds.



**Fig1:** The dependence of X-ray intensity on Cu and Mo secondary target

It can be found that V, Ti, Cr, Fe give higher in X-ray intensity when they are excited by Cu secondary target while X-ray intensity of Zr is higher when they are excited by Mo secondary target. However, due to the content of Zr in ilmenite mineral is high, so Cu secondary target usually are chosen.

3. Study on the optimum conditions such as high voltage, X-ray tube current for determining Ti, Fe, Cr, V, and Zr.

**Tab 1:** The X-ray Intensity at different values of high voltage U (kV) and tube current I (mA).

Elements	The X-ray Intensity at different values of high voltage U (kV) and tube current I (mA)				
	U=40 kV I=20 mA	U=35 kV I=10 mA	U=35 kV I=15mA	U=30 kV I=15 mA	U=30 kV I=10 mA
<b>Ti</b>	452700	216700	265600	198900	133000
<b>V</b>	6600	3500	4862	3800	2350
<b>Cr</b>	3560	2150	1957	2320	820
<b>Fe</b>	1115620	561650	655350	490950	328200
<b>Zr</b>	1583	470	701	431	260
<b>Dead time (%)</b>	45.75	24.2	29.3	18.8	13.3

It can be found that the intensity values increased with the increase of voltage and tube current. However, if the tube current was increased over a certain value, the stability of analysis decreased. By experiment, we can find that, for the high accuracy and the stability of X-ray fluorescence technique, the dead time doesn't exceed 20%.

From the studied results and for obtaining the sufficient excitation to all 5 elements Ti, Cr, Fe, V and Zr, the voltage of 30kV and tube current of 15mA were chosen.

#### *4. Fundamental parameter method*

Fundamental parameter is the most versatile method for quantification in the QXAC package and suited even for completely unknown samples. Practically, all modes of excitation with electromagnetic radiation in the range of X-rays can be covered and many parameters can be selected to match the assumptions needed for the calculations with the experiment.

#### *The fundamental parameter method in WinAxi Software Package*

The following modules compose WinAxi Software Package: WinAxi: basic X-ray spectrum analysis. WinSpector: a program to control and set up data acquisition. WaxLibMan: a program to organize and set up the parameter file into a database like environment. WinFunt: quantitative analysis program based on Fundamental Parameters

The quantitative analysis can be done in two different modes:

#### *Fundamental parameter mode:*

Using standard, or

Standarless

#### *Comparative mode*

The specially characteristics when calculating using fundamental parameters method are some factors such as absorption and enhancement correction are taken into consideration.

#### Results and Discussion

Table 2 and 3 give the results obtained when the real ilmenite mineral, and the Reference Material Standards were analyzed using fundamental parameter method. The synthesized standard L with content of TiO<sub>2</sub>: 52%, Fe: 33.21%; Cr<sub>2</sub>O<sub>3</sub>: 1%; 1%; V<sub>2</sub>O<sub>5</sub>, ZrO<sub>2</sub>: 2% was used as the standard. The good agreement between the standard values and the analysis in comparison with the different analytical methods was obtained.

Table 4 and 5 show the results received when the Reference Material Standards was analyzed using fundamental parameter method. In this study, the composition and the content of the used standards were various. It can be found that when synthesized standard A2 with the large content of V, Cr, or synthesized standard P2 with content of ZnO are 20%, or P4 with the absent of V, Cr, Zr and there is light element Al (at lower X-ray energy) were used, the results are so good. However, when A1 synthesized standard contains the different content (TiO<sub>2</sub>: 20%, Fe<sub>2</sub>O<sub>3</sub>: 80%) used as standard, the results received are at poor agreement.

From the obtained results, we can find that the analysis of ilmenite mineral by X-ray fluorescence using fundamental parameter method were so advantageous, especially when the real samples and used standard are not very similar composition. In general, the quantitative analysis results will be the most accurate if the standards and unknowns have very similar composition. In the case there are not sufficient grade chemical to make standards or the composition of our standards are not similar to the that of samples, we can still use a standard with closer compositions to the unknown and using fundamental parameter method for our analysis. However, in order to confirm how

different the type of standard and the real sample would be and how far the difference between standard compositions and unknown compositions should vary, while they still can be properly used in routine work it needs further additional research and practical experiences.

### Conclusion

For meeting the demands of mineral analysis for export of end-user and to introduce the sufficient advantageous technique, which has been employed for recent year in the world, we has studied the project” Study on the determination of V, Cr, Fe, Ti, Zr in ilmenite mineral by using X-ray fluorescence”

In the frame work of this project, the studies on the using Cu, Mo secondary fluorescence target, excited high voltage, tube current of X-ray generator, and sample preparation procedure for ilmenite mineral samples were carried out.

Some quantitatively analysis methods used in X-ray fluorescence such as calibration curve and fundamental parameter were studied.

Based on the obtained results, the procedure for analyzing these elements in ilmenite mineral by using X-ray fluorescence was established. The application of this procedure for analyzing the exporting ilmenite mineral in Vietnam showed the good and reliable results.

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**Tab 2.** Results received when analyzed the real Ilmenite mineral using the fundamental parameter method.  
The Reference Material Standards IM was used as standard

Sample Code	TiO <sub>2</sub> (%)			Fe(%)			Cr <sub>2</sub> O <sub>3</sub> (%)			V <sub>2</sub> O <sub>5</sub> (%)			ZrO <sub>2</sub> (%)		
	Found Value by XRF	Chemical method	Absol. Error	Found Value by XRF	Chemical method	Absol. Error	Found Value by XRF	AAS method	Absol. Error	Found Value by XRF	AAS method	Absol. Error	Found Value by XRF	AAS method	Absol. Error
488/03	5322±0.31	52.7	0.5	31.9±0.24	32.35	0.45	0.58±0.04	0.54	0.04	0.37±0.02	0.32	0.05	1.40±0.06	1.32	0.08
460/03	52.5±0.45	52.9	0.4	33.7±0.36	32.91	0.8	0.54±0.03	0.45	0.09	0.33±0.02	0.27	0.06	1.45±0.05	1.43	0.02
012/03	55.2±0.71	54.5	0.7	32.0±0.54	32.65	0.65	0.44±0.04	0.42	0.02	0.21±0.04	0.16	0.05	1.29±0.07	1.35	0.08
001/03	54.8±0.57	55.5	0.7	32.5±0.60	31.79	0.69	0.59±0.05	0.64	0.05	0.40±0.04	0.35	0.05	1.28±0.04	1.33	0.05
143/03	52.1±0.35	51.5	0.6	30.1±0.66	30.87	0.77	0.46±0.03	0.41	0.05	0.24±0.03	0.29	0.05	1.29±0.05	1.45	0.16

**Tab 3.** Results received when analyzed the Reference Material Standards using fundamental parameter method. The synthesized samples L with concentration TiO<sub>2</sub>:52%, Fe: 33.21%; Cr<sub>2</sub>O<sub>3</sub>:1%; V<sub>2</sub>O<sub>5</sub>:1%; ZrO<sub>2</sub>:2% was used as standard

Sample Code	TiO <sub>2</sub> (%)			Fe(%)			Cr <sub>2</sub> O <sub>3</sub> (%)			V <sub>2</sub> O <sub>5</sub> (%)			ZrO <sub>2</sub> (%)		
	Found Value by XRF	Certified Value	Absol. Error	Found Value by XRF	Certified Value	Absol. Error	Found Value by XRF	Certified Value	Absol. Error	Found Value by XRF	Certified Value	Absol. Error	Found Value by XRF	Certified Value	Absol. Error
IM	48.6±0.54	48.0	0.6	32.2±0.32	32.70	0.50	0.36±0.03	0.31	0.05	0.27±0.04			1.55±0.04	1.50	0.05

<b>HQ2</b>	55.4± 0.62	56.0	0.6	31.3± 0.38	30.76	0.54	0.46± 0.04	0.50	0.04	0.54± 0.05	0.50	0.04	0.98± 0.03	1.0	0.02
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**Tab 4.** Results received when analyzed the Reference Material Standards using fundamental parameter method The synthesized samples A2 with concentration: TiO<sub>2</sub>:35%, Fe<sub>2</sub>O<sub>3</sub>: 35%; Cr<sub>2</sub>O<sub>3</sub>:15%; V<sub>2</sub>O<sub>5</sub>:11.66%; ZrO<sub>2</sub>:3.34% was used as standard

Sample Code	TiO <sub>2</sub> (%)			Fe(%)			Cr <sub>2</sub> O <sub>3</sub> (%)			V <sub>2</sub> O <sub>5</sub> (%)			ZrO <sub>2</sub> (%)		
	Found Value by XRF	Certified Value	Absol. Error	Found Value by XRF	Certified Value	Absol. Error	Found Value by XRF	Certified Value	Absol. Error	Found Value by XRF	Certified Value	Absol. Error	Found Value by XRF	Certified Value	Absol. Error
<b>IM</b>	49.0± 0.80	48.0	1.00	32.4± 0.42	32.7	0.30	0.38± 0.04	0.31	0.07	0.28± 0.04			1.58± 0.05	1.50	0.08
<b>L</b>	51.83± 0.62	52.0	0.17	31.93± 0.46	33.21	1.28	0.92± 0.08	1.0	0.08	1.14± 0.03	1.0	0.14	2.12± 0.04	2.0	0.12

**Tab 5.** Results received when analyzed the Reference Material Standards using fundamental parameter method. The synthesized samples P4 with concentration: TiO<sub>2</sub>: 35%; Fe<sub>2</sub>O<sub>3</sub>: 35%; Al<sub>2</sub>O<sub>3</sub>: 30% was used as standard

Sample Code	TiO <sub>2</sub> (%)			Fe(%)			Cr <sub>2</sub> O <sub>3</sub> (%)			V <sub>2</sub> O <sub>5</sub> (%)			ZrO <sub>2</sub> (%)		
	Found Value by XRF	Certified Value	Absol. Error	Found Value by XRF	Certified Value	Absol. Error	Found Value by XRF	Certified Value	Absol. Error	Found Value by XRF	Certified Value	Absol. Error	Found Value by XRF	Certified Value	Absol. Error
<b>IM</b>	49.4± 0.70	48.0	1.40	32.45± 0.55	32.7	0.25	0.41± 0.05	0.31	0.10	0.32± 0.05			1.61± 0.07	1.50	0.11
<b>L</b>	52.19± 0.80	52.0	0.19	32.06± 0.46	33.21	1.14	0.85± 0.08	1.00	0.15	1.18± 0.03	1.0	0.18	2.21± 0.09	2.0	0.21

# 1.4 - Nuclear Medicine and Radioisotope Production



## STUDY ON THE SYNTHESIS OF AMP DERIVATIVES FOR LABELING WITH $^{153}\text{Sm}$ AND $^{166}\text{Ho}$

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Pham Ngoc Dien and Mai Phuoc Tho

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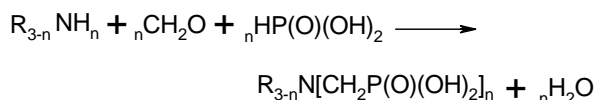
**Abstract:** This study describes the synthesis method and characterization of AMP- (Aminomethylene phosphonic acid): (PDTMP; BDTMP; DMPDTMP)

AMP is synthesized by the condensation of correlative diamine, phosphorous acid and formaldehyde using a modified Mannich reaction in the presence of hydrochloric acid. Recrystallization of the crude product from water yields white crystals of pure legend, and subsequently characterized using  $^1\text{H-NMR}$ , IR spectroscopy, melting point, crystal picture, element analysis, metal trace analysis. Synthesized AMP, when tagged with therapeutic radio nuclides such as  $^{153}\text{Sm}$  and  $^{166}\text{Ho}$  are quite good, Complexes with RC purity and labeling efficiency 20 - 98% and above could be prepared by ordinary reaction condition.

### I. Introduction

Within the last decade, there has been an increasing interest in developing new radiopharmaceuticals for therapy, especially those used for palliation of pain from bone metastases. At present an array of radio nuclides and their labeling compounds have been proposed for treating bone pain due to cancer is phosphonic acid legends. The most promising among these radiopharmaceuticals is AMP labeled  $^{153}\text{Sm}$  and  $^{166}\text{Ho}$ [2,6]

This paper reports a direct method for preparation of AMP in high yeilds by a modified Mannich reaction using phosphorous acid, formaldehyde, and correlative diamine. Their proceeds according to the general equation given below.



Where  $n = 1, 2$  or  $3$ . The hydrogen atom directly bonded to the phosphorus in phosphorous acid is the "acidic" hydrogen required for this type of reaction. [7,8]

The optimum result was obtained when the reaction was carried out at low pH, e.g. in the presence of concentrated hydrochloric acid. Concentrated hydrochloric acid (p.a.) was add drop by drop to 0.125 mole diamino compounds, followed slowly by 0.5 mole phosphorous acid dissolved in water. The mixture was refluxed for 30' ( min) and 1 mole 38% aqueous formaldehyde solution was drop wire, over 2 hours. The reaction was refluxed for a further 3 hours, and then allowed to cool. On standing for some days in the refrigerator, crystals precipitated out. They were filtered off and recrystallized twice from ethanol solution. They were the white crystalline materials. Recrystallization of the crude product from water yields white crystals of pure legend, and subsequently characterized using  $^1\text{H-NMR}$ , IR spectroscopy, melting point, crystal picture, element analysis, metal trace analysis.

## II. Materials and Methods

### A. Materials

- Chemicals: Correlative diamine: Propylene diamine, Buthylene diamine, Dimethylpropylene diamine, Formaldehyde 37% ( F.W.30.03 );  $H_3PO_3$  ( F.W. 62 ); HCl, NaOH, Ethanol, Methanol

- Tools: 1000ml Round flask (3 neck); Hot plate; Beaker; Melting point measuring instrument; Syringe (Glass); Stirring bar; Stopper; Septum; Needle; Spatula. Ice bath, electric stirrer, filtering funnel, extracting funnel, rotary evaporator.

### B. Preparation

The experimental procedure for the synthesis of the ligand is mole rate as follows.

- Ortho-phosphorous acid ( 4 mol.  $H_3PO_3$  ) and
- 4 mol. HCl ( of 37% aqueous solution of HCl )
- 1 mol. Correlative diamine was added slowly.
- 4 mol. Formaldehyde ( 30% aqueous solution formaldehyde) was added drop wire over 10 minute to a refluxing mixture comprising of above.

The temperature of the reaction mixture was maintained at 115 - 125°C, for 3 hours and then lowered to 60°C, thereafter; the mixture was cooled to room temperature (22°C) and was concentrated under vacuum ( about 5 days) when the solid AMP precipitated out. The crude AMP (phosphonate) was recrystallized from hot water or methanol : water (1:1) mixture to crystalline derivatives and dried.

### C. Characterization

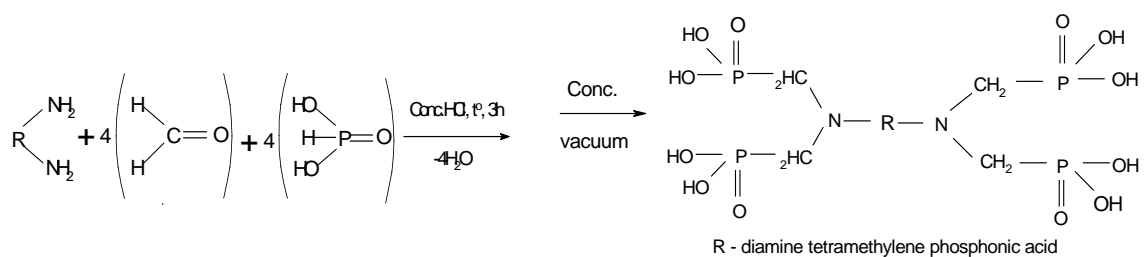
Final production quality control

To check the melting point, microscopic, crystal Picture , IR spectrum ,  $^1H$ -NMR spectrum, labeling efficiency of  $^{153}Sm$ ,  $^{166}Ho$ , element analysis, metal trace analysis.

## III. Results and Discussion

AMP could be easily synthesized by the modified Mannich reaction using phosphorous acid, formaldehyde, and correlative diamine. The product was found to be pure as characterized of melting point Crystal picture,  $^1H$ -NMR, IR spectrum, labeling efficiency, element and metal trace analysis.

As results shown the specification of the Synthesized AMP. Schema of synthesis is below.



Diamine Formandehyde Phosphorous acid

## 1. Elements analysis:

No	Name	P%	N%	Ashe%
01	PDTMP	28.31	5.61	1.35
02	BDTMP	27.35	5.50	1.37

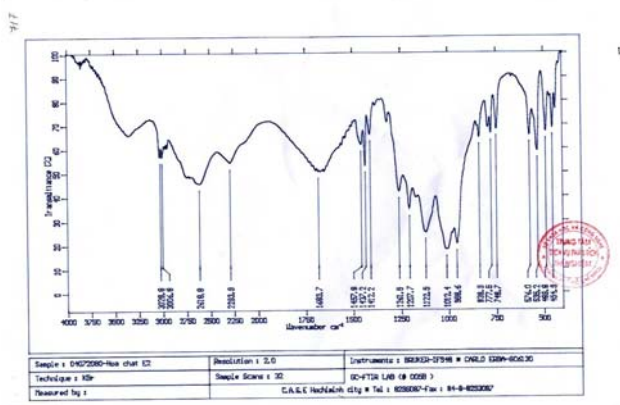
## 2. Metal trace Elements analysis: &lt; 0.01

## 3. Comparison of IR absorption spectrum

The characteristic IR bands of AMP are very similar to EDTMP, they were shown in Table

**Tab 1.** The characteristic IR bands of AMP

Range/cm <sup>-1</sup>	Band maximum	Assignment
2000-4000	3327s 3024s, 3005s 2950s, 2921s 2773sh,	OH, water NH CH <sub>2</sub> OH, POH
1500-2000	1657br	OH, water
1300-1500	1485m, 1437m 1411m, 1344m	CH <sub>2</sub> , CN
700-1300	1248s, 1167s, 1050s,	P=O, P-O
400-700	602m, 585m, 548m, 512..	P-O



**Fig. 1.** IR spectrum picture of AMP

The observed absorption bands are assigned to the quaternary nitrogen atom, the OH groups (of the water molecules and of the phosphonic groups), the P(O)(OH)<sub>2</sub> groups and the different CH<sub>2</sub> groups. Broadening of the bands and many local maximum could be observed in the ranges 2000–4000 cm<sup>-1</sup>, due to the presence of the strong hydrogen-bonding network, assigned to the phosphonic OH groups and to the water molecules. Two peaks are assigned to the quaternary N atom, which means that the two N atoms are not equivalent in the hydrogen-bonding sense. The band at 1657 cm<sup>-1</sup> supports the presence of water molecules in the AMP sample, as in the case of EDTMP.

Similarly as for EDTMP, 5 peaks of medium intensity could be observed in the range 1300–1500  $\text{cm}^{-1}$ , assigned to  $((\text{CH}_2)$  or/and  $(\text{CN}))$  vibrations. This is not surprising if we take into consideration the similar structures of EDTMP. In the ranges 700–1300 and 400–700  $\text{cm}^{-1}$ , broad peaks could be observed, with 5 defined local maxima and several shoulders, which could be assigned to the  $\text{P}(\text{O})(\text{OH})_2$  groups. The expected symmetry of the  $\text{P}(\text{O})(\text{OH})_2$  groups is  $\text{C}_{2v}$ , and consequently 3 peaks are expected in each of these wavenumber ranges. The number of peaks and shoulders indicated that there are at least two types of  $\text{P}(\text{O})(\text{OH})_2$  groups in different surroundings. The shoulders are caused by hydrogen-bonding with different strengths.

5.  $^1\text{H}$ -NMR spectrum,

$\text{CH}_2\text{-N}$ : 2.905ppm ;  $\text{CH}_2\text{-CH}_2$ : 3.325ppm ;  $\text{OH}$ : 4.144ppm; (DMSO- $\text{D}_6$ : 270MHz)

(They were shown in Fig.2)

6. Labeling efficiency = 97% (Paper and column chromatography method)

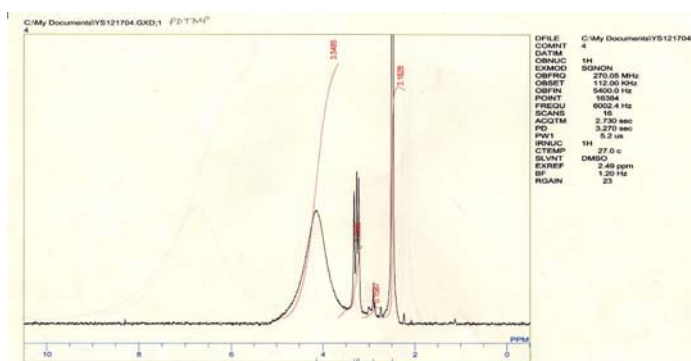
(They were shown in Fig.4-9)

Paper chromatography method were used. This was performed using Whatman No. 1 paper. 5  $\mu\text{l}$  of the reaction mixture was applied to 2cm from one end of the paper strip of 10cm. The strip was developed in the solvent mixture (NaCl 0,9%, ) until the solvent reached 10cm from the point of application. The strip was dried and cut into 1cm sections and the radioactivity was measured.

-  $^{153}\text{Sm}$ -AMP and  $^{166}\text{Ho}$ -AMP are detected at  $R_{f(0)} = 0,95 - 1$  and uncomplexed  $^{153}\text{Sm}$  at the origin. Complexing yields were determined using this formula follows:

$$\text{CY}(\%) = [1 - (\text{activity at the origin} / \text{total activity})] \times 100$$

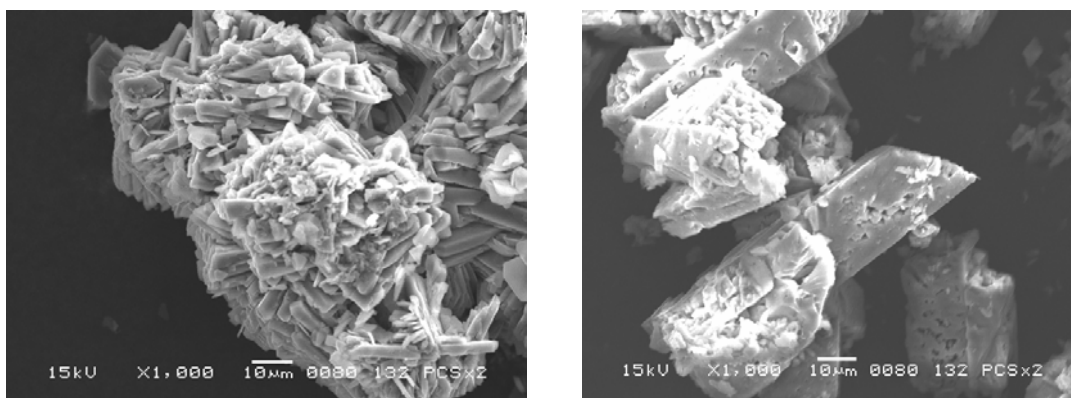
- By ionic exchange in Sephadex C-25 columns: Aliquots of the complex ( 100-200 $\mu\text{l}$ ) were put on the top of the top of the 1.2 cm diameter x 2 cm height Sephadex C – 25 columns ( approximately 0.5g of dry resin). The complex was eluted with 40ml of saline solution at 1.5 – 2.0 ml/min whereas the  $^{153}\text{Sm}^{3+}$  and  $^{166}\text{Ho}^{3+}$ , eventually formed, were retained in the columns. The columns radioactivity were measured in a dose calibrator before and after the elution and decay corrections were performed. The completing yields ( CY) was calculated using this formula:  $\text{CY}(\%) = [1 - (\text{residual activity} / \text{initial activity})] \times 100$ .



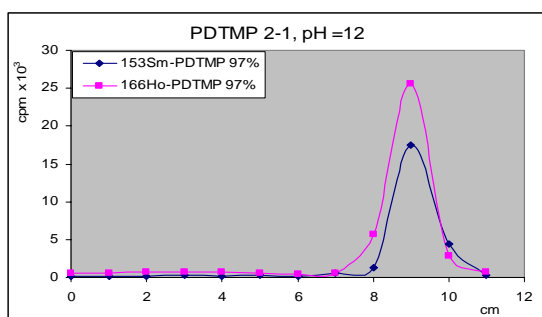
**Fig. 2.**  $^1\text{H}$ -NMR spectrum picture of AMP

$\text{CH}_2\text{-N}$ : 2.905ppm ;  $\text{CH}_2\text{-CH}_2$ : 3.325ppm ;  $\text{OH}$ : 4.144ppm; (DMSO- $\text{D}_6$ : 270MHz)

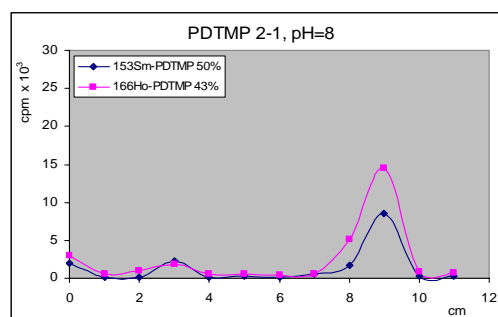
7. Color : white crystals



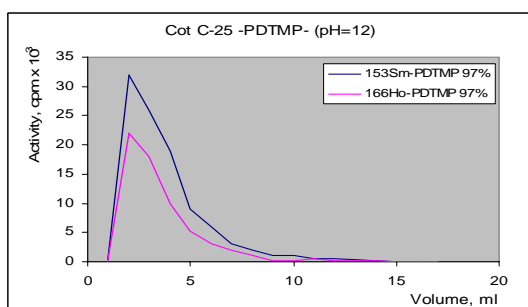
**Fig. 3.** Microscopic Crystal Picture of AMP after recrystallization are similar



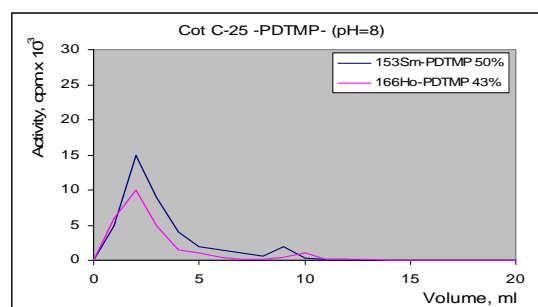
**Fig. 4.** Paper chromatography Schema of  $^{153}\text{Sm}$ -PDTMP and  $^{166}\text{Ho}$ -PDTMP Labeling efficiency = 97%, pH=12



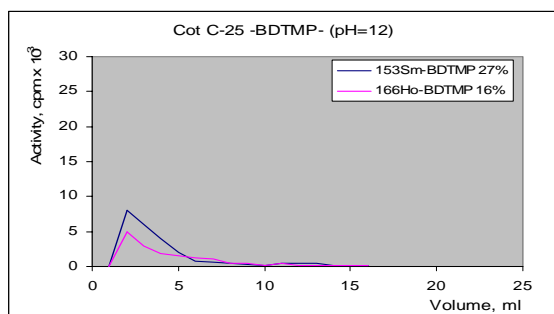
**Fig. 5.** Paper chromatography Schema of  $^{153}\text{Sm}$ -PDTMP and  $^{166}\text{Ho}$ -PDTMP Labeling efficiency < 50%, pH=8



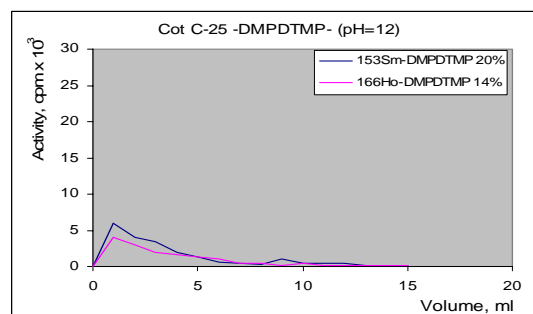
**Fig. 6.** Column chromatography Schema of  $^{153}\text{Sm}$ -PDTMP and  $^{166}\text{Ho}$ -PDTMP Labeling efficiency 97%, pH=12



**Fig. 7.** Column chromatography Schema of  $^{153}\text{Sm}$ -PDTMP and  $^{166}\text{Ho}$ -PDTMP Labeling efficiency < 50%, pH=8



**Fig. 8.** Column chromatography Schema of  $^{153}\text{Sm}$ -BDTMP and  $^{166}\text{Ho}$ -BDTMP Labeling efficiency < 30%, pH=12



**Fig. 9.** Column chromatography Schema of  $^{153}\text{Sm}$ -DMPDTMP and  $^{166}\text{Ho}$ -DMPDTMP Labeling efficiency < 20%, pH=12

### Conclusion

AMP could be easily synthesized by the modified Mannich reaction using phosphorous acid, formaldehyde, and correlative diamine. The product was found to be pure as results shown above.

Basing on the results obtained the following conclusion were outdrawn

The methods of AMP synthesis are quite good and applicable for production of vehicle used in labeling with radionuclide  $^{153}\text{Sm}$ ,  $^{166}\text{Ho}$

The quality of synthesized AMP products is suitable for purpose of labeling and application.

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## STUDY ON THE PREPARATION OF METHYLENE DIPHOSPHONATE(MDP) LABELING WITH $^{99m}\text{Tc}$ FOR BONE SCINTIGRAPHY

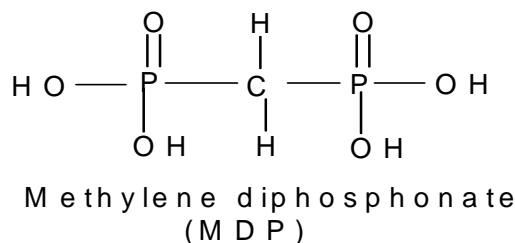
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**Abstract:** The  $^{99m}\text{Tc}$ -MDP kit was prepared by using aseptic technique. The composition of MDP in vivo kit including 5 mg MDP, 0.5 mg stannous chloride, 0.5 mg ascorbic acid and 5 mg sodium chloride. The kit produces  $^{99m}\text{Tc}$ -MDP with more than 95% labeling efficiency at pH 6-7 when mixed with requisite amount of  $^{99m}\text{Tc}$ -pertechnetate. The preparation has been found sterility, pyrogen free, to be sufficiently stable invitro as well as in vivo, blood clearance. After intravenous administrations about 50% of the dose is accumulated and retained by the skeleton. The kit provides quality product in high yield, more stable than other phosphonate kit, high bone uptake. High avidity of  $^{99m}\text{Tc}$ -MDP for bone imaging makes it a promising agent for the detection of bone diseases.

### Introduction

Since the early 1970s, a number of  $^{99m}\text{Tc}$  phosphate compounds have been introduced for bone imaging such as  $^{99m}\text{Tc}$  tripolyphosphate,  $^{99m}\text{Tc}$  polyphosphate,  $^{99m}\text{Tc}$  pyrophosphate. The improvement in bone imaging has been developed when diphosphonate compounds were introduced. These compounds possess P-C-P bonds, which are more stable in vivo than P-O-P compounds. The molecular structure of MDP is shown in figure 1.



**Fig. 1.** Molecular structure of methylene diphosphonate

In the field of medical diagnostics,  $^{99m}\text{Tc}$  with a half life of 6 hr and the monochromatic 140 KeV photons is ideal used for imaging purposes. Currently, the  $^{99m}\text{Tc}$ -MDP is widely used in hospitals in Vietnam. But almost the kit are imported. The local need is on the increase. So that, the matter for the producer is seeking for the optimum radio labeling condition for the preparation of this radio pharmaceutical. For this purpose, the study on the preparation of MDP labeling with Tc-99m for bone scintigraphy are currently under development.

In this paper the investigation of the optimal condition for the preparation of  $^{99m}\text{Tc}$ -MDP and the physiochemical and biologic quality control, blood clearance and biologic distribution of  $^{99m}\text{Tc}$ -MDP are described.

## Experimental

### A. Materials:

- MDP (methylene diphosphonate), PA, Lot No. S32649 051, MERCK - Schuchardt
- $^{99m}\text{Tc}$ -Pertechnetate was obtained from Nuclear Research Institute (NRI), Dalat, Vietnam
- $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , PA, Lot. No. B554315 945, MERCK
- Thyoglycolate Medium USP CM-173, England
- Trypton Soya Broth (Soybean –Casein Digest Medium) USP, England
- Trypton Soya Agar CM-131, OXOID LTD. Basingstoke, Hampshire, England
- LAL (Lymulus Amebocyte Lysate) ETO 0200, Lot No. 034K 6405, Sigma
- Endotoxin Standard, Lot. No. E 8029, Sigma.

### B. Procedure:

*Preparation of stannous kit MDP:* All procedure must be performed aseptically in a laminar flow hood in clean room. Prepare for 100 vials:

1. Purge 250 ml distilled water for injection with nitrogen gas 0.22 $\mu\text{m}$ , filter for 1 hour
2. Dissolve 0.5 g of methylene diphosphonate in 80ml  $\text{N}_2$  purge water (from Step 1)
3. Add 0.05 g acid ascorbic to the methylene diphosphonate solution
4. Dissolve 0.05 g of stannous chloride dihydrate in 1ml of 2N hydrochloride acid in a sterile test tube
5. Drop stannous chloride solution to the methylene diphosphonate solution (from Step 3), mix gently
6. Adjust the pH to 6.5 - 7 with 3 ml of sterile 2N sodium hydroxide
7. Add sterile water to get 100 ml final solution, fill this solution with 0.22  $\mu\text{m}$  Millipore filter
8. Aseptically transfer 1 ml aliquot sample into sterile empty vials (10 ml size) using sterile syringe
9. Freeze the sample at  $-40^\circ\text{C}$
10. Freeze drying the sample within 32 hours

**Radiolabelling:**  $^{99m}\text{Tc}$ -MDP was prepared by using MDP kit which consists of 5 mg methylene diphosphonate, 0.5 mg acid ascorbic, 0.5 mg stannous chloride dihydrate and 5mg sodium chloride and the requisite amount of  $^{99m}\text{Tc}$ -pertechnetate app. 10 – 20 mCi (370 - 740 MBq). The contents were mixed thoroughly and incubated at room temperature for 15 min.

**Radiochemical purity:** The radiochemical purity of  $^{99m}\text{Tc}$ -MDP was assessed by ascending instant thin layer chromatography (ITLC) using solvent system, namely 1M sodium acetate and acetone 100% as mobile phases. The radioactive contaminants were identified as reduced/hydrolyzed  $^{99m}\text{Tc}$  and free  $^{99m}\text{Tc}$ -pertechnetate.



**Invitro stability:** The radiolabel was tested for its in vitro stability by ascending paper chromatography. Labeling  $^{99m}\text{Tc}$  with MDP kit at differential pH such as 3, 5, 6, 7, 8. Each of radiolabel was mixed with 2ml of 0,9% NaCl and 2ml human serum, respectively. Paper chromatography were carried out to assess the labeling efficiency after incubating at 37°C for different time intervals (1, 2, 3, 4, 24 hours).

**Sterility tests:** The MDP is incubated in thyoglycolate medium (30-35°C) for aerobic and anaerobic bacteria and in soybean casein medium (20-25°C) for fungi, molds, aerobic and facultative anaerobic bacteria. The test medium is observed for 7-14 days.

**Pyrogenicity tests:** The rise in temperature after injected radio pharmaceutical in rabbits, and the determination of endotoxin in MDP kit using LAL (Limulus Amebocyte Lysate) kit.

**Blood clearance and plasma protein binding:** Blood clearance of  $^{99m}\text{Tc}$ -MDP was studied in 2 rabbits, weighing 2 kg each. After labeling, 1.9 mCi of  $^{99m}\text{Tc}$ -MDP was administered into the ear vein of each rabbit and blood samples were collected at different time intervals 0.5, 1, 2, 3, 5, 24 hours. The radioactivity in blood was calculated as percentage of the injected dose. The plasma was separated from the blood samples and equal volumes of plasma and 12.5% trichloroacetic acid (TCA) were mixed to precipitate the plasma proteins. The radioactivity in the precipitate and supernatant was measured in a gamma counter.

**Biodistribution:** In vivo distribution of  $^{99m}\text{Tc}$ -MDP was studied in 2-3 month old mice. 50  $\mu\text{l}$  of  $^{99m}\text{Tc}$ -MDP (20  $\mu\text{Ci}$ ) was administered into the tail vein of each mouse weighing 20-30 g. the animal was sacrificed at difference time intervals 0.5, 1, 2, 4, 24 hours after giving an overdose of chloroform (or ether). Difference were quickly removed, washed with normal saline and dried in the paper folds. The radioactivity was counted in each organ and expressed as percent inject dose.

**Scintigraphy of bone:** 1ml  $^{99m}\text{Tc}$ -MDP (4 mCi) was administered into the ear vein of rabbit weighing 2 Kg. The scintigraphy was carried out at 2 hours after injected.

## Results and Discussion

The maximum labeling yield (>95%) and stability was achieved when 0.5 mg stannous chloride was used for complexing 5mg MDP with 370-740 MBq  $^{99m}\text{Tc}$ -pertechnetate at pH 6.5 – 7 (Table 1 and 2) The radiochemical purity of  $^{99m}\text{Tc}$ -MDP was assessed by ascending instant thin layer chromatography (ITLC) using solvent system, namely 1M sodium acetate and acetone 100% as mobile phases. The radioactive contaminants were identified as reduced/hydrolyzed  $^{99m}\text{Tc}$  and free  $^{99m}\text{Tc}$ -pertechnetate. The labeling yield more than 95% was achieved (Figure 2 and 3)

**Tab 1.** Effect of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  concentration on radiochemical purity of  $^{99m}\text{Tc}$ -MDP. PH of all the preparation was keep constant at 7.

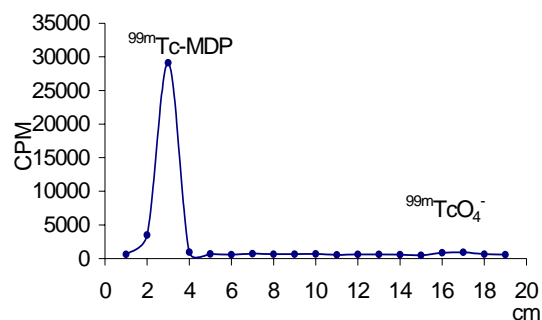
The labeling efficiency were carried out by ITLC

$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ( $\mu\text{g}$ )	% free $^{99m}\text{Tc}$ -pertechnetate	% Reduced/ Hydrolyzed $^{99m}\text{Tc}$	% $^{99m}\text{Tc}$ -MDP
1	98,6	0,22	1,18
25	2,5	5,4	92,1

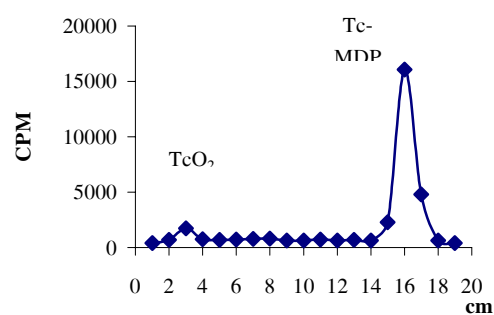
50	0,9	3,5	93,2
100	2,1	3,9	94,0
150	1,7	3,8	94,5
250	1,9	3,3	94,8
500	1,2	2,0	96,8
750	0,5	3,5	97,0
1000	0,6	3,9	95,5

**Tab 2.** Effect of pH on the formation of  $^{99m}\text{Tc}$ -MDP. While keeping other reaction condition constant, only the pH was varied from 3-8. In vitro stability of the product was ascertained along with labeling efficiency at various time periods of incubation at  $37^{\circ}\text{C}$  by paper chromatography

% Labeling efficiency at different incubation periods						
pH	0 h	1h	2h	3h	4h	24h
3	95,5	99,9	99,7	99,9	99,9	-
5	99,9	97,2	95,8	99,8	99,8	-
6	99,9	99,3	99,6	99,1	99,1	99,4
7	98,2	93,2	96,0	85,5	85,7	-
8	61,3	36,1	27,7	14,2	14,3	68,7



**Fig. 2.** Radiochemical purity of  $^{99m}\text{Tc}$ -MDP. The labeling efficiency were carried out by ITLC in MEK



**Fig. 3.** Radiochemical purity of  $^{99m}\text{Tc}$ -MDP. The labeling efficiency were carried out by ITLC in 1M sodium acetate

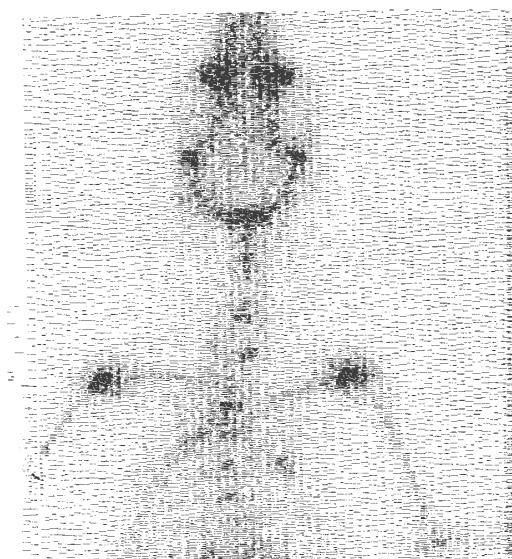
The concentration of  $^{99m}\text{Tc}$ -MDP declined in whole blood following the intravenous administration in rabbits. The first component declined rapidly followed by a relatively slow elimination. Plasma protein binding was less initially (50% at 30 min) but increased gradually with time.

Biodistribution of  $^{99m}\text{Tc}$ -MDP in liver, spleen, kidney, skeleton, muscle, lung, heart, blood, intestine and stomach in mice at various time intervals after its administration is shown in Table 3. Among all the organs studied, skeleton and skeletal

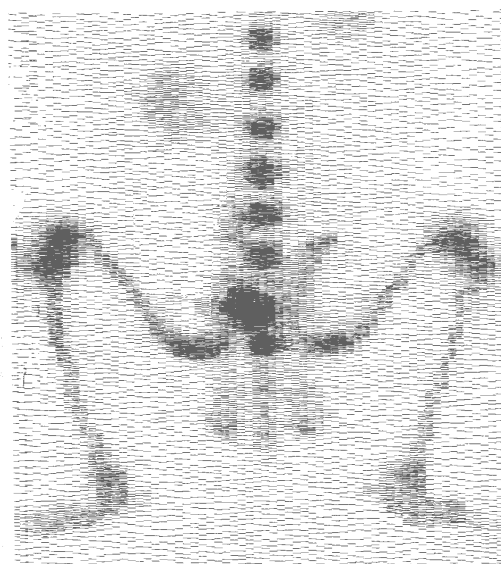
muscle exhibited maximum uptake of the radio pharmaceutical (43 –58% of the radioactive dose at 0.5 - 3 hours) which decreased to 15% at 24 hours . The accumulation of radioactivity in other organs less than in skeleton. Normal bone scintigraphy obtained with  $^{99m}\text{Tc}$ -MDP after intravenous 2 hr (4 mCi) Figure 4 and 5.

**Tab 3.** Biodistribution of  $^{99m}\text{Tc}$ -MDP in organs/Tissue at different time after intravenous administration. Data expressed as percent of injected dose  $\pm$  SD of 5 animals

Percent of injected dose					
Organs	0,5 h	1 h	3 h	5 h	24 h
Liver	1,04 $\pm$ 1,4	1,41 $\pm$ 0,17	0,35 $\pm$ 0,12	1,19 $\pm$ 0,31	0,122 $\pm$ 0,08
Spleen	0,15 $\pm$ 0,07	0,11 $\pm$ 0,01	0,01 $\pm$ 0,005	0,03 $\pm$ 0,01	0,006 $\pm$ 0,005
Kidney	0,73 $\pm$ 0,37	1,00 $\pm$ 0,16	0,52 $\pm$ 0,16	0,66 $\pm$ 0,1	0,096 $\pm$ 0,03
Skeleton	43,97 $\pm$ 1,54	51,7 $\pm$ 7,15	58,8 $\pm$ 15,21	47,7 $\pm$ 7,56	15,90 $\pm$ 2,42
Muscle	9,67 $\pm$ 1,5	19,2 $\pm$ 8,35	4,16 $\pm$ 1,79	3,89 $\pm$ 3,66	5,02 $\pm$ 10,01
Lung	0,12 $\pm$ 0,08	0,31 $\pm$ 0,35	0,05 $\pm$ 0,005	0,11 $\pm$ 0,10	0,02 $\pm$ 0,01
Heart	0,03 $\pm$ 0,01	0,41 $\pm$ 0,08	0,023 $\pm$ 0,01	0,06 $\pm$ 0,05	0,06 $\pm$ 0,006
Blood	0,45 $\pm$ 0,06	0,55 $\pm$ 0,25	0,57 $\pm$ 0,006	0,66 $\pm$ 0,13	0,28 $\pm$ 0,17
Intestine	5,53 $\pm$ 4,36	2,97 $\pm$ 0,47	6,88 $\pm$ 0,7	1,44 $\pm$ 0,86	0,19 $\pm$ 0,03
Stomach	0,22 $\pm$ 0,1	0,45 $\pm$ 0,09	0,31 $\pm$ 0,1	0,84 $\pm$ 0,09	0,04 $\pm$ 0,02



**Fig. 4.** Normal bone scintigraphy obtained with  $^{99m}\text{Tc}$ -MDP 2 hr after injection into rabbit (first part)



**Fig. 5.** Normal bone scintigraphy obtained with  $^{99m}\text{Tc}$ -MDP 2 hr after injection into rabbit (end part)

## Conclusion

In conclusion, the preparation of  $^{99m}\text{Tc}$ -MDP using stannous chloride as a reducing agent, ascorbic acid as a stabilizer has been developed and applied for bone scanning. The  $^{99m}\text{Tc}$ -MDP was sterile, non-pyrogenic radio pharmaceutical, high labeling efficiency. Requirements of quality control of this radio pharmaceutical were satisfied followed the USP XXII inquiry and used for intravenous administration in patients.

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# 1.5 - Radiation Protection and Radioactive Waste Management

# **STUDY ON APPLICATION OF AEROBIC BIOLOGICAL METHOD FOR PROCESSING WASTEWATER OF BEER FACTORY**

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**Abstract:** Purpose of the theme includes practical investigation of biochemical properties of the beer effluent, calculation, design, installation and test of a lab equipment system using aerobic biological method for cleaning beer factory waste.

Base on general theory [1], opened references published in local and from abroad [2] and also experiences obtained from practical investigation in the factories, the theme have been carried out and completed as below.

**Key words:** Beer Wastewater.

## **Content**

### **1. Design, manufacture, installation of a lab equipment system in capacity of 2 L/h using aerobic biological method for beer waste effluent.**

Main parameters of the lab equipment: Capacity of process :  $Q = 2$  L/h.

Characteristics of the input waste effluent (feed liquid):

$$\text{COD} = 1500 \text{ mg/l, BOD}_5 = 1000 \text{ mg/l, SS} = 320 \text{ mg/l, pH} = 5 - 11,$$

$$\Sigma\text{N} = 30 - 100, \text{pH} = 5 - 11,$$

Characteristics of the output waste effluent (processed liquid):

$$\text{COD} = 100 \text{ mg/l, BOD}_5 = 50 \text{ mg/l; pH} = 5 - 11, \text{SS} = 50 \text{ mg/l, pH} = 5.5 - 9.$$

#### *1.1. Gelatinous sedimentary equipment*

The gelatin clarified bulk is made of PVC with capacity/batch of 20 L for decreasing input content of  $\text{BOD}_5$  in aeroten. The bulk is stirred by mechanical agitator.

#### *1.2. Two-order clarified aeroten bulk*

##### a) Aeroten bulk

Capacity of the bulk :  $Q = 2$  L/h or 48 L/day

Geometry parameters of the bulk: L.W.H = 280.180.550(mm)

Air flow is plunged into the aeroten through a air distribution tube with  $Q_{kk} = 61.24$  L/h

Characteristics of the input feed:

$$\text{COD} = 900 \text{ mg/l, BOD}_5 = 600 \text{ mg/l, SS} = 180 \text{ mg/l, pH} = 7-7.5.$$

##### b) Secondary clarified bulk

The bulk is designed as a vertical sediment bulk with a flow tube located on center site.

Geometry parameters of the bulk: L.W.H = 120.120.400(mm)

Liquid flow in the center tube :  $V_{tt} = 7.1$  mm/s,

Raising liquid flow in settler bulk :  $V_1 = 0.005$  mm/s .

While using aerobic biological method, the system consists of aeroten and secondary clarified bulk that are applied to process beer waste effluent with feed flow of 2 L/h. Results of the test could provide a lot of essential data for design, manufacture and operation of large scaled equipment.

1. Study on effects of main technology parameters on yield of treating process

- Study on effect of organic substance content in the waste water feed,
- Effect of pH of the feed,
- Effect of soluble oxygen on treating yield,
- Effect of resident time on the yield while using aerobic biological method.

## **2. Establishment of suitable procedure for beer waste effluent**

Base on experiment and practical investigation data, the aeroten biological method is able to applied successfully for processing beer waste effluent. However, several mechanical, chemical processes should be combined with the method. A complex procedure consists of chemico-mechanical process and biological method permit minimum decrease of pollutants at allowable concentration as of standard of TCVN 5945-1995.

The procedure includes several stages as below:

- Collect and store of the waste effluent

The waste water from all sources of the beer factory is collected and stored in a waste container after removal of all kinds of rubbish.

- Feed into a regulator tank and plunge of air

The effluent from stored container is separated sand sediment and oil, after that fed into a regulator tank. The tank is plunged air for increasing stirring rate and to avoid sediment of suspended substances.

- Transfer to a primary sediment- filtered tank

Amount of gelatinous and ingelatin agents are controlled automatically for increasing rate of clarification and filtration.

- Feed into a aeroten tank

In the tank, the wastewater is distributed uniform through a inert material coated microorganism. pollution organic substances in the feed solution is degraded by microorganism in the presence of air and organic mud.

- Transfer to a secondary sediment- filtered tank

The effluent from the aeroten tank is flowed into a secondary sediment- filtered tank and sterilized then discharged into common sewerage.

**3. To scale the lab equipment system up to capacity of 400 m<sup>3</sup>/day of beer waste effluent**

- 1) Collect storage container:  $V_{lv} = 1.25 \text{ m}^3$  a each unit,
- 2) Sand sediment – Oil separate tank:  $V_{lv} = 2.5 \text{ m}^3 \cdot 2$  unit,
- 3) Regulator tank:  $V_{lv} = 150 \text{ m}^3$  a unit, two air plunge machine installed under water :  $Q = 60 \text{ m}^3/\text{h}$ ,  $H = 5 \text{ m H}_2\text{O}$ , type of JA-40,
- 4) Primary sediment – filter tank:  $V_{lv} = 32 \text{ m}^3 \cdot 2$  unit,
- 5) Advance capacity aeroten tank:  $V_{lv} = 160 \text{ m}^3 \cdot 2$  unit, three air plunge machine installed over surface of the water:  $Q = 5.55 \text{ m}^3/\text{min}$ ,  $H = 5 \text{ m H}_2\text{O}$ , type of LT-080
- 6) Secondary sediment – filter tank:  $V_{lv} = 25 \text{ m}^3 \cdot 2$  unit,
- 7) Mud degraded tank:  $V_{lv} = 20 \text{ m}^3$  a unit
- 8) Sterilized tank:  $V_{lv} = 8 \text{ m}^3$  a unit,
- 9) Two pump installed under water: :  $Q = 17 - 20 \text{ m}^3/\text{h}$ ,  $H = 10 \text{ m H}_2\text{O}$ ,
- 10) A mud pump installed over surface of the water:  $Q = 6- 12 \text{ m}^3/\text{h}$ ,  $H = 15 -20 \text{ m H}_2\text{O}$ , type of RA-100,
- 11) Adjust system of pH using calibrated fix pump:  $Q = 0 - 18.5 \text{ L/h}$ ,  $P = 4\text{bar}$ , type of ALPB 0419
- 12) Two calibrated fix pumps:  $Q = 0 - 18.5 \text{ L/h}$ ,  $P = 4\text{bar}$ , type of ALPB 0419.

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## **STUDY, DESIGN AND BUILD UP THE LAB-SCALE WASTE TREATMENT UNIT BY MOLTEN SALT OXIDATION (MSO)**

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**Abstract:** Molten salt oxidation (MSO) is a robust thermal process has the inherent capability of completely destroying organic constituents of mixed waste, hazardous waste and explosive. MSO is an ideal way to treat a variety of difficult waste stream while producing low level of fugitive emission in the off-gas. With its nature, in MSO process organic materials are converted into carbon dioxide, nitrogen and water vapor; radio nuclides, metals and inorganic materials in the waste stream are captured in the melt salt.

*In awareness of above advantages, study on the application of MSO technology for waste treatment is great meaning while the requirement to solve waste, especially hazardous and persistent organic, is essential more and more in Vietnam.*

*Initially, building up MSO lab-scale unit is fundament and premise for the program studying on the waste treatment technology further. A lab-scale unit simulating for MSO process is designed with a reactor, an off-gas treatment subsystem and some assistant equipment to help safe and needed testing operation condition.*

### **Introduction**

#### ***Essential requirement for waste treatment***

With the economic development in Vietnam, a huge amount of waste having potential high pollution is increasingly generated through out the country. Statistical data show that annual increasing amount of wastes is about 30-40%, including 50.27-60.22% of organic; 12-25% of medical hazardous and 35-40% of industrial hazardous wastes in almost of cities.

In addition to municipant and industrial waste, waste from agriculture activities such as usage of pesticides also plays significant environmental pollution role. The quickly increasing pesticides as well as uncontrolled and prohibited for usage pesticides in great bulky stock are needing to solve.

One of such a kind of waste which requires to treat is mixed waste from Nuclear Research Installation and Medical Facilities. Treatment mixed waste is the demand for the radioactive waste management at present and in near future with usage of nuclear power and high-medium capacity research reactor in Vietnam.

#### ***Situation of waste treatment solution research***

Incineration has been an universally and favorable solution for waste treatment to alternative mean in ultimate disposal option for long time. Incineration has been considered as one of most effective mean of dealing with many wastes, to reduce their harmful potential. Incineration, however, shows many major shortcoming due to there is potential to generate uncontrolled and significant secondary waste sources in environment, especially, during treating halogenated organic wastes. Therefore incineration is facing to difficulty to permit because of strong public opposition.

The world tendency of waste management is finding out high effective and environmental friendly alternative solution to incineration that is universally but disable for detoxification of the environment.

### ***Goal and content of the project***

The program of study on MSO technology aims verify the advantages of MSO technology by testing run on a lab- scale unit and determine the feasible of this technology met by technical ability in Vietnam. Therefore this project need to show the scientific foundation of the high effective and safe technology for treatment of hazardous and difficult waste in Vietnam. Also, another study content of the project is the design to build up a lab-scale MSO unit that is essential basement for main study stages.

### **Study on MSO technology for waste treatment**

#### ***What is MSO***

Molten salt oxidation is the thermal flameless process which completely destroys organic constituents in waste compound, hazardous waste and explosive. MSO can treat a wide variety of solid, liquid and gaseous waste at low level temperature while producing insignificant amount of unstable production and particles in off-gas.

The non-flame process in MSO technology prevents many problems occurring in incinerators. Radio nuclides, metals and inorganic materials in the waste stream are captured and held in the salt bath. chlorine, fluorine, bromine phosphorous sulfur and other acidic productions are captured in the salt as chlorides, fluorides, bromides and sulfates, respectively.

The test results and reports show that MSO process does not produce dioxin/furan for treating POPs because of approximately absolutely dichloride efficiency (>99,999%).

#### ***MSO processing and its advantages***

In MSO process both feeding either hazardous or organic waste and oxidizing gas are introduced into the melt from the bottom of molten salt tank in the a reactor. The alkaline salt is heated initially up to molten point about 700-950°C. There are two following simultaneously processing in melt medium when waste and oxygen/air are fed into reactor:

- The organic materials are destroyed by pyrolysis in heat medium. By thermal-dynamic mechanism of salt, alkaline oxide and dioxide are formed. Halogen and other composition such as sulfur converted into acid gases are neutralized by alkaline oxide and then are captured in the melt.

- At the same time, the flameless oxidation processing fed waste occurs in the reactor. Fed waste and oxygen/air force to through the full depth of the melt, maximizing contact between waste and molten salt thereby the degree and overall rate of oxidation of the waste.

#### ***MSO process has several advantages over incineration:***

1. The destruction efficiency is high up to 99,999%. The chemical environment in the melt favors the formation of super oxide ions ( $O_2^-$ ) which catalyze oxidation of

the waste. The melt as liquid medium in MSO process create intimate contact between the reactants therefore enhances completion of the chemical reaction.

2. There is just trace of acidic gas in off-gas due to these productions is neutralized immediately by alkaline oxide. Large particles are also held in the salt bath. This minimizes emission and hence reduces of off-gas treatment equipment.

3. Additionally, the treatment process without supplemental fuel and with the relatively simple structures makes MSO technology become the economic solution because of saving energy and less maintenance cost.

4. MSO process does not produce dioxin and furan since chlorine in waste stream is completely destroyed. .

5. The medium in MSO process provides stable heat transfer medium that resists thermal surges, and ensures temperature uniformity and is therefore able to tolerate rapid process fluctuation. Flame-outs is completely avoided. since MSO is a non-flame process that proceeds by catalytic liquid-phase oxidation reaction.

6. Operation of MSO is lower temperature than that in flame-combustion unit, minimizing emission of  $\text{NO}_x$  and nuclides in off-gas.

With several advantages MSO process is promising alternative solution to incineration for treatment of hazardous and difficult waste stream, global and stressing waste at present.

### **The Design of MSO Lab-Scale Unit**

#### ***Fundament for design calculation***

- Basing on bubble mechanism in the process to choose shape of reactor and ration between diameter and length of this structure.

- Basing on the general reaction in the process to calculate amount of salt and volume of feeding waste.

- Choosing of kind of salt and waste for design bases on experimental requirements. Chosen salt is sodium carbonate since this is very stable alkaline salt and then with carbonate radical expected productions are  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . as feeding waste is organic. Regarding to efficiency of MSO technology in difficult treatment condition chosen waste is DDT pesticide, a persistent organic waste.

#### ***Description of the MSO lab-scale unit***

The lab-scale unit consists of two subsystems, which includes a process vessel and an off-gas system. The vessel is combined from two chambers for two treatment stage. The volume of the vessel meets capacity of 0,3 -0,5 kg/h of feeding waste in primary treatment stage and resident time of about 2s in secondary treatment stage. The reactor's material is an alloy of nickel and chromium - SUS317 which can resistances corrosion by salt in heat medium. Materials for the surrounding of the reactor is firebrick and ceramic filaments. A heater unit by electrical-radiation assemblies can supply heat to the reactor up to 1000°C. An automatic temperature control equipment is used to set operation temperature and adjust it.

Feeding waste unit is flexible system for many kinds of wastes, including a hopper, air ejector chamber and screw feeder. The injector conducting waste is insulated by cold air to keep low waste temperature until they contact with the melt salt.

A blower is design to supply oxygen/air not only for easily feeding and processing waste but also for cooling waste in the injector.

The off-gas treatment system consists a heat-exchange equipment, absolute filter. and exhauster system including a fan and pipes.

#### ***Feature of the MSO lab-scale unit***

- The secondary chamber giving in the vessel is secondary oxidation stage to completely oxidize highly oxygen-demanding waste by the MSO.

- With insulated injector of waste, this prevents unexpected reactions before waste contact with molten salt.

- The air blower system has three functions: supplying oxygen/air to processing waste; supplying compressed air for easily feeding waste that their particle size is very small; cooling feeding waste.

#### **Conclusion**

Basing on theoretical factual foundation of molten salt oxidation process, considering as the best demonstration available technology for waste treatment, a lab-scale for testing some chosen problematic waste is considered carefully and designed. With some major and essential equipment, the MSO lab-scale unit is expected to meet meaningful requirement of the study on the application of this technology for waste treatment in Vietnam..

#### **Aknowledgement**

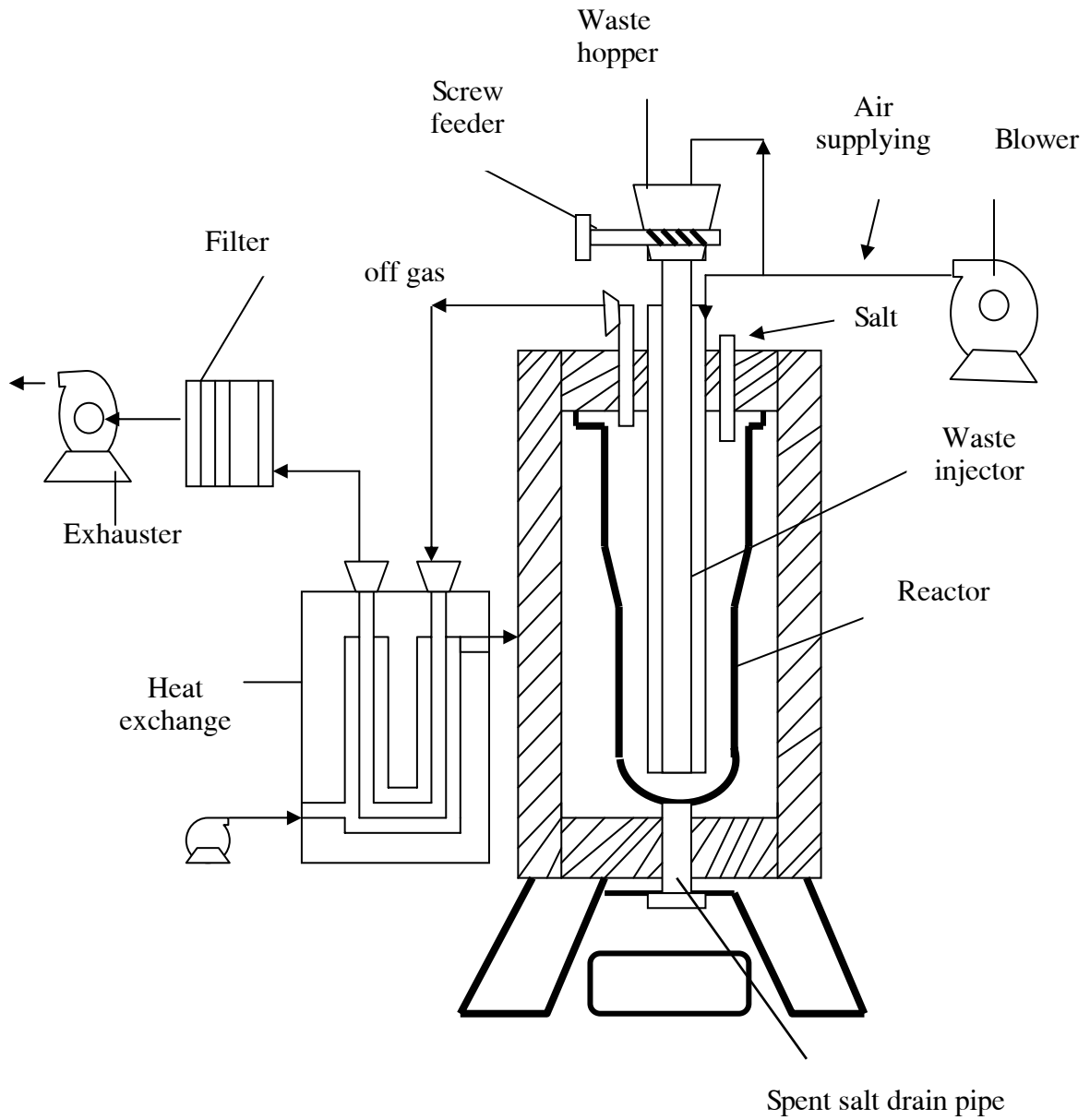
The authors wish to thank to following people who contribute in this work: Administration and Planning Departments of VAEC/INST, Radiation Protection and Environment Center, Eng. Thai Van An, Eng. Nguyen Dinh Tho, Eng. Do Hong Quan and, especially, Dr. Hee-Chul Yang, Dr. Yong-Jun Cho, the researcher group studying on MSO technology at KAERI.

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DIAGRAM OF LAB-SCALE MSO UNIT



# **INTERNAL RADIATION DOSIMETRY FOR SOME OF GAMMA EMITTING NUCLIDES BY A CHAIR-TYPE WHOLE-BODY COUNTER USING A SCINTILLATION DETECTOR**

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**Abstract:** *The research on method and establishment of a procedure on whole-body dosimetry for some of gamma-emitting radionuclides (such as I-131, Mo-99, Cr-51, Fe-59, Hg-203, Sb-124, Zn-65, Ag-110m, Cs-134 và Co-60) by in-vivo measuring technique using a chair-type whole-body counter with a scintillation detector and the code of LUDEP 2.0 was carried out.. The research result was applied to determine internal dose of I-131 for whole-body for radiation workers working at the Nuclear Research Institute. This has had important significance in routine control of internal dose for radiation workers contacting with unsealed radioactive sources emitting gamma-rays.*

## **Introduction**

The use of unsealed radioactive sources emitting gamma-rays has been developed in society, in particular at the Nuclear Research Institute and in nuclear medicine departments of hospitals. Therefore, research and establishment of a procedure on internal dosimetry have been very necessary in order to guarantee radiation safety for radiation workers contacting with unsealed radioactive sources emitting gamma-rays.

The researches carrying out here are study on method and establishment of a procedure on whole-body radiation dosimetry for some of gamma-emitting radionuclides (such as I-131, Mo-99, Cr-51, Fe-59, Hg-203, Sb-124, Zn-65, Ag-110m, Cs-134 và Co-60) by a chair-type whole-body counter with a scintillation detector and applying the code of LUDEP 2.0. The studied result has been applied to determine whole-body doses for radiation workers contacting with the unsealed radioactive source of I-131 at the Nuclear Research Institute.

## **Experimental**

### ***1. Studying some of features for the multi-channel scintillation gamma spectrometer***

Counting efficiency and FWHM according to energies were determined for the multi-channel scintillation gamma spectrometer of GR 111M (India) using NaI(Tl) with crystal size of 2 $\times$ 2 inches and the code of gamma-spectrum measuring and processing of PHAST Version 3.4 (with using some of the point-type standard sources emitting gamma-rays such as Ba-133, Cs-137, Mn-54, Na-22 and Co-60).

### ***2. Determination of radioactive activity for some of gamma-emitting radionuclides***

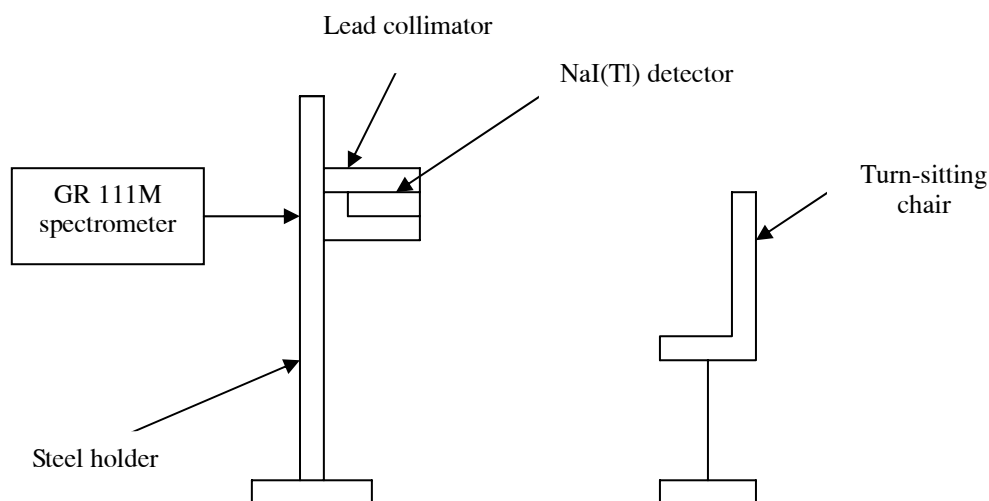
Solid standard material of Mo, Cr, Fe, Hg, Sb, Zn, Ag, Cs and Co were prepared and irradiated by neutrons for 20 hrs at the rotary specimen rack of Dalat nuclear reactor

operating at the power of 500 kW. After that, they were measured by the gamma spectrometer in order to determine radioactive activities based on the known counting efficiencies above (The solution of I-131 was also prepared and measured as the irradiated samples above).

### 3. Determination of total counting efficiency and detection limit for the chair-type whole-body counter

#### \* Chair-type whole-body counter

The chair-type whole-body counter was established. It consists of the scintillation gamma spectrometer of GR 111M, the steel holder with lead collimator adjustable around, the whole-body standard phantom by plastic material and the turn-sitting chair for the phantom/ subject. Experimental diagram of this counter was shown in figure 1.



**Fig. 1.** Experimental diagram of the chair-type whole-body counter.

#### \* Determination of total counting efficiency and detection limit using the whole-body standard phantom

The every sample with known activity was mixed regularly with water into radioactive solution. After that, it was filled in blocks of the phantom (in which 1/3 of I-131 activity was in thyroid block and the remainder was in the remain blocks of the phantom; the samples of Mo-99, Cr-51, Fe-59, Hg-203, Sb-124, Zn-65, Ag-110m, Cs-134 vař Co-60 were regularly filled into whole blocks of the phatom. The phantom was set on the turn-sitting chair and gamma spectrum was measured by the counter at different geometry-positions of phantom-detector in order to determine counts at energy peaks of interest. Based on the known radioactive activities and the measured counting rates, total counting efficiencies for radionuclides above at the energy peaks of interest and at different geometry-positions of phantom-detector were determined. Determination of total counting efficiencies was carried out at different geometry-positions of H and L (H = 40, 60, 80, 100 and 110 cm; L = 15, 20, 40, 60 and 70 cm; in which H was height from central axis of horizontal detector to the bottom plate of the steel holder and L was horizontal distance from front side of the thyroid block to horizontal detector). Based on the total counting efficiencies, corresponding detection

limits at the energy peaks of interest for every radionuclides above were determined. Table 1 showed features of radionuclides, geometries for measuring phantom/ subject, total counting efficiencies (having largest values at H = 100 cm and L = 15 cm) and corresponding detection limits.

**Tab 1.** Features of radionuclides, geometries for measuring phantom/ subject, total counting efficiencies (as Eff) and corresponding detection limits (as LD) measured with time of 1 hr.

No.	Nuclide	<i>E</i> (in keV)	$\eta$ (in %)	<i>H</i> (In cm)	<i>L</i> (in cm)	<i>Eff</i> (in %)	<i>LD</i> (in Bq)
1	I -131	364.5	81.20	100	15	0.0317	4,173
2	Mo-99	739.6	12.13	100	15	0.0161	5,081
3	Cr-51	320.1	10.08	100	15	0.0274	17,665
4	Fe-59	1,099.2	56.50	100	15	0.0078	858
5	Hg-203	279.2	81.46	100	15	0.0120	1,256
6	Sb-124	602.7	97.80	100	15	0.0068	982
7	Zn-65	1,115.5	50.70	100	15	0.0084	2,447
8	Ag-110m	657.8	94.64	100	15	0.0176	4,939
9	Cs-134	795.8	85.44	100	15	0.0111	235
10	Co-60	1,173.2	99.90	100	15	0.0254	631

#### **4. Measuring and evaluating whole-body dose using the code of LUDEP 2.0.**

Measurement and evaluation of whole-body dose for some of gamma-emitting radionuclides of interest above by the chair-type whole-body counter with using the code of LUDEP 2.0 were carried out through two steps as follows:

##### *\* Measuring radioactive activity for whole-body*

A contaminated subject was sited at a fixed geometry-position (with known total counting efficiency) by the chair-type whole-body counter; measuring gamma spectrum for a subject; determination of counts at energy peaks of interest in the measured gamma spectrum; calculation of total radioactive activity for whole-body from the measured counts and the total counting efficiency known in the table 1.

##### *\* Calculation and evaluation of whole-body dose*

Running the code of LUDEP 2.0; entering file of experimental data on the measured radioactive activities into the code; choosing input parameters: exposure regime, radionuclide, physiological parameters of the subject (such as height, mass, etc.); bio-kinetic model of radionuclide of interest; calculating whole-body dose for intake of 1 Bq (as dose coefficient for whole-body. The result of calculating dose coefficients for whole-body for Vietnamese adult was shown in table 2); calculating total activity of radionuclides of interest in the subject (as intake in Bq) such as choosing retention regime of radionuclide of interest, entering the file of experimental data on the measured radioactive activities into the code; calculating whole-body dose by multiplying the total radioactive activity by dose coefficient for whole-body.



**Tab 2.** The result of calculating dose coefficients for whole-body (as DC in Sv) for some of radionuclides of interest by the code of LUDEP 2.0.

No.	Nuclide	DC (in Sv)	No.	Nuclide	DC (in Sv)
1	I-131	$2.209 \times 10^{-8}$	6	Sb-124	$1.885 \times 10^{-9}$
2	Mo-99	$4.353 \times 10^{-10}$	7	Zn-65	$4.092 \times 10^{-9}$
3	Cr-51	$3.946 \times 10^{-11}$	8	Ag-110m	$7.369 \times 10^{-9}$
4	Fe-59	$6.000 \times 10^{-9}$	9	Cs-134	$1.335 \times 10^{-8}$
5	Hg-203	$1.236 \times 10^{-9}$	10	Co-60	$9.438 \times 10^{-9}$

**5. Establishment of a procedure on whole-body dosimetry for some of gamma-emitting radionuclides by the chair-type whole-body counter**

Based on the study above, the procedure on whole-body dosimetry for some of gamma-emitting radionuclides by the chair-type whole-body counter was established. It consists of: Brief outline; equipment and tools; procedure (preparation of measuring system and subject, steps carried out, evaluation of efficiency, quality control, caution for carrying out the procedure); scope of application and main references.

**6. Application of whole-body dosimetry for I-131 for radiation worker**

**Tab 3.** The measuring result on total radioactive activity (intake) for “Cu” subject and corresponding whole-body doses in the production times of I-131.

No.	Production time	Measuring date	Measuring time	Intake $\pm$ Standard error (in Bq)	Whole-body dose for I-131 (in $\mu$ Sv)
1	24/4/2005	26/4/2005	1	$(2.77 \pm 0.80) \times 10^4$	$537 \pm 155$
		4/5/2005	2		
2	22/5/2005	30/5/2005	1	$(7.52 \pm 1.25) \times 10^2$	$15 \pm 2$
		19/6/2005	2		
3	14/8/2005	17/8/2005	1	$(7.28 \pm 2.70) \times 10^3$	$141 \pm 52$
		20/8/2005	2		

The researched result above was applied to determine whole-body dose for the radiation worker working directly on the production line of I-131 at the Nuclear Research Institute. Dosimetry was carried out for three times of I-131 production and the result on whole-body doses were shown in table 3. Comparing them with the result on whole-body dosimetry by in-vitro technique (urine analysis) was shown that they were corresponding in error range.

**Conclusion**

The researches on method and establishment of procedure of whole-body dosimetry for some of gamma-emitting radionuclides (such as I-131, Mo-99, Cr-51, Fe-59, Hg-203, Sb-124, Zn-65, Ag-110m, Cs-134 vaú Co-60) by the chair-type whole-body counter with a scintillation detector and applying the code of LUDEP 2.0 were carried out. From that, internal dosimetry for whole-body for the radiation worker contacting

with unsealed radioactive source of I-131 was carried out at the Nuclear Research Institute. Therefore, it is possible to application of whole-body dosimetry in routine for radiation workers contacting with unsealed radioactive sources emitting gamma-rays.

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## 1.6 - Ecology and Environment

# INVESTIGATION INTO DETERMINATION OF URANIUM AND THORIUM ISOTOPES IN SOIL SAMPLES BY PRECIPITATION METHOD

Ngo Quang Huy, Nguyen Van Suc, Trinh Thi Bich, Tran Van Luyen,  
Nguyen Van Mai, Thai My Phe and Dao Van Hoang

*Center for Nuclear Techniques, VAEC*

**Abstract:** *The paper presents the procedure to prepare the soil samples for measurement in the alpha spectrometer according to the method of coprecipitation with LaF<sub>3</sub>. In this procedure the deduce of oxidation states of uranium from U(VI) to U(IV) was performed by the Zn metal of analytical grade in HCl 4M solution. The recoveries of chemical separation equal to  $\varepsilon_{U\text{-chemistry}} = (78 \pm 4) \%$  for uranium and  $\varepsilon_{Th\text{-chemistry}} = (82 \pm 4) \%$  for thorium. The alpha spectrometer has 4 measurement chambers with PIPS detectors of A-1200-37-AM Model, which has 1200 mm<sup>2</sup> active area. The geometrical efficiency of the measuring system equals to  $\varepsilon_{\text{geometry}} = 18 \%$  and the total efficiencies were  $\varepsilon_U = \varepsilon_{\text{geometry}} \times \varepsilon_{U\text{-chemistry}} = (14,0 \pm 0,7)\%$  for uranium and  $\varepsilon_{Th} = \varepsilon_{\text{geometry}} \times \varepsilon_{Th\text{-chemistry}} = (14,7 \pm 0,7)\%$ .*

*The recoveries of chemical separation were rather high (about 80%), that leads to the use of a small weight of soil sample (about 0.5 g). The efficiencies were also stable, that allows analyzing the soil sample without using radiotracers. They are advantages of the sample preparation procedure of this work.*

## I. Introduction

The sample preparation procedure plays an important role in the analysis of radioactive nuclides by alpha spectrometer. At the present time there are four main methods of sample preparation, which are vacuum sublimation, direct evaporation, electrodeposition and micro-coprecipitation. Most publications of radioactive nuclide analysis by alpha spectrometry applied the electrodeposition technique [1-4]. This method was commonly employed because it can form a thin layer of sample onto polished metallic surfaces that decreases the self-absorption effect. However the method of electrodeposition requires special reagents and relatively elaborate equipment. To overcome this difficulty some authors suggested to separate U, Th, Pu and Am elements in environmental samples by the method of coprecipitation with lanthanum fluoride, LaF<sub>3</sub> or neodymium fluoride, NdF<sub>3</sub>, and filter the microprecipitates on the nucleon membrane filters for measurement of alpha particles by alpha spectrometers [5-7]. This technique is more convenient than the electrodeposition method because of the simplicity of chemical separation process, time economy and simultaneous separation of some nuclides in the same conditions. However the coprecipitation with LaF<sub>3</sub> or NdF<sub>3</sub> should be improved because the recovery of chemical separation significantly depends on oxidation states of considered elements and on the amount of La or Nd and HF. This paper presents the investigation into the soil sample preparation for alpha analysis according to the coprecipitation with LaF<sub>3</sub> for determining the activities of <sup>238</sup>U, <sup>234</sup>U, <sup>232</sup>Th, <sup>230</sup>Th, <sup>228</sup>Th radionuclides in soil samples.

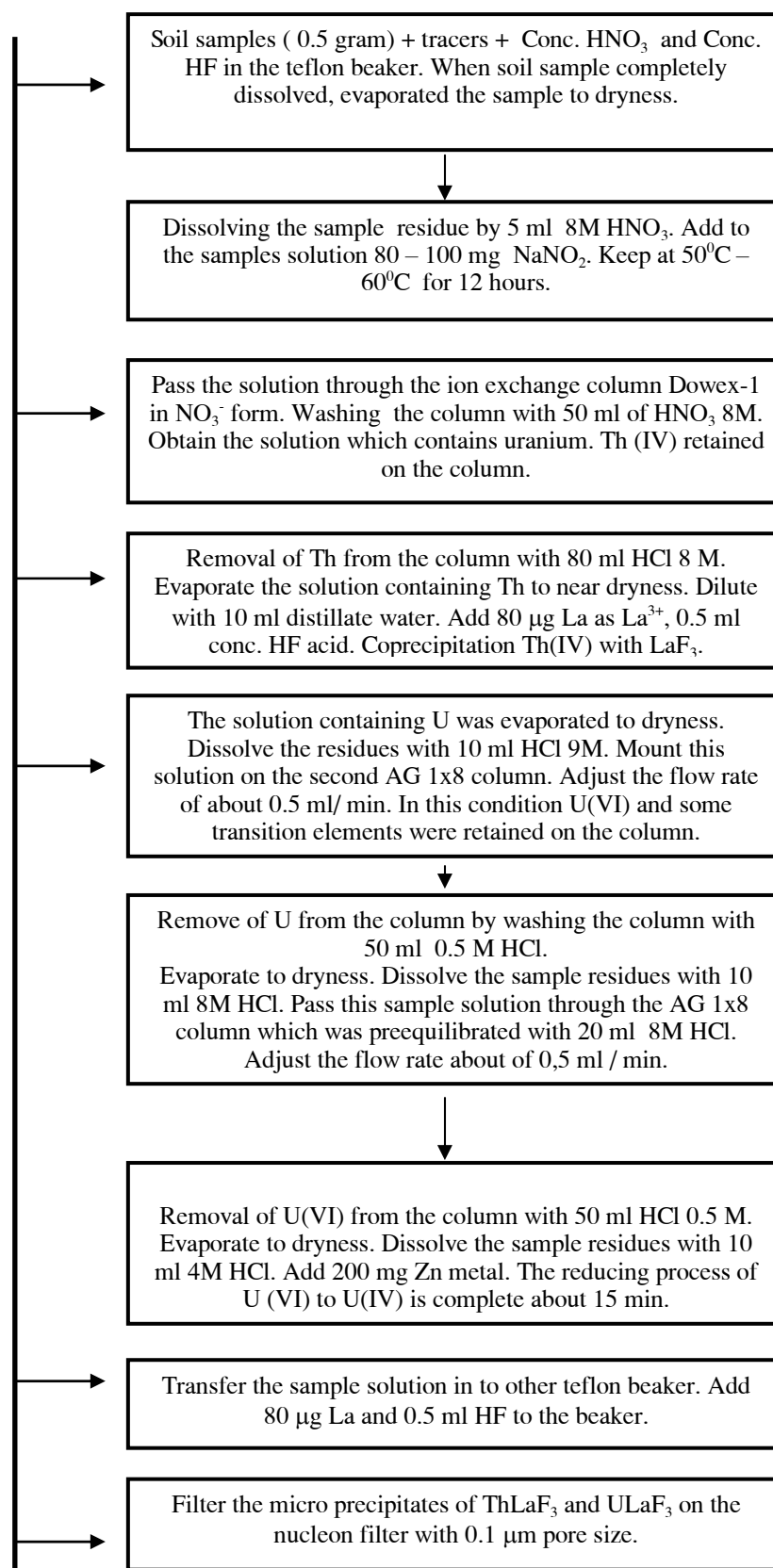
## II. Coprecipitation of U(IV) and Th(IV) with LaF<sub>3</sub>

A disadvantage of the electrodeposition method in published papers is the instability of the recovery of chemical separation and as its consequence the use of radiotracers in the process of sample preparation is necessary. The chemical separation yield of uranium in this method is very low and depends on many factors as separation process, removal of interfering elements, etc... In the coprecipitation method, chemical yield could be improved if completely reducing U(VI) to U(IV) by the suitable reagents and the reduced medium. In the most case, TiCl<sub>4</sub> is one of the reagents used for reducing U(VI). However, this reagent is not convenient for preserving and harmful to the health. In this work, the Zn metal was used as reduced reagent and results of our study show that the reducing of U(VI) to U(IV) by Zn in a large amount of Fe<sup>3+</sup> is very quantitative and that is not effected to coprecipitation of U(IV) with LaF<sub>3</sub> [8]. The procedure of analysis of <sup>238</sup>U, <sup>234</sup>U, <sup>232</sup>Th, <sup>230</sup>Th, <sup>228</sup>Th radionuclides with the sample preparation by coprecipitation with LaF<sub>3</sub> is showed in Fig.1. The recoveries of chemical separation were measured by addition of <sup>232</sup>U and <sup>229</sup>Th tracers into soil samples for uranium and thorium analysis. The results obtained were  $\varepsilon_{\text{U-chemistry}} = 78.4 \%$  for uranium and  $\varepsilon_{\text{Th-chemistry}} = 82.4 \%$  for thorium.

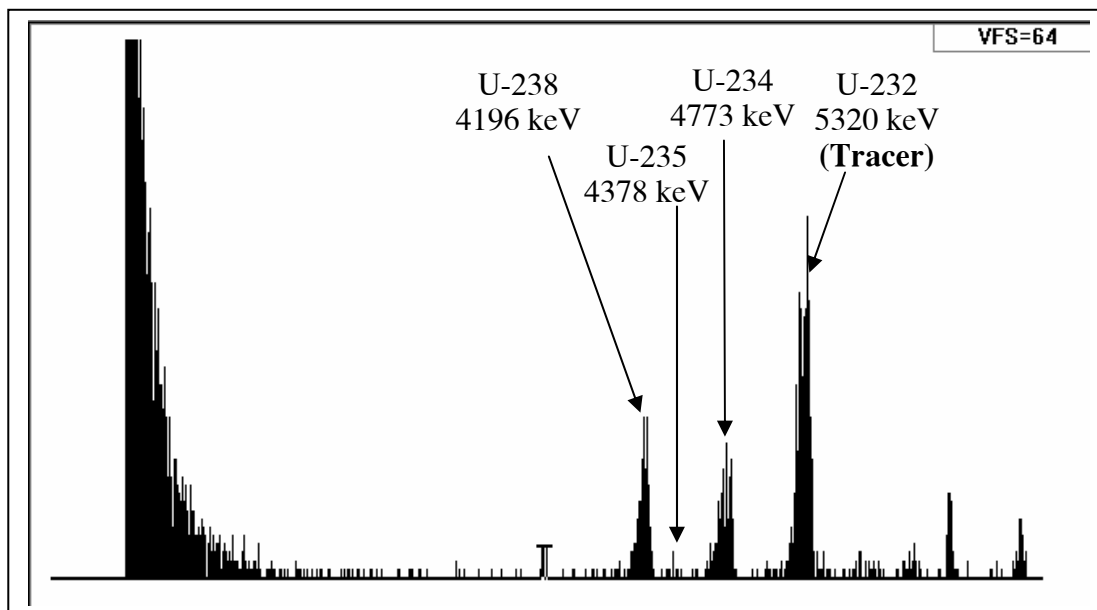
Our procedure gave high and stable recoveries of chemical separation (from 79 to 82% for all analytical samples). In the paper of Joshi [6] the recovery of chemical separation reached from 92% to 97% for uranium in a pure <sup>232</sup>U tracer solution, but it fluctuated in a range (20 – 85) % with the mean value of 32%. The high recoveries of chemical separation in our work lead to the use of a small weight of soil sample (about 0.5 g) and their stability allows analysing the soil sample without using radiotracers. They are advantages of the sample preparation procedure of this work.

## III. Alpha spectrometer and the efficiency of measurement system

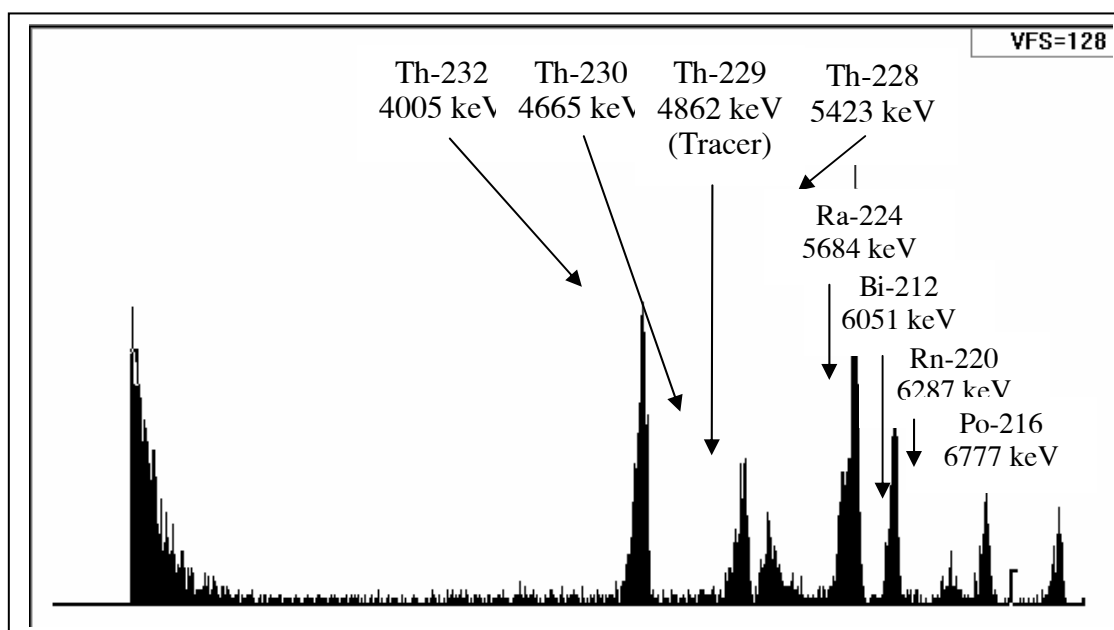
The alpha spectrometer “Alpha Analyst” of Canberra Industries Inc., USA, has four measurement chambers with PIPS detectors of A-1200-37-AM Model, which has 1200 mm<sup>2</sup> active area, FWHM = 37 keV energy resolution and 16 counts/day background. The alpha spectra of uranium and thorium obtained according to the above-said procedure of sample preparation are illustrated in Fig. 2 and Fig. 3. For uranium (Fig. 2) there are two main peaks of <sup>238</sup>U (4194 keV), <sup>234</sup>U (4773 keV) and the peak of <sup>232</sup>U (5320 keV) tracer, whilst the peak <sup>235</sup>U (4378 keV) can be ignored because of its insignificant intensity. For thorium (Fig. 3) there are three main peaks of <sup>232</sup>Th (4005 keV), <sup>230</sup>Th (4665 keV), <sup>228</sup>Th (5423 keV) and the peak of <sup>229</sup>Th (4862 keV) tracer. In the spectrum of thorium four additional peaks of <sup>224</sup>Ra (5684 keV), <sup>212</sup>Bi (6051 keV), <sup>220</sup>Rn (6287 keV) and <sup>216</sup>Po (6777 keV) are also obtained. The geometrical efficiency was determined by two reference alpha sources of 7400-SRC-59940 and 7400-SRC-0375. With the distance of 15 mm between the sample and the detector it equals to  $\varepsilon_{\text{geometry}} = 18 \%$  and does not depend on energy of alpha particle in the range (4 – 6) MeV. The total efficiencies of sample preparation and measurement were  $\varepsilon_{\text{U}} = \varepsilon_{\text{geometry}} \times \varepsilon_{\text{U-chemistry}} = (14,0 \pm 0,7)\%$  for uranium and  $\varepsilon_{\text{Th}} = \varepsilon_{\text{geometry}} \times \varepsilon_{\text{Th-chemistry}} = (14,7 \pm 0,7)\%$ .



**Fig. 1.** Flow schema of soil sample preparation for alpha spectroscopic analysis.



**Fig. 2.** Uranium spectrum of the soil sample No. 19 with  $^{232}\text{U}$  tracer of 17.7 mBq activity. Three main peaks are  $^{238}\text{U}$  (4196 keV),  $^{234}\text{U}$  (4773 keV) and  $^{232}\text{U}$  (5320 keV).



**Fig. 3.** Thorium spectrum of the soil sample No. 37 with  $^{229}\text{Th}$  tracer of 17.7 mBq activity. Four main peaks are  $^{232}\text{Th}$  (4005 keV),  $^{230}\text{Th}$  (4665 keV),  $^{228}\text{Th}$  (5423 keV) and  $^{229}\text{Th}$  (4862 keV).

#### IV. Validation of the analytical method

The validation of the analytical method was checked by measurement of activities of  $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{228}\text{Th}$  radionuclides in the IAEA-135 reference sample (Table 1), two rock samples and five soil samples (Table 2). The measurement was carried out with using the above-said total efficiencies and without adding

radiotracers. The analytical result was compared to those obtained by gamma spectrometry, instrumental neutron activation and ICP-MS methods.

**Tab 1.** Comparison of activities of  $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{228}\text{Th}$  radionuclides of IAEA-135 reference sample measured in this work with reference values.

Nuclide	Activity of this work (Bq/kg)	Reference activity (Bq/kg)	Range of reference activity (Bq/kg)	Recommendation / Information
$^{238}\text{U}$	$32,6 \pm 1,8$	30	27 – 36,5	I
$^{234}\text{U}$	$28,5 \pm 1,6$	28,3	20,9 - 32	I
$^{232}\text{Th}$	$42,5 \pm 2,2$	36,9	35 - 38	R
$^{230}\text{Th}$	$60,8 \pm 3,1$	69,1	61 – 73,4	I
$^{228}\text{Th}$	$41,3 \pm 2,2$	38,2	25,7 - 72	I

Table 2. Comparison of activities of  $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{228}\text{Th}$  radionuclides of two rock samples and five soil samples measured in this work by alpha spectrometry (AS) with those obtained by gamma spectrometry (GS), instrumental neutron activation (INAA) and ICP-MS methods.

#### URANIUM

Sample	Activity $^{238}\text{U}$ (Bq/kg)				$^{234}\text{U}$ (Bq/kg)
	AS	GS	INAA	ICP-MS	AS
Rock R <sub>3</sub>	$95.6 \pm 5.0$			98.8 (8 ppm)	$99.4 \pm 5.0$
Rock R <sub>4</sub>	$119.8 \pm 6.0$			123.5 (10 ppm)	$113.4 \pm 6.0$
Gray soil No. 16	$134.3 \pm 6.8$	$126.8 \pm 9.0$	$152.0 \pm 10.0$ (12.31 ± 0.80 ppm)	$138.6 \pm 1.2$ (11.22 ± 0.10 ppm)	$163.5 \pm 8.0$
Red soil No. 19	$21.7 \pm 2.1$	$19.6 \pm 2.0$	$21.5 \pm 2.0$ (1.74 ± 0.17 ppm)	$27.5 \pm 0.3$ (2.23 ± 0.02 ppm)	$21.7 \pm 2.1$
Alluvial soil No. 35	$225.2 \pm 15.0$	$219.8 \pm 7.5$		$232.2 \pm 6.5$ (18.80 ± 0.53 ppm)	$265.3 \pm 15.0$
Alluvial soil No. 37	$66.8 \pm 3.5$	$66.2 \pm 6.0$		$72.6 \pm 1.1$ (5.88 ± 0.09 ppm)	$77.9 \pm 4.0$
Alluvial soil No. 47	$41.6 \pm 2.0$	$47.3 \pm 4.5$	$45.6 \pm 4.5$ (3.69 ± 0.40 ppm)	$40.1 \pm 0.4$ (3.25 ± 0.03 ppm)	$40.5 \pm 2.0$



## THORIUM

Sample	Activity $^{232}\text{Th}$ (Bq/kg)				$^{230}\text{Th}$ (Bq/kg)	$^{228}\text{Th}$ (Bq/kg)
	AS	GS	INAA	ICP-MS	AS	AS
Rock R <sub>3</sub>	253.1 ± 12.5			242 (60.2ppm)	107.1 ± 5.0	247.2 ± 12.5
Rock R <sub>4</sub>	159.2 ± 8.0			167 (41.7ppm)	113.8 ± 6.0	171.0 ± 8.5
Gray soil No. 16	45.4 ± 2.5	51.7 ± 4.5	43.1 ± 4.3 (10.51 ± 1.05 ppm)	39.0 ± 1.4 (9.5 ± 0.3 ppm)	34.5 ± 2.0	37.6 ± 2.0
Red soil No. 19	23.5 ± 2.4	34.9 ± 3.5	32.5 ± 3.2 (7.91 ± 0.79 ppm)	24.2 ± 1.2 (5.9 ± 0.3 ppm)	15.1 ± 1.5	22.4 ± 2.2
Alluvial soil No. 35	66.4 ± 3.5	74.6 ± 6.5		62.8 ± 1.6 (15.3 ± 0.4 ppm)	59.6 ± 3.5	71.1 ± 4.0
Alluvial soil No. 37	73.6 ± 3.5	82.8 ± 5.5		76.4 ± 4.3 (18.6 ± 0.9 ppm)	50.0 ± 3.0	79.2 ± 4.0
Alluvial soil No. 47	85,7 ± 4,5	87,2 ± 6,5	73,7 ± 5,5 (17,97 ± 1,34 ppm)	92.5 ± 1.5 (22.5 ± 0.4 ppm)	57.9 ± 3.0	70.0 ± 3.5

From the Table 2 it is seen that the experimental values lie in the range of reference values of IAEA-135 sample for  $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{230}\text{Th}$  and  $^{228}\text{Th}$  radionuclides. Table 3 reveals that the results of four analytical methods are in good agreement with relative uncertainties of (5 – 10) %.

### V. Conclusion

1. In this work a procedure of soil sample preparation for alpha measurement according to the method of coprecipitation with  $\text{LaF}_3$  was established. The reducing of uranium from U(VI) to U(IV) was used by the Zn metal in HCl 4M solution.

2. The recoveries of chemical separation were rather high (about 80%), that leads to the use of a small weight of soil sample (about 0.5 g). The recoveries were also stable, that allows analyzing the soil sample without using radiotracers. They are advantages of the sample preparation procedure of this work.

3. The validation of the suggested analytical method was checked by measurement of an IAEA-135 reference sample, two rock samples and five soil samples. The measurement results of the alpha spectrometer were in good agreement with those of the gamma spectrometry, neutron activation analysis and ICP-MS methods.

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## STUDY OF THE CORRELATION BETWEEN EACH OF RADIONUCLIDES $^{238}\text{U}$ , $^{226}\text{Ra}$ , $^{232}\text{Th}$ , $^{230}\text{Th}$ , $^{137}\text{Cs}$ AND THE OTHERS FOR SOILS AND SEDIMENTS

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**Abstract:** *The spatial distribution of  $^{230}\text{Th}$  and other radionuclides, as well as their correlations was investigated based on 15 soil samples collected in an 250 m<sup>2</sup> Rhodic Ferralsols area and 10 soil sample in an area of 150 m<sup>2</sup> of Ferralic Acrisols. The results showed that: (i) The concentration of radionuclides varies with sampling points in a wide range; this variation is not attributed only to the uncertainty of analytical data but also to geochemistry processes of Actinides; (ii) There is existence of good linear correlation between  $^{226}\text{Ra}$  and  $^{232}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{232}\text{Th}$ ,  $^{228}\text{Ra}$  and  $^{228}\text{Th}$  for two study sites with correlation coefficients  $r^2$  varying from 0.7 to 0.99; (iii) The correlations between  $^{238}\text{U}/^{226}\text{Ra}$  and  $^{238}\text{U}/^{232}\text{Th}$ , between  $^{238}\text{U}/^{232}\text{Th}$  and  $^{226}\text{Ra}/^{232}\text{Th}$ , and between  $^{40}\text{K}/^{232}\text{Th}$  and  $^{40}\text{K}/^{226}\text{Ra}$  were found with  $r^2 = 0.7 - 0.92$ .*

*In order to study the depth distribution of radionuclides and their correlations in sediment, 5 sediment cores were collected at 5 reservoirs in Lamdong province. Results show that: (i) The concentration of radionuclides widely varies with depth for all study sites; the standard deviation is much greater than analytical errors; (ii) The mean value of radionuclide concentrations at 5 locations is much different from site to site, varying from 10-15 Bq/kg for Tay Di Linh to 95-100 Bq/kg for Pro; (iii) Radionuclides  $^{226}\text{Ra}$  and  $^{232}\text{Th}$ ,  $^{228}\text{Ra}$  and  $^{228}\text{Th}$  have good correlation with  $r^2 = 0.71 - 0.98$ ; Ratios  $^{238}\text{U}/^{226}\text{Ra}$  and  $^{238}\text{U}/^{232}\text{Th}$ ,  $^{40}\text{K}/^{232}\text{Th}$  and  $^{40}\text{K}/^{226}\text{Ra}$  also have rather good correlation with  $r^2 = 0.60 - 0.99$ ; (iv) There is existence of linear correlation between  $^{226}\text{Ra}$  and  $^{232}\text{Th}$  for all 5 investigated sites with the angular co-efficient of correlation lines varying from 0.69 to 1.65.*

*Results obtained from the distribution of radionuclides in different grain size components of soil and sediment samples showed that: (i) Radionuclides  $^{226}\text{Ra}$  and  $^{232}\text{Th}$ ,  $^{228}\text{Ra}$  and  $^{228}\text{Th}$  have good correlation with  $r^2 > 0.92$ ; (ii) Ratios  $^{238}\text{U}/^{226}\text{Ra}$  and  $^{238}\text{U}/^{232}\text{Th}$ ,  $^{40}\text{K}/^{232}\text{Th}$  and  $^{40}\text{K}/^{226}\text{Ra}$  also have good correlation for soil and sediment samples; (iii) There is existence of weak linear correlation between  $^{238}\text{U}$  and  $^{226}\text{Ra}$ ,  $^{238}\text{U}$  and  $^{232}\text{Th}$  for all 2 investigated sites with the correlation coefficients  $r^2$  varying from 0.59 to 0.68; this weak correlation is easy broken in natural soil and sediment environments.*

### Introduction

In the recent years, in the world as well as in Vietnam the requirement of understanding and amelioration of environmental problems is increasing. In order to understand present and future environmental phenomena, we have to rest on secure knowledge of their origin in the recent past. Consequently, environmental contexts which preserve a temporally well-resolved record of recent environmental changes have received increasing attention. Such contexts include lake and near-shore marine sediments and areas of peat accumulation. Therefore, sediment sources are important information for the sedimentology field, as well as environmental science.

Characteristics of sediments such as mineral, colour, magnetics or major elements were studied and successfully applied for identification of sediment sources in many countries over the world in the early years of the 80 decade of the century XX. However, there is not any tracer that can apply for any geological area.

The utilization of naturally – occurring radionuclides in environment for identification of sediment sources was initiated and investigated in the last years of the 80 decade of the century XX. The issue has been much interested scientists and many studies have been carried out after that. Remarkable achievements have been obtained from such studies. In recent years, research programmes have been set up in many countries for understanding the behaviour of radionuclides in environments and establishing the protocol for using environmental radionuclides in identifying sediment sources.

The objective of research project of the year 2004 is to study the correlation between each of radionuclides  $^{238}\text{U}$ ,  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$ ,  $^{230}\text{Th}$ ,  $^{137}\text{Cs}$  and the others for soils and sediments. Therefrom, the capability of using environmental radionuclides for identification of sediment sources for some regions in Vietnam is examined.

## Experiments

### 2.1 Study of spatial variation in radionuclides in the soil environment

#### a) Study sites

In order to study the spatial distribution, as well as correlation between radionuclides, 25 soil samples were collected at two locations with soil types of Ferralic Acrisols and Rhodic Ferrasols. For Rhodic Ferrasols 15 bulk soil cores with the depth of 30 cm were collected in the area of 250 m<sup>2</sup>. Similarly, 10 bulk soil cores were collected in the area of 150 m<sup>2</sup> for Ferralic Acrisols. All soil samples were processed at the Laboratory for gamma and alpha counting.

#### b) Results and discussion

##### *Concentration of radionuclides in soils*

Results showed that concentrations of radionuclides at 25 sampling points vary highly, exceeding the analytical errors. This means that the migration of radionuclides is significant at two study sites. The concentration of  $^{238}\text{U}$ ,  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{228}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{232}\text{Th}$  in Ferralic Acrisols is much higher than in Rhodic Ferrasols.

##### *The correlation of radionuclides at Rhodic Ferrasols area*

Statistical analysis of concentration of radionuclides at 15 sampling points showed that nuclide couples  $^{226}\text{Ra}$  and  $^{232}\text{Th}$ ,  $^{228}\text{Ra}$  and  $^{228}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{232}\text{Th}$  have good relationship. Besides, the correlation between ratio  $^{238}\text{U}/^{226}\text{Ra}$  and  $^{238}\text{U}/^{232}\text{Th}$ , between  $^{238}\text{U}/^{232}\text{Th}$  and  $^{226}\text{Ra}/^{232}\text{Th}$  with correlation coefficient  $r^2$  ranges between 0.71 and 0.89 was found. Therefore, concentrations of nuclides although vary from site to site, there are an existence of correlations between them.

##### *The correlation of radionuclides at Ferralic Acrisols area*

Statistical analysis of concentration of radionuclides at 15 sampling points showed that the correlation of  $^{238}\text{U}$  and  $^{232}\text{Th}$ ,  $^{226}\text{Ra}$  and  $^{232}\text{Th}$ ,  $^{228}\text{Ra}$  and  $^{228}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{232}\text{Th}$  is rather good with  $r^2$  varying from 0.85 to 0.99. Radionuclide ratios  $^{238}\text{U}/^{226}\text{Ra}$  and  $^{238}\text{U}/^{232}\text{Th}$ ,  $^{40}\text{K}/^{232}\text{Th}$  and  $^{40}\text{K}/^{226}\text{Ra}$  also have correlation with  $r^2 = 0.90 - 0.92$ .

### *Overall remark*

There is an existence of the correlation between  $^{226}\text{Ra}$  and  $^{232}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{232}\text{Th}$ ,  $^{228}\text{Ra}$  and  $^{228}\text{Th}$  for all two study sites. The correlation between  $^{228}\text{Ra}$  and  $^{228}\text{Th}$  with the angular coefficient of about unit indicates the secular equilibrium of these nuclides. The correlation of  $^{226}\text{Ra}$  and  $^{232}\text{Th}$ , of  $^{230}\text{Th}$  and  $^{232}\text{Th}$  means that the concentration of these couples varies with a given rate.

## **2.2 Investigation of the concentration level of radionuclides in sediments**

### *a) Study sites*

In order to study the concentration level of radionuclides in sediments, as well as the correlation between nuclides, sediment cores were collected at five reservoirs located in Lamdong province including Chien-thang, Tuyen-lam, Pro, Tay-di-linh and Dateh. Sediment cores with the diameter of 6.3 cm were taken and then sectioned at 2 cm intervals.

### *b) Results and discussion*

#### *Variation of nuclide concentrations with depth*

Analysis of radionuclides for 5 sediment cores showed that (i) the concentration of radionuclides much varies with depth for all investigated reservoirs; (ii) The standard deviation of radionuclide concentrations is much higher than analytical uncertainties; (iii) The average concentration of radionuclides in sediment is much different from reservoir to reservoir, ranging between 10 – 15 Bq/kg (Tay-di-linh) and 100 Bq/kg (Pro).

#### *The correlation of radionuclides in sediments*

Although the concentration of radionuclides varies very much with core depth, there is good correlation between  $^{226}\text{Ra}$  and  $^{232}\text{Th}$ , between  $^{228}\text{Ra}$  and  $^{228}\text{Th}$ . Besides the correlation between  $^{238}\text{U}/^{226}\text{Ra}$  and  $^{238}\text{U}/^{232}\text{Th}$ ,  $^{40}\text{K}/^{232}\text{Th}$  and  $^{40}\text{K}/^{226}\text{Ra}$  also found.

The correlation between  $^{228}\text{Ra}$  and  $^{228}\text{Th}$  with the angular coefficient of about unit ( $r^2 = 0.87 - 0.98$ ) indicates the secular equilibrium of these nuclides.  $^{226}\text{Ra}$  correlates with  $^{232}\text{Th}$  with  $r^2 = 0.71 - 0.95$  and the angular coefficient ranging between 0.69 and 1.65 for 5 study sites.

Ratio of  $^{238}\text{U}/^{226}\text{Ra}$  correlates with  $^{238}\text{U}/^{232}\text{Th}$  with high correlation coefficient ( $r^2 = 0.80 - 0.99$ ) and the angular coefficient varying from 1.05 to 2.74.

## **2.3 The variation of concentration of radionuclides with grain size**

### *a) Method and materials*

A soil sample was collected in a catchment and a sediment sample was collected in an outlet of a lake. Different grain size fractions were separated using the EFL2 MK3 shaker for grains  $> 50 \mu\text{m}$  and settling method for grains  $< 50 \mu\text{m}$ . Parts with different grain size were analyzed for radionuclides using low background gamma spectrometers.

### *b) Results and discussion*

The results showed that the concentration of radionuclides in different rain size fractions is quite different for both soil and sediment sample.

### *The correlation between radionuclides*

Statistical analysis of concentration of radionuclides in different grain size components showed that correlations between radionuclides are existent for soil and sediment sample.

There are good correlations between  $^{226}\text{Ra}$  and  $^{232}\text{Th}$ , between  $^{228}\text{Ra}$  and  $^{228}\text{Th}$  with  $r^2 > 0.92$  for both soil and sediment sample. Therefore, the correlation between  $^{226}\text{Ra}$  and  $^{232}\text{Th}$ ,  $^{228}\text{Ra}$  and  $^{228}\text{Th}$  was also found in natural sediment environment, where the grain size separation is usually happened.

The correlation between  $^{238}\text{U}/^{226}\text{Ra}$  and  $^{238}\text{U}/^{232}\text{Th}$ ,  $^{40}\text{K}/^{226}\text{Ra}$  and  $^{40}\text{K}/^{232}\text{Th}$  is rather good for soil and sediment samples.

There are weak correlations between  $^{238}\text{U}$  and  $^{226}\text{Ra}$ ,  $^{238}\text{U}$  and  $^{232}\text{Th}$  with correlation coefficient  $r^2 = 0.59 - 0.68$ . This weak correlation is easily broken in natural environment. That why the correlation between  $^{238}\text{U}$  and  $^{226}\text{Ra}$ ,  $^{238}\text{U}$  and  $^{232}\text{Th}$  is rarely found in natural sediments.

There are some correlations which are only found in soil or sediment such as correlation between  $^{40}\text{K}$  and  $^{226}\text{Ra}$ , between  $^{238}\text{U}/^{232}\text{Th}$  and  $^{226}\text{Ra}/^{232}\text{Th}$ . These correlations are sometimes encountered in natural sediment environment.

### **Conclusion**

Results obtained from two study soil types with 25 sampling points showed that (i) the concentration of radionuclides much varies from point to point for each soil type; (ii) There is an existence of the good correlation between  $^{226}\text{Ra}$  and  $^{232}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{232}\text{Th}$ ,  $^{228}\text{Ra}$  and  $^{228}\text{Th}$  for all two study sites; (iii) The correlations between  $^{238}\text{U}/^{226}\text{Ra}$  and  $^{238}\text{U}/^{232}\text{Th}$ ,  $^{238}\text{U}/^{232}\text{Th}$  and  $^{226}\text{Ra}/^{232}\text{Th}$ ,  $^{40}\text{K}/^{232}\text{Th}$  and  $^{40}\text{K}/^{226}\text{Ra}$  are also existent.

For sediment environment, experimental data showed that (i) the concentration of radionuclides highly varies with depth for all investigated reservoirs; (ii) The average concentration of radionuclides in sediments is much different from site to site; (iii) there is good correlation between  $^{226}\text{Ra}$  and  $^{232}\text{Th}$ ,  $^{228}\text{Ra}$  and  $^{228}\text{Th}$ ,  $^{238}\text{U}/^{226}\text{Ra}$  and  $^{238}\text{U}/^{232}\text{Th}$ ,  $^{40}\text{K}/^{232}\text{Th}$  and  $^{40}\text{K}/^{226}\text{Ra}$ ; (iv)  $^{226}\text{Ra}$  correlates with  $^{232}\text{Th}$  with  $r^2 = 0.71 - 0.95$  and the angular coefficient ranging between 0.69 and 1.65 for 5 study sites.

For different grain size fractions, obtained results showed that (i) the concentration of radionuclides in different grain size fractions is quite different; (ii) There are good correlations between  $^{226}\text{Ra}$  and  $^{232}\text{Th}$ ,  $^{228}\text{Ra}$  and  $^{228}\text{Th}$ ,  $^{238}\text{U}/^{226}\text{Ra}$  and  $^{238}\text{U}/^{232}\text{Th}$ ,  $^{40}\text{K}/^{226}\text{Ra}$  and  $^{40}\text{K}/^{232}\text{Th}$  for both soil and sediment sample. Besides, there are some correlations which are only found in soil or sediment such as correlation between  $^{40}\text{K}$  and  $^{226}\text{Ra}$ , between  $^{238}\text{U}/^{232}\text{Th}$  and  $^{226}\text{Ra}/^{232}\text{Th}$ .

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## **DETERMINATION OF PESTICIDE RESIDUES SUCH AS TPN, DIFENOCONAZOLE, FENVALERATE, FENTHOAT AND PARATHION IN SAFE VEGETABLES PRODUCED IN DALAT CITY BY GAS CHROMATOGRAPHY**

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**Abstract:** *The existence of an intensive agricultural system provides favorable conditions for pest prevalence in Vietnam. Therefore, farmer use pesticides to protect plants and increase yields. To reduce the tendency of using agricultural chemicals, human beings provide methods: Integrated Pest Management (IPM) or production of safe vegetables. However, safe vegetable products have not desirable responded yet.*

*Monitoring and inspecting for pesticide residues in fruits and vegetables are essential. Chromatography methods and a recent method GT test kit are applied for analyzing.*

*Gas chromatography equipped Electron Capture Detector (ECD) and Flame Ionization Detector (FID) and based on the procedure of liquid – liquid extraction, preconcentration and clean - up methods. The suitable conditions for separating and analyzing of Fenvalerate, Phenthoate, Chlorothalonil, Difenconazole and Methyl Parathion were investigated and employed to determine these pesticides residues in export purpose. This work is respond to require of customers. The studied method showed that there is high recoveries. Phenthoate showed recovery 98.7%, Fenvalerate 91.6%, Chlorothalonil 97.4%, Difenconazole 92.8% and Methyl Parathion 94.6%. LOD and LOQ are trustable.*

*In this work, use of the method enable plant material to be extracted and cleaned up for gas chromatographic determination of residues of 5 compounds of the organophosphorus and pyrethroid groups as TPN, DIFENOCONAZOLE, FENVALERATE, FENTHOAT AND PARATHION compounds by one or the same procedure. Limit of detection and limit of quantitation are determined in range of 5-15ng and 0.002-0.005 ppm.*

### **1. Outline of method**

Samples with a high water content such as spinach, tomatoes are homogenized with acetone, those with a low water content as soy-bean, potatoes are homogenized with a mixture of water and acetone. After evaporation of acetone, the aqueous residue is saturated with sodium chloride and extracted with ethyl acetate. After procedure of clean-up, elution, and dilution, the pesticide residues are determined by Gas-chromatography using an Electron Capture Detector and Flame Ionization Detector.

### **2. Reagents and Apparatus**

- Buchner porcelain funnel. 9cm dia.
- Separatory funnel, 250ml, 500ml
- Rotary vacuum evaporator
- Liquid - liquid extractor for extraction with heavy solvents



- Chromatographic tube, 20mm i.d., 30cm long
- Volumetric flasks, various sizes ranging from 2ml to 200ml
- Gas-chromatograph equipped with FID and ECD
- Microsyringe
- Acetone, dist.
- Etylacetate, dist.
- Dichloromethane, dist.
- Acetone-water mixture 2:1 v/v
- Sodium chloride, p.a.

### 3. Sampling and sample preparation

More than 100 samples of 3 kinds of vegetables such as: soy-bean, potatoes and Spinach were collected from the vegetable farms of Dalat City and Duc Trong District.

After delivery to the residue analysis laboratory, the laboratory sample should be further processed as required and reduced to an analytical size sample. If, for some exceptional reason, this cannot be done on the same day, the laboratory sample should be stored immediately in a refrigerator.

Firstly, the laboratory sample should be assessed for appearance, aroma and, if applicable, flavor (taste): particular note should be taken of any variations from the normal physical state or appearance. At the same time, any contamination or visible deposits possibly arising from application of crop protection measures should be noted.

The next step is to remove any impurities like stones or perhaps even pests as well as any visibly blemished, spoiled or rotten portions. The material should not be washed. However root vegetables, potatoes and the like should be rinsed lightly to remove adhering soil. Then the laboratory sample should be weighed and, if applicable, the number of units it contains should be counted

## 4. Procedure

### 4.1. Extraction

#### 4.1.1. Sample with a high water content (vegetable: spinach)

Homogenize 50g of the largely comminuted spinach (G) with 100ml of acetone for 3 min. Filter the homogenate with suction through a fast flow rate filter paper in a Buchner funnel. Rinse with 30ml acetone. Transfer the filtrate to a 150ml flask, dilute to mark by acetone ( $V_{Ex}$ ).

#### 4.1.2. Potatoes, soy-bean

Grind 50g of potato (G), add 150ml acetone-water mixture and homogenize for 3min. Filter the homogenate with suction through a fast flow rate filter paper in a Buchner funnel. Rinse with 30ml acetone. Transfer the filtrate to a 150ml flask, dilute to mark by acetone ( $V_{Ex}$ ).

## 5. Cleanup

### 5.1. Liquid – liquid partition

Transfer an aliquot of ( $V_{Ex}$ ) to a separatory funnel, add 30ml of saturated sodium chloride, and then extract three times with 10ml portion in the separatory funnel for 3 min. dry the combined organic phases on 50g sodium sulfate, and filter through a filter paper into 11-round bottomed flask. Wash the sodium sulfate and the filter paper with 50ml of ethyl acetate. Rotary-evaporate the combined filtrates almost to dryness.

### 5.2. Column chromatography

Fill a chromatographic tube with 50ml diethyl ether, tamp a flux of cotton wool to the bottom of the tube, add 15g silicagel and let the supernatant liquid drain to the surface of the silicagel. Cover the silicagel with sodium sulfate. Dissolve the residue derived from in 5ml diethyl ether and add to the column. Rinse the flask several times with 5ml portions of diethyl ether and elute part of the co-extractives with 100ml diethyl ether. Then rewash with 100ml eluting mixture 1. Rotary-evaporate the eluate containing the residues almost to dryness.

### 5.3. Gas-chromatographic determination

Dissolve the residue derived from in acetone and make up to a given volume ( $V_{End}$ ) which should not be less than 2ml. Inject an aliquot of this solution ( $V_i$ ) into the gas chromatograph.

#### Operating condition

Gas chromatograph	Shimadzu GC-17A V3
Column	SPB™-1
Column temperature	80°C
Injection port temperature	230°C
Detector	ECD, 300°C
Gas flow rate	30ml/min
Injection volume	1µl

## 6. Evaluation

Calculation of residues

$$R = \frac{Q_A \cdot V_{End} \cdot W_{St}}{Q_{St} \cdot V_i \cdot G}$$

G - sample weight (in g)

$V_{End}$  - terminal volume of sample solution (in ml)

$V_i$  - portion of volume  $V_{End}$  injected into gas chromatography (in µl)

$W_{St}$  - amount of residue injected with standard solution (in µg)

$Q_A$  - peak area of residue

$Q_{St}$  - peak area of standard

## 7. Results

**Tab 1. Recovery (%)**

Residue	Concentration added ( $\mu\text{g/g}$ )	Concentration found ( $\mu\text{g/g}$ )	RSD	Recovery (%)
TPN	0.5	0.487	$\pm 0.054$	97.4
Fenvalerate	1.0	0.916	$\pm 0.137$	91.6
Phenthoate	1.0	0.897	$\pm 0.152$	89.7
Parathion	0.5	0.473	$\pm 0.073$	94.6
Difenoconazole	1.0	0.938	$\pm 0.133$	93.8

**Tab 2. LOD, LOQ and MRL.**

Pesticide	LOD ( $\mu\text{g/ml}$ )	LOQ ( $\mu\text{g/g}$ )	MRL ( $\mu\text{g/g}$ )
TPN	0.005	0.008	0.05
Fenvalerate	0.002	0.003	0.05
Phenthoate	0.002	0.005	0.05
Parathion	0.0015	0.003	0.03
Difenoconazole	0.0015	0.003	0.05

**Tab 3. a, b,  $R^2$  and the regression line**

Pesticide	a	b	$R^2$	$S_i = aC_i + b$
TPN	352	0.54	0.9969	$Y=352x+0.54$
Fenvalerate	2358	104	0.9943	$Y= 2358x+104$
Phenthoate	460	13.7	0.9994	$Y=460x-13.7$
Parathion	1163	17.9	0.9986	$Y=1163-17.9$
Difenoconazole	40.2	1.1	0.9996	$Y=40.2x-1.1$

**Tab 4.** Results of pesticide residues in spinach (fresh), collected from dry season in 2004 in Ductrong province and Dalat city

No	Pesticides	Residue content in range (ng/g)/ % number of contaminated samples				MRL (ng/g)
		0 -1ng/g	1- 10ng/g	10-100ng/g	100-1000ng/g	
1	Phenthoate	50%	35%	10%	5%	100-2000
2	Difenoconazole	95%	4%	1%	0%	100-500
3	Methyl parathion	99%	1%	0%	0%	10-100
4	TPN	70%	28%	2%	0%	100-2000
5	Fenvalerate	35%	40%	20%	5%	100-2000

**Tab 7.** Results of pesticide residues in spinach (fresh), collected from rainy season in 2004 in Ductrong province and Dalat city

No	Pesticides	Residue content in range (ng/g)/ % number of contaminated samples				MRL (ng/g)
		0 -1ng/g	1-10 ng/g	10-100ng/g	100-1000ng/g	
1	Phenthoate	60%	34%	6%	0%	100-2000
2	Difeno-conazole	80%	18%	2%	0%	100-500
3	Methyl parathion	99%	1%	0%	0%	10-100
4	TPN	63%	35%	2%	0%	100-2000
5	Fenvalerate	40%	47%	10%	3%	100-2000

## 8. Conclusions

We studied and established successfully the method for determining of Phenthoate, Difenoconazole, Methyl parathion, TPN and Fenvalerate pesticide residue in vegetables .

We applied this method for analyzing these pesticide residues in the real samples of fresh, and frozen spinach, soybean and potato around Lamdong province.

The pesticide residues mentioned above in spinach collected from Dalat city and Ductrong district are in low level.

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## DETERMINATION OF As, Hg, Sb and Se IN WATER AND VEGETABLE SAMPLES AT DALAT BY HYDRIDE GENERATOR - ATOMIC ABSORPTION SPECTROPHOTOMETRY

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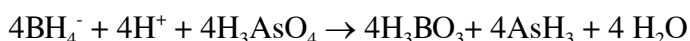
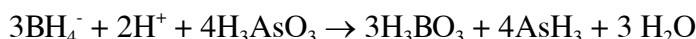
**Abstract:** To determine volatile elements in water and vegetable samples, atomic absorption spectrophotometry were developed. Arsenic, mercury, antimony and selenium were determined by hydride generator - atomic absorption spectrophotometry (HG-AAS). Concentration of elements were analyzed ranged As (0.54 - 2.35  $\mu\text{g/L}$ ), Hg (0.32-0.96  $\mu\text{g/L}$ ), Sb (0.42-2.32  $\mu\text{g/L}$ ) and Se (0.17-0.39  $\mu\text{g/L}$ ) in water samples and As (0.018 - 0.063 mg/kg.wet), Hg (6.5-15.6  $\mu\text{g/kg.wet}$ ), Sb (5.9-15.6  $\mu\text{g/kg.wet}$ ) and Se (0.027-0.063 mg/kg.wet) in vegetable samples.

### I. Introduction

The atomic absorption spectrophotometry AAS techniques in which including Flame - Atomic Absorption Spectrophotometry (F-AAS) has been applied for determination of Ca, Mn, Cu, Zn,... However, the technique is often quite difficult to analyze some elements such as: Se, As, Sb, Hg... because of detection limit not high and low concentration of the elements in water and environmental samples. An analytical technique has been developed in the present work. It is based on hydride generation systems.

For Arsenic, Antimony and Selenium

Arsenic, Antimony and Selenium were formed hydrides ( $\text{AsH}_3$ ,  $\text{SbH}_3$ ,  $\text{SeH}_2$ ) in acidic solution with  $\text{NaBH}_4$  for example the reaction of  $\text{As}^{3+}$  with  $\text{NaBH}_4$  forms arsine  $\text{AsH}_3$  and can be presented as follows:



Hydride generation involves several steps: the hydride is generated by chemical reaction, it is swept out of the solution into the atomizer by a carrier gas and they are determined by F-AAS and measured at 193.7nm, 231.2nm and 196nm for As, Sb and Se, respectively.

*For mercury.*

Mercury is determined by cold - vapour technique, it is unique the metallic elements because of its significant vapour pressure at room temperature. Mercury ions in solution can be reduced by  $\text{SnCl}_2$  ( $\text{Sn}^{2+} + \text{Hg}^{2+} \rightarrow \text{Sn}^{4+} + \text{Hg}^0$ ) to metallic mercury, mercury is swept out of the solution into the atomizer by a carrier gas and measured at 253.7nm.

Detection limit of method for As (0.01ppm), Hg (0.0005ppm), Sb (0.002ppm) and Se (0.01ppm).

## II. Experiments

### 1. Apparatus

- Atomic Absorption Spectrophotometer system connected to computer.
- Balance, micropipette, glassware, glass beakers. etc.

### 2. Reagents

- All chemicals used were of analytical grade. Deionized water was obtained by processing distilled water in an ion exchange unit
- Hydrochloric acid (density 1.12 g/cc), Nitric acid (density 1.4 g/cc) Sulphuric acid (density 1.84 g/cc) etc.
- Standard Reference Material (SRM) Mixed Human Diet H-9 and Pine Needle 1575 were obtained from the National Institute of Standards and Technology (NIST) and used for quality control. Single-element solutions standards ( $1000 \mu\text{g ml}^{-1}$ ) of arsenic, mercury, antimony and selenium were obtained from Merck (Germany)
- All equipments used for sampling and storing were washed with soap and water, treated with dilute nitric acid and then thoroughly rinsed with deionized water.

### 3. Sample collection and preparation

More than 30 samples in which including 16 water samples and 16 kinds of difference vegetables were collected from Dalat city.

- Water samples were collected from 6 lakes such as: Xuan Huong lake, Than tho lake, Tuyen Lam lake...
- Vegetable samples were purchased from some market and some co-operative in Dalat, after being cleaned, the samples were dried at  $60^{\circ}\text{C}$  until the dried weight reached a constant value.

### 4. HG-AAS method for determining As, Sb and Se in water samples

500ml of water sample was filtered through with size  $0.45\mu\text{m}$  membrane filter in order to remove suspending materials. Nitric acid was added to adjust  $\text{pH} < 1$  and quantitative transfer the sample in flask of ratovapor system, then evaporate at low pressure until dryness. Solution were transferred to 10ml measuring flask and diluted with water to make 10 ml.

### 5. HG - AAS method for determining Hg in water samples

100ml of water sample was filtered through with size  $0.45\mu\text{m}$  membrane filter in order to remove suspending materials. Add 5ml  $\text{HNO}_3$ , 2.5ml  $\text{H}_2\text{SO}_4$  and 15ml potassium permanganate then solution were taken on hot place at  $90^{\circ}\text{C}$  in 2 hours, after that solution was added 1-2 drops  $\text{NH}_2\text{OH} - \text{HCl} - \text{NaCl}$  to uncolor of  $\text{KMnO}_4$ . mercury ions in solution is reduced with  $\text{SnCl}_2$  to element mercury and measured by the conventional cold vapor atomic absorption technique.

### 6. HG-AAS method for determining As, Hg, Sb and Se in vegetable samples

Quantitative weight of 0.5 gram of each sample and Quantitative transfer the samples in different teflon bomb, add 5 ml nitric acid (density 1.4 g/cc) and 1 ml

sulphuric acid (density 1.84 g/cc). Then the samples were digested in hot water at 90°C. Generally it took 8-10 hours for complete digestion, solution were transferred to 10ml measuring flask and diluted with water to make 10 ml.

### 7. HG-AAS method for deterring Hg in vegetable samples

Quantitive weight of 0.5 gram of each sample and Quantitative transfer the samples in different teflon bomb, add 5 ml nitric acid (density 1.4 g/cc) and 1 ml sulphuric acid (density 1.84 g/cc). Then the samples were digested in hot water at 90°C. Generally it took 8-10 hours for complete digestion, solution were transferred to 100ml flask and diluted with water to make 100 ml. Add 5ml HNO<sub>3</sub>, 2.5ml H<sub>2</sub>SO<sub>4</sub> and 15ml potassium permanganate, then solution were taked on hot place at 90°C for 2 hours, after that solution was added 1-2 drops NH<sub>2</sub>OH – HCl –NaCl to uncolor of KMnO<sub>4</sub>. mecury ions in solution is reduced with SnCl<sub>2</sub> to element mecury and measured by the coventional cold vapor atomic asborption technique.

**Tab 1.** Concentration of As, Hg, Sb and Se in water samples in Dalat (10<sup>-3</sup>mg/lit).

No	Name of sample	As	Hg	Sb	Se
01	Doi co lake	2.35 ± 0.23	0.87 ± 0.08	2.32 ± 0.22	0.32 ± 0.03
02	Xuan huong lake (1)	1.45 ± 0.12	0.65 ± 0.06	1.61 ± 0.15	0.28 ± 0.03
03	Xuan huong lake (2)	1.31 ± 0.11	0.81 ± 0.08	1.45 ± 0.14	0.36 ± 0.04
04	Xuan huong lake (3)	1.96 ± 0.12	0.96 ± 0.09	1.36 ± 0.14	0.39 ± 0.04
05	Xuan huong lake (4)	1.84 ± 0.12	0.75 ± 0.07	1.41 ± 0.13	0.29 ± 0.03
06	Xuan huong lake (5)	1.65 ± 0.11	0.81 ± 0.08	1.47 ± 0.15	0.31 ± 0.03
07	Da thien lake	0.98 ± 0.11	0.55 ± 0.05	0.89 ± 0.09	0.21 ± 0.02
08	Tuyen Lam lake (left)	0.78 ± 0.07	0.42 ± 0.04	0.78 ± 0.07	0.22 ± 0.02
09	Tuyen Lam lake (right)	0.94 ± 0.10	0.51 ± 0.05	0.87 ± 0.08	0.28 ± 0.03
10	Chien Thang lake	2.01 ± 0.22	0.97 ± 0.09	1.87 ± 0.15	0.24 ± 0.02
11	Than tho lake (1)	1.36 ± 0.11	0.92 ± 0.09	2.31 ± 0.19	0.28 ± 0.02
12	Than tho lake (2)	1.57 ± 0.15	0.88 ± 0.08	1.65 ± 0.17	0.25 ± 0.03
13	Cam ly fall	1.98 ± 0.18	0.96 ± 0.09	1.98 ± 0.19	0.31 ± 0.03
14	Phan Dinh Phung stream	1.65 ± 0.15	0.84 ± 0.08	2.14 ± 0.25	0.33 ± 0.03
15	Suoi vang lake	0.54 ± 0.05	0.35 ± 0.04	0.42 ± 0.04	0.17 ± 0.02
16	Tap water	0.66 ± 0.07	0.32 ± 0.04	0.52 ± 0.06	0.21 ± 0.02
	Total mean	1.49 ± 0.51	0.76 ± 0.22	1.44 ± 0.66	0.27 ± 0.06



**Tab 2.** Concentration of As, Hg, Sb and Se in vegetable samples.

No	Name of sample	As mg/kg wet	Hg µg/kg wet	Sb µg/kg wet	Se mg/kg wet
01	Mustard	0.025 ± 0.003	8.2 ± 0.8	11.5 ± 1.5	0.032 ± 0.003
02	Field cabbage	0.019 ± 0.002	9.6 ± 0.9	7.6 ± 0.9	0.029 ± 0.003
03	Watercress	0.034 ± 0.003	15.6 ± 0.9	9.8 ± 1.0	0.032 ± 0.003
04	Spinach	0.025 ± 0.003	11.2 ± 1.3	12.7 ± 1.5	0.054 ± 0.005
05	Broccoli	0.033 ± 0.003	8.6 ± 0.9	15.6 ± 1.6	0.042 ± 0.005
06	Salad	0.014 ± 0.002	6.8 ± 0.7	11.2 ± 1.1	0.036 ± 0.004
07	Corol	0.016 ± 0.001	9.3 ± 0.9	8.7 ± 1.1	0.027 ± 0.003
08	cabbage	0.023 ± 0.002	7.5 ± 0.6	14.8 ± 1.2	0.036 ± 0.004
09	Chi. Cabbage	0.036 ± 0.004	8.6 ± 0.8	7.8 ± 0.7	0.055 ± 0.005
10	Celery	0.034 ± 0.003	7.6 ± 0.8	12.5 ± 1.2	0.029 ± 0.003
11	Cauliflower	0.045 ± 0.005	9.6 ± 0.9	9.7 ± 0.9	0.036 ± 0.003
12	Carrot	0.063 ± 0.006	12.0 ± 1.2	14.5 ± 1.5	0.055 ± 0.005
13	Potato	0.054 ± 0.005	14.0 ± 1.1	10.9 ± 1.2	0.041 ± 0.004
14	Green pepper	0.018 ± 0.002	6.5 ± 0.6	5.9 ± 0.5	0.063 ± 0.006
15	Tomatoes	0.024 ± 0.002	6.8 ± 0.6	6.6 ± 0.7	0.044 ± 0.004
16	French bean	0.022 ± 0.002	7.8 ± 0.8	10.5 ± 0.9	0.036 ± 0.004
	Total mean	0.030 ± 0.014	9.7 ± 3.0	10.6 ± 2.9	0.040 ± 0.010

### III. Conclusion

1. Establish procedures for determination of arsenic, mercury, antimony and selenium in water and vegetable samples by hydride generator - Atomic Absorption Spectrophotometry.
2. Determination of arsenic, mercury, antimony and selenium in 16 water and 16 vegetables in Dalat city.
3. The concentration of As, Hg, Sb and Se in water and vegetable samples which collected from Dalat is lower respective permissible limits according to Vietnam standard.

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## **MONITORING AND STUDYING PM-10 AIR DUST POLLUTION AT THE LANG METEOROLOGICAL STATION, HANOI**

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**Abstract:** *The approved contents of the regular task named “Monitoring and Studying PM-10 Air Dust Pollution at the Lang Meteorological Station, Hanoi” in 2004 have been completed well.*

*312 air dust samples have been collected with two kinds of air samplers (GENT-SFU and ASP) on every Wednesday and Sunday for 24 hours at the Lang Meteorological Station, Hanoi.*

*PM<sub>2.5</sub>, PM<sub>2.5-10</sub>, PM<sub>10</sub> and BC concentrations in 208 air dust samples have been determined by gravimetric and light reflection methods.*

*Ground meteorological parameters (T, Rain, WS, WD, RH) during monitoring have been collected and processed.*

*Variations of air dust concentrations of PM<sub>2.5</sub>, PM<sub>2.5-10</sub>, PM<sub>10</sub> and BC concentrations monthly in 2004 have been assessed. The yearly average air dust concentrations have been compared with those of previous years.*

*Participated in implementation of the contents of the IAEA/RCA/RAS/7/013 Project on "Support of Urban Air Quality Management" and international program of ACE.*

*With the obtained results, the studying group has been integrating step by step in the general trend presently of the region and the world in the field of studying and applying nuclear and related analytical techniques to solve air dust pollution problem.*

### **1. Contents of the task**

#### ***Contents of the task***

The approved contents of the regular task named “Monitoring and Studying PM-10 Air Dust Pollution at the Lang Meteorological Station, Hanoi” in 2004 have been completed well:

- 312 air dust samples have been collected with two kinds of air samplers (GENT-SFU and ASP) on every Wednesday and Sunday for 24 hours;
- PM<sub>2.5</sub>, PM<sub>2.5-10</sub>, PM<sub>10</sub> and BC concentrations in 208 air dust samples have been determined by gravimetric and light reflection methods;
- Ground meteorological parameters (T, Rain, WS, WD, RH) during monitoring have been collected and processed;
- Monthly variations of PM<sub>2.5</sub>, PM<sub>2.5-10</sub>, PM<sub>10</sub> and BC concentrations in 2004 have been assessed. The yearly average air dust concentrations have been compared with those of previous years;
- Participated in implementation of the contents of the IAEA/RCA/RAS/7/013 Project on "Support of Urban Air Quality Management" and international program of ACE;

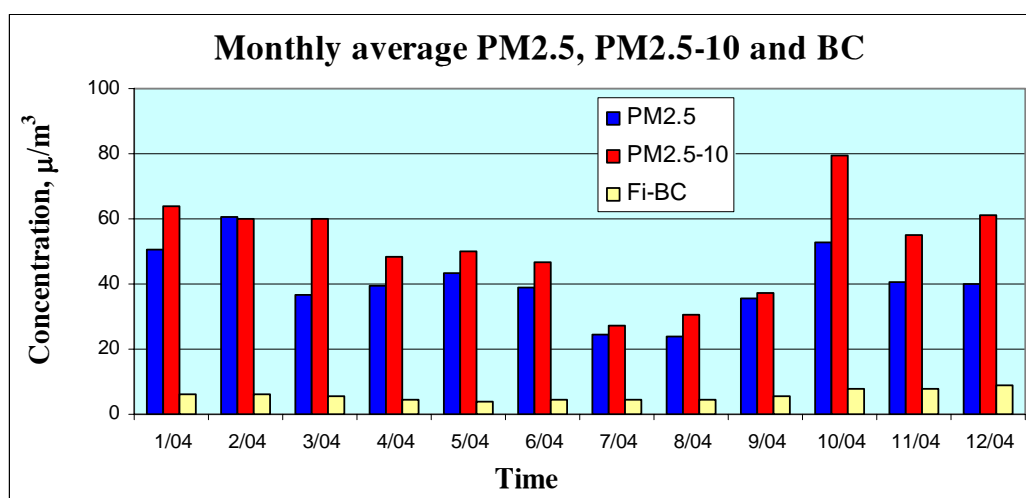
- Received technical supports of the RAS/7/013 project;
- Processed data of previous years, wrote paper for publishing.

## 2. Some of results

### 2.1. Time series of $PM_{2.5}$ , $PM_{2.5-10}$ and BC in 2004 Hanoi

$PM_{2.5}$ ,  $PM_{2.5-10}$ ,  $PM_{10}$  and BC concentrations at the Lang Station in 2004 have been observed continuously from January to December. Monthly average concentration in 2004 is presented on Fig.1.

Mean  $PM_{2.5}$  concentration from April to September (rainy season) is  $34.39 \mu\text{g}/\text{m}^3$ , from March to October (dry season) is  $46.54 \mu\text{g}/\text{m}^3$ . Mean  $PM_{10}$  concentrations in the same periods are  $46.54 \mu\text{g}/\text{m}^3$  and  $109 \mu\text{g}/\text{m}^3$ . They are higher than those in rainy season 1.35 and 1.46 times, respectively.



**Fig. 1.** Monthly average  $PM_{2.5}$ ,  $PM_{2.5-10}$ ,  $PM_{10}$  and BC concentrations at Lang Station in 2004

### 2.2. Yearly average $PM_{2.5}$ , $PM_{2.5-10}$ , $PM_{10}$ and BC concentrations at Lang Station from 8/98 up to now

Yearly average  $PM_{2.5}$ ,  $PM_{2.5-10}$ ,  $PM_{10}$  and BC concentrations at Lang Station from 8/98 up to now are given in Tab. 1. Generally,  $PM_{2.5}$ ,  $PM_{2.5-10}$ ,  $PM_{10}$  and BC concentrations tend to decrease slightly but not clear. However, they seem to increase in 2004.

In order to have scientific conclusions, it is necessary to analyse chemical compositions in collected samples and then to apply detailed statistical process technique.

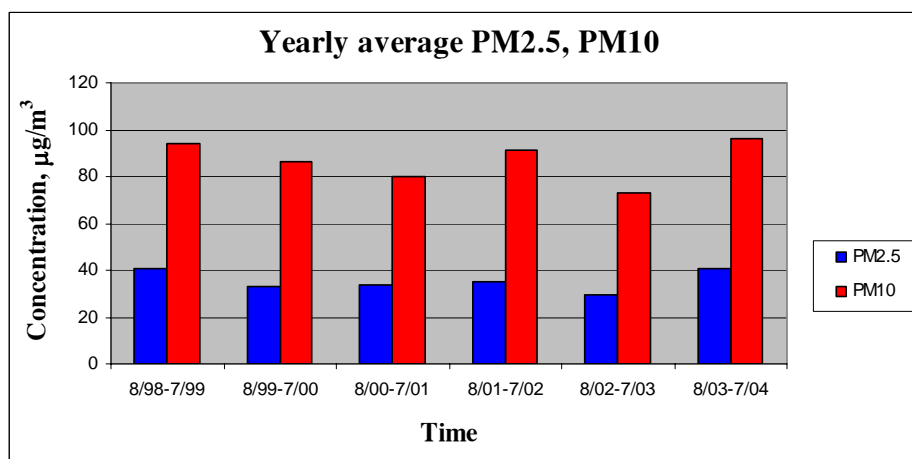
Yearly means of  $PM_{2.5}$  and  $PM_{2.5-10}$  from 6 years observed are  $35.6 \mu\text{g}/\text{m}^3$  and  $86.7 \mu\text{g}/\text{m}^3$ , respectively. They are 2.37 times for  $PM_{2.5}$  and 1.73 times for  $PM_{10}$  higher than those comparing to the USA air quality standards.

Numbers of days have 24h  $PM_{2.5}$  and  $PM_{10}$  that are exceeded the USA air quality standards are 10.17% and 10.7%, respectively.

**Tab. 1.** Yearly average PM, Pb and Fi-BC at Lang Station ( $\mu\text{g m}^{-3}$ )

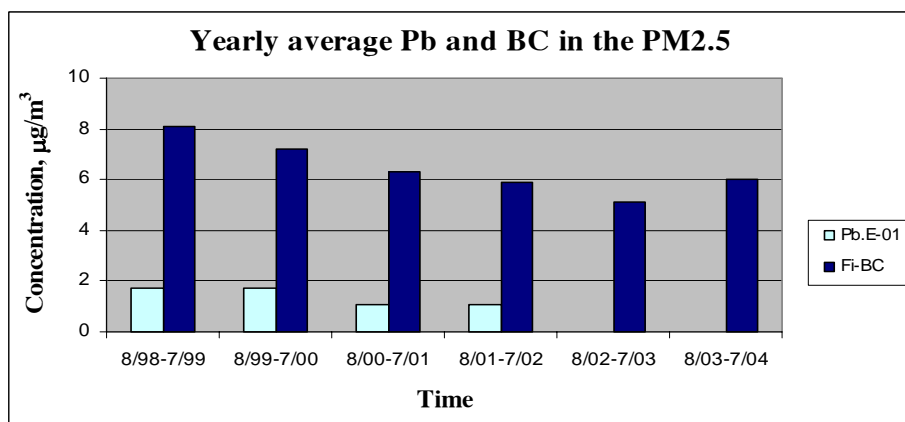
Duration	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>	PM <sub>10</sub>	Pb	Fi-BC
8/1998-7/1999	41.0	58.0	94.1	0.17	8.1
8/1999-7/2000	33.2	49.4	86.5	0.17	7.2
8/2000-7/2001	34.0	45.3	79.8	0.11	6.3
8/2001-7/2002	34.9	53.0	91.0	0.11	5.9
8/2002-7/2003	29.6	42.8	72.7	(*)	5.1
8/2003-7/2004	40.9	55.3	96.2	(*)	6.0

(\*) Not yet data



**Fig. 2.** Time series of yearly average PM<sub>2.5</sub>, PM<sub>10</sub> at Lang Station

Working group would like to acknowledge the VAEC, the INST, the Center Radiation Protection and Environment, the Environmental Radiation Monitoring Session and it's colleagues for they believed, entrusted and facilitated the group to perform the task well.



**Fig. 3.** Yearly average Pb and BC in the PM<sub>2.5</sub> at Lang Station.

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## DETERMINATION OF TRITIUM CONCENTRATION IN PRECIPITATION AT A STATION OF HANOI

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**Abstract:** The precipitation samples have been collected monthly and time, the analysis was followed the procedure of Subproject CS/03/04-03.

The procedure was improved to be adopted with some particular samples. After preliminary distillation, the samples would be recycle distilled in red-ox media for 4 – 8 hrs, the temperature at the output of the vigroux column was  $< 30^{\circ}\text{C}$ . The obtained conductivity was  $c \leq 30 \mu\text{S}$ .

The Liquid Scintillation Counting was carried out with the 1:1 (w/w) ratios to the scintillator (Ultima-Gold LLT) and counting time was 100 min/cycle x 10 cycles. Low limit detection of the analysis is  $A_T = 0.5 \text{ TU}$ .

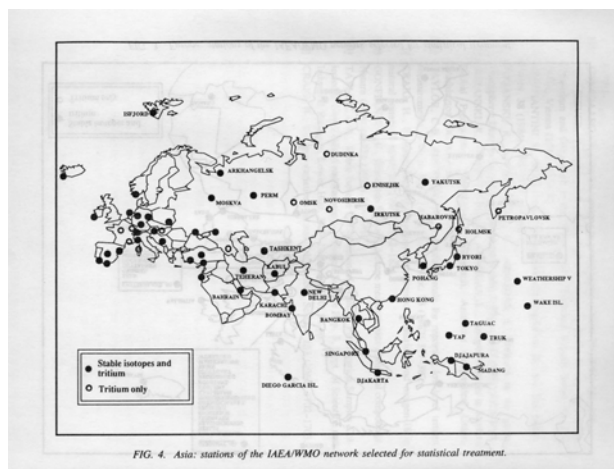
The results have shown that tritium concentration was highest ( $3.51 \pm 0.76 \text{ TU}$ ) on June 2004 and lowest ( $0.5 \pm 0.46 \text{ TU}$ ) on August 2004.

Making comparison to IAEA's Isotope Hydrology Laboratory obtained the 20% error with  $A_T < 1.0 \text{ TU}$  sample and 10% with  $A_T < 5.0 \text{ TU}$ , respectively.

### Introduction

Nowadays, the water source for industry and living is difficult problem to solve that we have been to face and it will become more serious in the near future. To give an exact conclusion about the capacity and resource of underground water which will be used for our life, the hydrological geologists must have a lot of data and tritium concentration is one of them.

Besides of the application that mentioned above, monitoring of tritium concentration may also give us some information about the change of radioactive background of environment. For these purposes, a monitoring network of isotopes in precipitation was set up (GNIP), it consists the global and national stations.



**Fig 1.** Stations of the IAEA/WMO network selected for statistical treatment.

The tritium concentration is very different between regions and depends on season, weather, latitude, distance from sea coast etc. A large part of the  $^3\text{H}$  produced by the nuclear explosions has been injected into the stratosphere and returns to the troposphere each year during spring and early summer. This causes the seasonal variation in both  $^3\text{H}$  and  $^{14}\text{C}$ , more pronounced in the former, because the residence time of  $\text{H}_2\text{O}$  to which  $^3\text{H}$  is coupled in the atmosphere is very small (in the order of weeks).

## Experiment

### 1. Sampling.

The precipitation samples were collected from January to December 2004 by sampling equipment that was made following the IAEA's model. It has been settling on the top of the INST building (Nghia do, Cau giay, Ha noi). After collecting, the samples were kept in 500 mL sealed plastic bottles to prevent air exchange.



**Fig 2.** The equipment for sample collection.



**Fig 3.** The bottles for sample preservation.

Number of the collected samples is 69 and as following:

**Tab 1.** Samples collected in 2004

Month	1	2	3	4	5	6	7	8	9	10	11	12
Number of samples	0	0	12	13	9	7	11	6	5	1	3	2

### 2. Sample treatment

The collected samples have been treated following the procedure I-4 of CS/03/04-03 so that obtained  $\text{pH}=6.8-7.0$  and conductivity  $c<30 \mu\text{S}$ . This procedure based on distillation.

With normal samples (low concentration of solid residue, small among of organic impurity), we have carried out treatment by single distillation. And with others (high conductivity, high organic impurity), after single distillations, their conductivity



was still high, so we must use recycle distillation technique in the diluted  $\text{KMnO}_4$  medium by vigroux column (fig. 4); the temperature of output was  $30^\circ\text{C}$ . This is to prevent the isotope classification. The results are followings.

**Tab 2.** The results of single distillation

No	Code of sample	Conductivity before single distillation ( $\mu\text{S}$ )	Conductivity after single distillation ( $\mu\text{S}$ )	Remarks
1	BM-1	373	80	Not suitable for electrolysis.
2	SN-3	305	73	
3	P3B-7	725	107	
4	P3A-7	554	202	
5	P2A-7	599	123	
6	P89B-7	768	190	
7	P89A-7	518	129	
8	P2B-7	1340	390	
9	P23N-7	1195	43	

**Tab 3.** The results of recycle distillation.

No.	Code of sample	Conductivity ( $\mu\text{S}$ )		Mass of samples			
		Before treatment	After treatment	Before treatment	After treatment	Lost mass (g)	Lost mass (%)
1	BM-1	80	30.0	666.58	666.07	0.51	0.08%
2	SN-3	73	14.0	670.97	670.45	0.52	0.08%
3	P3B-7	107	4.5	521.44	520.14	1.30	0.25%
4	P3A-7	202	10.0	522.95	521.24	1.71	0.33%
5	P2A-7	123	10.0	519.66	519.33	0.33	0.06%
6	P89B-7	190	5.0	536.94	536.32	0.62	0.12%
7	P89A-7	129	6.0	515.76	515.13	0.63	0.12%
8	P2B-7	390	30.0	520.85	519.04	1.75	0.33%
9	P23N-7	43	6.0	516.15	515.50	0.65	0.13%



**Fig. 4.** The equipment for recycle distillation.

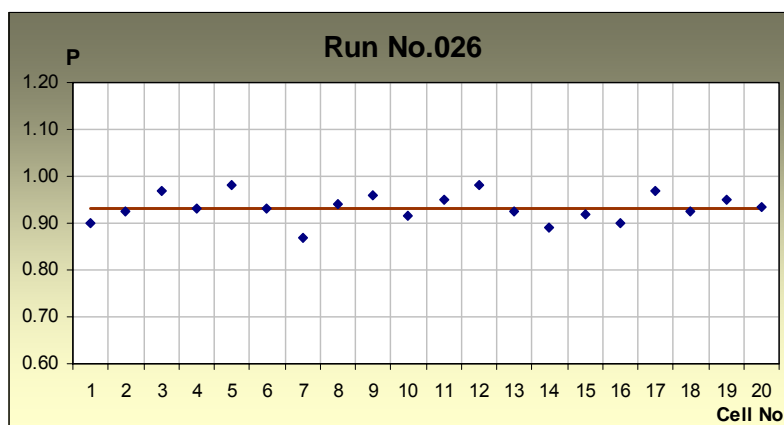
3. *Improvement of the enrichment electrolysis procedure.*

- *Electrolysis procedure.*

The schedule of electrolysis was 1430 Ah charge and was distributed as follow:

3.5A	200Ah
6.0A	400Ah
8.0A	500Ah
10.0A	1100Ah
8.0A	1200Ah
6.0A	1300Ah
3.5A	1430Ah

The enrichment procedure has been improved. This is illustrated on P value graphs of run No.26 and No.39. The P values have increased from 0.93 to 0.96 and P error has decreased from 0.04 to 0.012. (Fig. 5 and 6)



**Fig. 5.** P value of run 026

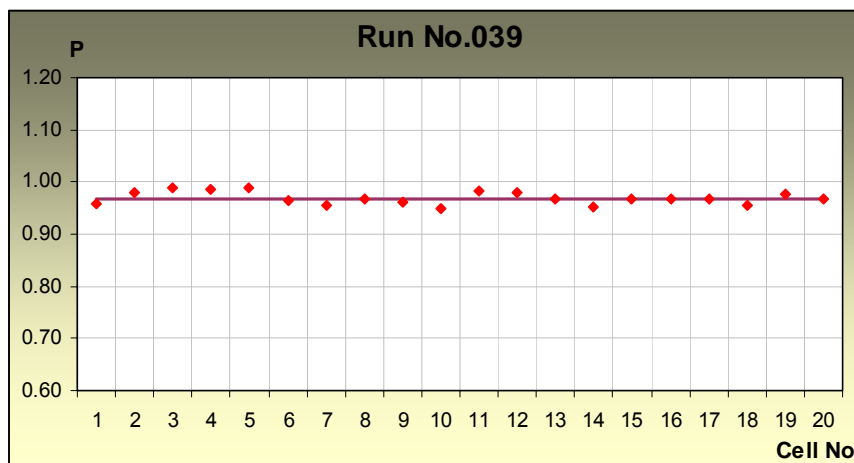


Fig. 6. P value of run 039

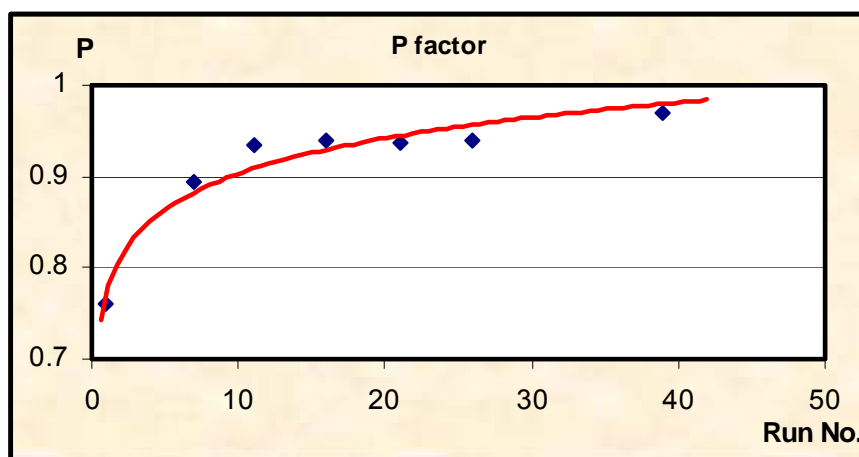


Fig. 7. The progression of P value

- *Liquid scintillation counting.*

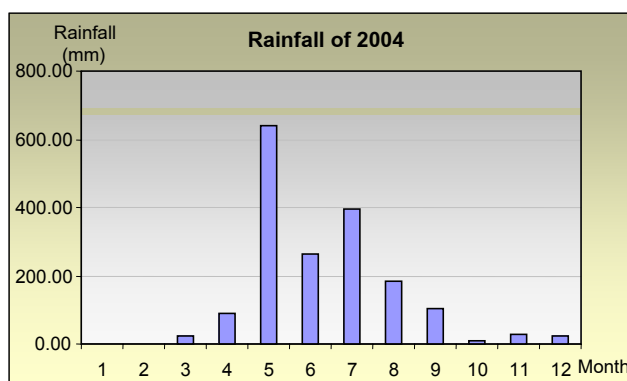
The liquid scintillation counting was carried out in 1:1(w/w) ratios of the purified enriched samples and cocktail on the Packard Perkin Elmer 3170 TR/SL. The used cocktail was Ultima Gold LLT.

4.The rainfall in 2004.

Base on rainfall data at the collecting location, a rainfall chart was built. This chart has shown that the highest rainfall was on May (640 mm) and the lowest one (7.54 mm) was on October 2004. It was almost no rain on January and February. (Fig. 8)

Tab 4. The rain fall in 2004 at the collecting station

Month	1	2	3	4	5	6	7	8	9	10	11	12
Rain fall (mm)	0	0	24,33	91,26	640,05	263,07	394,98	185,43	105,72	7,54	25,94	23,40



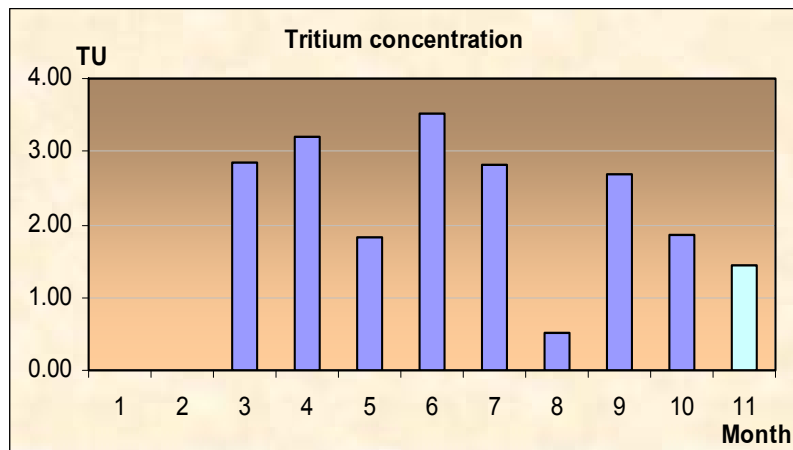
**Fig. 8.** Rainfall in 2004

5. *Tritium concentration in precipitation.*

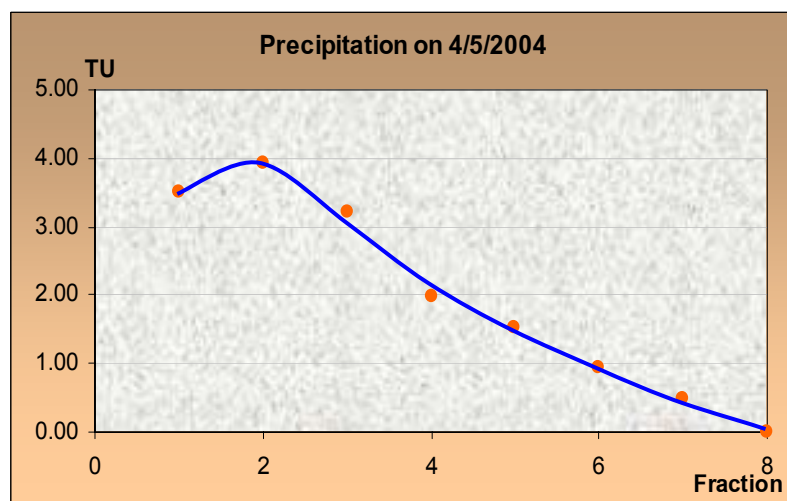
The results of tritium concentration analysis in several collected samples are followings.

**Tab 5.** Tritium concentration of analyzed samples

No.	Code	Month	CPMave.	NSA	E(Zi)	At (TU)
1	04-01	3	2.01	0.99	23.24 ± 7.75 %	2.85 ± 2.68
2	04-02	4	2.09	1.07	22.43 ± 7.66 %	3.21 ± 0.74
3	04-03	5	1.62	0.60	22.46 ± 7.66 %	1.81 ± 0.58
4	04-04	6	2.33	1.31	25.41 ± 7.97 %	3.51 ± 0.76
5	04-05	7	1.96	0.94	22.90 ± 7.71 %	2.81 ± 0.73
6	04-06	8	1.23	0.21	23.08 ± 7.73 %	0.50 ± 0.46
7	04-07	9	1.93	0.91	25.14 ± 7.95 %	2.68 ± 0.60
8	04-08	10	1.75	0.73	23.03 ± 7.73 %	1.86 ± 0.66
9	04-09	11	1.58	0.56	24.50 ± 7.88 %	1.43 ± 0.78
10	04-05.1	5	2.35	1.23	23.69 ± 7.8 %	3.50 ± 0.85
11	04-05.2	5	2.52	1.40	26.77 ± 8.11 %	3.94 ± 0.98
12	04-05.3	5	2.18	1.06	23.31 ± 7.76 %	3.23 ± 0.83
13	04-05.4	5	1.78	0.66	22.97 ± 7.72 %	1.98 ± 0.80
14	04-05.5	5	1.46	0.34	25.09 ± 7.94 %	1.52 ± 0.54
15	04-05.6	5	1.63	0.51	25.5 ± 7.25 %	0.93 ± 0.52
16	04-05.7	5	1.25	0.13	22.6 ± 7.68 %	0.50 ± 0.68



**Fig. 9.** Tritium concentration of the monthly samples in 2004



**Fig. 10.** Tritium concentration of samples collected on 4/5/2004

Because of the increase of P value and the decrease P error, the enrichment factor E increased from 23 to 25 and the low limit detection was down from 1.0 TU to 0.5 TU. The tritium concentration of samples in the year 2004 was highest (3.51 TU ± 0.76) on June and lowest (0.50 ± 0.46 TU) on August (Fig. 9).

6. *Uncertainty.*

The uncertainty of tritium concentration was calculated by two steps:

- Enrichment factor error

$$\sigma_{E_s} = \sqrt{\left(\frac{\partial E_s}{\partial Q}\right)^2 (\sigma(Q))^2 + \left(\frac{\partial E_s}{\partial P}\right)^2 (\sigma(P))^2 + \left(\frac{\partial E_s}{\partial W_I}\right)^2 (\sigma(W_I))^2 + \left(\frac{\partial E_s}{\partial W_F}\right)^2 (\sigma(W_F))^2}$$

- Tritium concentration error

$$\sigma_{A_T} = \sqrt{\left(\frac{\partial A_T}{\partial N_{NS}}\right)^2 (\sigma(N_{NS}))^2 + \left(\frac{\partial A_T}{\partial N_{STD}}\right)^2 (\sigma(N_{STD}))^2 + \left(\frac{\partial A_T}{\partial A_{STD}}\right)^2 (\sigma(A_{STD}))^2 + \left(\frac{\partial A_T}{\partial E_s}\right)^2 (\sigma(E_s))^2 + \left(\frac{\partial A_T}{\partial D}\right)^2 (\sigma(D))^2}$$

## 7. Conclusion.

It is not efficient to give a conclusion about the relationship between tritium concentration and meteorological data based on tritium data of one year. Otherwise, the monitoring of tritium concentration in precipitation during several years will give us a figure of difference of tritium concentration between Hanoi and some stations surrounding us such as Bangkok, Hong Kong, etc. Hence, hydrological geologists can adjust the tritium data of our region in the past years. So, to get a more complete database of tritium which can be used for hydrological metrology and environment it should extend the period for tritium monitoring.

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# STUDY ON THE APPLICATION OF COLD VAPOR ATOMIC ABSORPTION SPECTROMETRY AND HYDRIDE GENERATION ATOMIC ABSORPTION SPECTROMETRY FOR THE DETERMINATION OF HG AND AS TRACES IN SEA WATER SAMPLES

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**Abstract:** *The trace amount of total mercury (Hg) and arsenic (As) in sea water samples were quantitatively determined by using the Atomic Absorption Spectrometry connected with the hydride generation technique (HG-AAS) for As, and with the cold vapor technique (CV-AAS) for Hg. The experiments were carried out at room temperature on a Hydride System Module (HS55) combined with an Atomic Absorption Spectrometer (VARIO 6, Analytic Jena AG). The effect of reductants concentration, and that of matrix on the absorption intensity of each analyzed element was studied in details. The sea water sample after filtrating through a membrane with 0.45  $\mu\text{m}$ -hole size was pre-treated with an oxidant or a reductant to obtain the identical medium. The absorption intensity of each element was then measured on the VARIO-6 under the optimum parameters for spectrometer such as: maximum wavelength, current of hollow cathode lamp, and that for hydride system such as cell temperature, speed of peristaltic pump, pump time, reaction time and rewash time, etc.*

*The analytical procedures were set-up and applied for the determination of these above mentioned elements in the synthesized sea water sample and in the real sea water samples with high precision and accuracy.*

**Key words:** *mercury, arsenic, cold vapor, hydride generation, AAS, sea water*

## **I. Introduction**

Sea water has been the precious resource for the human due to the role of climate regulation and that of the insurance of mankind life. Oceans and seas contain a huge volume of water, and they thus became the human's ideal places for waste deposition from long time ago[1]. As the risk of environmental pollution caused by the human activities has been increased, the research on hydrometeorology (including marine hydrometeorology) over the world has been concentrated for finding out the causes and the regulation of pollution. The estimation of chemical compositions of sea water and the content of soluble heavy and toxic metal ions such as Hg, As...[2,3,4,5] in sea-water areas, where the monitoring was taken place by the seasons and time as well as by their changes has been the important task on the research of marine environment, that was carried out systematically via the monitoring stations setting up along the coastal sea's region of our country by several research institutions on marine Hydrometeorology and Navigations.

The quantitative determination of arsenic and mercury is rather difficult due to their low contents in high salinity. Nowadays, the popular methods for analysis of these trace amounts are often the advanced techniques such as ICP-AES, ICP-MS, TXRF, Ed-



XRF, NAA...in conjunction with the chemical pre-treatment [6-12]. For serving the demands from the research of marine environment, and to introduce the sufficient analytical procedures in the routine works, an advantageous technique, which has been employed for many years in the world, the atomic absorption spectrometry (AAS) with the support of a mercury/hydride system is selected. With the use of this technique, the trace elements in high salinity matrix can be determined quantitatively.

## **II. Experimental**

### ***1. Chemicals and Apparatus***

All chemicals are of the analytical grade. The standard stock solutions (Cu, Pb, Zn, Cd) 1000 µg/ml for AAS (made of Merck company) were used for the study. High purity deionized distilled water (with the resistance ~18MΩ) was used for further dilution.

Argon Gas with high purity (99,999%).

Atomic Absorption Spectrometer VARIO-6 (Analytic Jena AG, equipped with the auto-optimization of selected parameters) with graphite furnace function (the atomization took place in a graphite wall-type tube) in connection to an Auto-sampler MPE50.

Vacuum pump (GAST DOA-P725-BN, made in USA) was used for the filtration of the sample solutions (through the filtrate membrane with 0.45 µm hole-size).

### ***2. Procedures***

The experiments were carried out at room temperature. The test solutions were prepared by mixing the standard solutions at a certain concentration.

The sea water samples in accordance with specifications[5] after receiving from the sender were filtered through a membrane with 0.45 µm hole-size and these solutions were chemically treated before the measurement if it was required.

A portion of 20-25 ml of sample was pipetted into a 25 ml volumetric flask. It was added a certain volume of concentrated HCl for getting 3% HCl (for determining Hg) or 0.6M (for determining As) in the final solution. This solution was transferred to a 50 ml-reaction vessel on the Mercury/Hydride system HS55 combined with AAS main body instrument VARIO 6, then the measurement of the absorption intensity of each element was taken place on AAS under the optimum parameters such as the max. wavelength, hollow-cathode current for spectrometer, measured mode (Peak Height or Peak Area), the inert gas flow rate, reagent (reductant) pumping rate, reagent pumping time, reaction time, and integration time.

## **III. Results and Discussion**

### ***III.1. The effect of Reductant Concentration on the Absorption Intensity of Hg and As***

SnCl<sub>2</sub> solution prepared in HCl [6,7,13] was often used as a reductant for the quantitative determination of Hg in water samples. It is the selective reductant for Hg<sup>2+</sup> and the exceed of SnCl<sub>2</sub> in sample solution did not interfered with the transport of Hg vapor into the quartz tube. The experiments showed that the absorption intensity (Abs.) of Hg reached the max. value when SnCl<sub>2</sub> concentration was over 2.5%. However, the

concentration of  $\text{SnCl}_2$  was chosen for further experiments as 5% due to the high reproducibility of Abs. values at this value of reductant.

Sodiumborohydride ( $\text{NaBH}_4$ ) is also a popular reductant for the quantitative determination of Hg.  $\text{Hg}^{2+}$  is easily reduced to  $\text{Hg}^0$  vapor at room temperature due to the nascent H atom. The study on the effect of  $\text{NaBH}_4$  concentration on the Abs. of Hg depicted that the use of 0.75%  $\text{NaBH}_4$  gave more reproducible value of Hg Abs. than that of the lower concentration, while the max. value of Hg Abs. was obtained with the usage of 0.5%  $\text{NaBH}_4$ .

These reductants for Hg determination were effective. However, the use of  $\text{NaBH}_4$  was more convenient if the analyses included both Hg and As.

Many authors [6,8,14,15,16] showed that dilute  $\text{NaBH}_4$  solution in alkali medium was used to be the effective reductant for the hydride formation of many metal ions such as arsenic, antimony,... at room temperature due to the role of nascent H atom. Since the formation of  $\text{H}_2$  gas (forming foam) has occurred during the reduction in acidic medium, the concentration of  $\text{NaBH}_4$  solution is limited. If over 3%  $\text{NaBH}_4$  is used, the adding of small amount of defoamed substances such as silicon or octanol is necessary. [17] The experiments showed that using 0.5%  $\text{NaBH}_4$  solution resulted in higher reproducibility of Arsenic Abs. than the use of lower concentration, though the max value of As Abs. was reached with 0.2%  $\text{NaBH}_4$  reductant.

### ***III.2. The effect of acidity on the Absorption Intensity of Hg and As***

The reduction of  $\text{Hg}^{2+}$  to  $\text{Hg}^0$  took place easily in acidic medium at room temperature. The acidic concentration influenced with the yield of this reduction, and with the absorption intensity of Hg. The experimental results showed that Hg Abs. reached the max. value at 3% of HCl in sample solution. This result is similar to that obtained by other authors.[18]

The reductant of As(III) to  $\text{AsH}_3$  also took place in HCl acidic medium. The effect of HCl concentration on the As Abs. was studied in the wide range from 0.01M to 10M.[16] However, from our results, it can be concluded that the As Abs. reached the max. value when the HCl concentration in sample solution varied from 0.55 to 0.67 M. This data seemed rather similar to those got from other authors.[16]

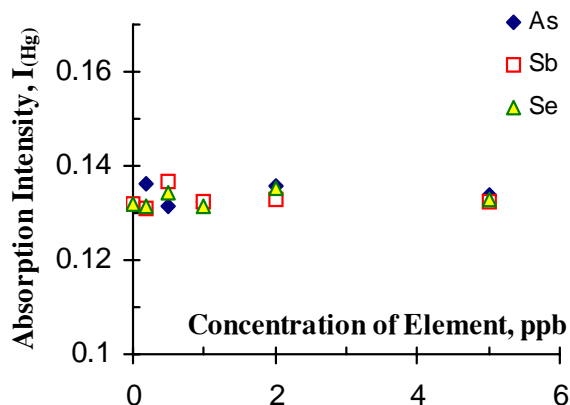
### ***III.3. The Effect of sea water matrix on the Absorption Intensity of Hg and As***

Sea water gave a rather thick matrix with the high content of NaCl and other major components such as Mg, Ca, and K. The highest constituent of sea water matrix, NaCl was selected for the representative study of the effect of the major elements on the Abs. of trace Hg and As.

From the experimental results, it can be summarized that the increase of NaCl concentration in solution does not interfere the Abs. of Hg and As because almost metal ions in sea water could not be reduced to volatile forms except for  $\text{Hg}^0$  and  $\text{AsH}_3$  (and other metallic hydrides). The special property of Hg and that of metallic hydride forming group at room temperature after reducing gives the high selectivity for their determination.

### III.4. The Effect of some trace elements, and mutual effect of the analyzed elements on the Absorption Intensity of Hg and As

At the same level of concentration in sea water, only few trace elements showed the interference with each other on its determination due to the advantages of the selectivity, which was supplied by the hollow cathode lamps and the working conditions of mercury/hydride system. Figure 1 showed an example of the mutual effect of some trace elements (As, Se, Sb) being present at the background on Abs. of Hg trace. Since their concentration in sea water was similar to that of Hg, they did not cause any interference on the Abs. of Hg. Our results agreed well with other conclusions. [18]



**Fig.1** Effect of some trace elements in sea water on the Hg Absorption Intensity

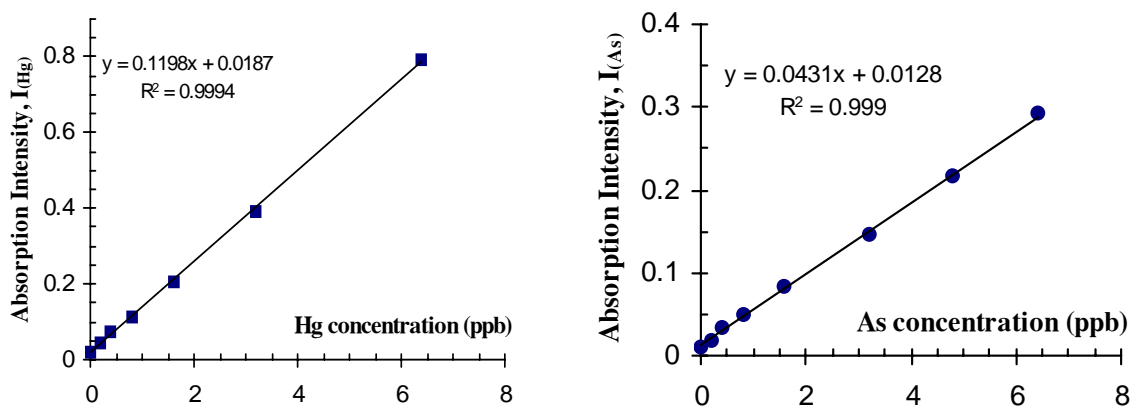
### III.5. The effect of an oxidant or reductant in pre-treatment stage on the quantitative determination of Hg and As

The adding of an oxidation or a reductant in pre-treatment stage supported the later reduction. Due to the natural exist of Hg and As in sea water, many inorganic and organic compounds of each element could be found. However, only the  $\text{Hg}^{2+}$  and As(III) forms can be easily reduced in the reaction using a reductant as  $\text{NaBH}_4$  (or  $\text{SnCl}_2$  for Hg also), it is necessary to convert all compounds of Hg or As into the uniform. For Hg in sea water, it consists of  $\text{Hg}^{2+}$ , and organo-mercury compound, and a small amount of  $\text{Hg}_2^{2+}$ . The adding of 0.2 ml of an effective oxidation such as  $\text{KMnO}_4$  (or  $\text{K}_2\text{Cr}_2\text{O}_7$ ) stabilized the sample after standing the sample for about 2 hrs and resulted in the higher Abs. of Hg in the comparison with the sample without pre-treatment. Arsenic in sea water consist of  $\text{H}_2\text{AsO}_3^-$ ,  $\text{HAsO}_4^{2-}$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{CH}_3\text{As}$ ,  $((\text{CH}_3)_2\text{As})$ , [6,7,14] and some other forms[7], but the percentage of inorganic compounds of As(III) and As(V) is much higher among all arsenic forms. [6,8] it thus needs adding a small amount of a sufficient reductant for converting all As(V) to As(III). 10% L-Cysteine solution was selected for this purpose due to its selectivity. The experiment showed that the adding of 0.5 ml of L-Cysteine into the sea water sample and left it standing for about 1 hr gave the higher value of Abs. of As, which compared with that obtained from the sample without pre-treatment. Our conclusion is similar to other author [19].

### III.6. Linearity and the Calibration of Hg and As

The linearity was received for all analyzed trace elements within the studied range of concentration. The dependency of the absorption intensity of each element on its concentration was studied in the presence of an artificial sea water background [6]

and the calibrations were then plotted for each element trace. Figure 2 showed the results.



**Fig. 2** The Calibration for the quantitative determination of Hg and As in Sea Water

### III.7. Analysis of sea water samples

**Tab 1.** Analysis of an Artificial Sea Water Sample (SSTD)

Trace Element	Certified Value ( $\mu\text{g/l}$ )	Found Value ( $\mu\text{g/l}$ ) by CV-AAS/HG-AAS	Error (%)	Found Value ( $\mu\text{g/l}$ ) By ICP-AES
Hg	1,000	$0,989 \pm 0,025$	-1,10	$1,052 \pm 0,013$
As	1,100	$1,090 \pm 0,023$	- 0,91	$1,198 \pm 0,012$

**Tab 2.** Analysis of the Sea Water Samples

Sample Code	Hg ( $\mu\text{g/l}$ )		As ( $\mu\text{g/l}$ )	
	by CV-AAS	by ICP-MS	by HG-AAS	by ICP-MS
<b>04-01</b>	$0,206 \pm 0,027$	$0,212 \pm 0,032$	$0,497 \pm 0,045$	$0,476 \pm 0,036$
<b>04-02</b>	$1,075 \pm 0,024$	$1,253 \pm 0,021$	$0,297 \pm 0,010$	$0,307 \pm 0,025$
<b>04-03</b>	$0,116 \pm 0,014$	$0,108 \pm 0,023$	$0,553 \pm 0,039$	$0,577 \pm 0,022$
<b>04-04</b>	$0,068 \pm 0,007$	$0,070 \pm 0,019$	$0,956 \pm 0,036$	$1,080 \pm 0,019$
<b>04-05</b>	$0,497 \pm 0,034$	$0,512 \pm 0,026$	$2,165 \pm 0,046$	$2,233 \pm 0,021$

ICP-MS = Inductively couples plasma -mass

An artificial sea water sample and five sea water samples were analyzed according to the studied procedure. The metal ion concentration was then calculated on

the base of calibration, and the result was given in Tables 1 and 2. Due to the lack of the Certified Reference Materials, the artificial sea water sample, which was prepared [5] and the contents of trace elements was analyzed by using a standard procedure on ICP-AES [7,8] was used for the statistic evaluation and for the comparison of the accuracy obtained from the studied analytical technique. The results agreed well with that received from an advanced technique (ICP-MS) and the data showed reasonable deviation and high reproducibility.

#### IV. Conclusion

The work has been fully achieved the aiming goals as the following.

- The necessary physical parameters for the determination of Hg and As on the AAS VARIO 6 with the cold vapor (CV-AAS) or hydride generation (HG-AAS) techniques;

- The effect of the effective reductants such as  $\text{SnCl}_2$  or  $\text{NaBH}_4$ , of acidity, of some mainly major components such as NaCl and that of some metallic trace elements in matrix of sea water sample solution on the determination of Hg and As was studied, and the optimum conditions for determining these elements were established;

- The analytical procedures were then set up for the quantitative analysis of trace Hg and As in sea water samples. The application of this procedure in the analysis of sea water samples was thus carried out in the laboratory of Center for Analytical Chemistry & Environment, ITRRE for supplying the demands from customers. The statistic data showed the reliable reproducibility and high precision and accuracy.

#### Acknowledgement

Our work was accomplished with the financial support of Project CS/03/03-05, ITRRE, VAEC. The authors are thankful to the help of the Institute leadership and to the co-operation of their colleagues in Center for Analytical Chemistry and Environment as well as their colleagues in FU Berlin for their experiments in comparison.

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## **APPLICATION OF BIOSORPTION IN RADIOACTIVE LIQUID WASTE TREATMENT**

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**Abstract:** *In biomasses which were researched in the world, Rhizopus arrhizus was interested in research because of high uranium and thorium selectivity and high performance adsorption capacity more than 5 times compare with other ion-exchange resins were in use. In this research, Vietnamese biomass Rhizopus arrrhizus was investigated and researched to separate uranium and thorium from radioactive liquid waste. The results showed that uranium and thorium adsorption al capacity of Vietnamese biomass is correlative to which were reached of previous researches in the world. Uranium and thorium adsorbed in biomass can be reached from 95,6 to 97,95% in HCl media at pH=2.5, extracted by alkaline bicarbonates, up to 99,94% by NaHCO<sub>3</sub>, but only 3,9 to 84% by NH<sub>4</sub>HCO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub>. A maximum load of ca 350mgU/g biomass and 150mgTh/g biomass, as analysed by UV-Spectrophotometer and ICP-MS , was obtained after chemical treatment.*

**Key words:** *biomasses, Rhizopus arrhizus, adsorption*

### **Introduction**

Since the late 1980s, when biotechnology have been developed, the researches and applications of biosorptions from Beer, Liquor Factories or Mushroom Field waste to treat industrial and radioactive wastes based on initial researches of heavy metals absorption ability of some natural mushrooms. In present, the application of biosorption to treat heavy metals in industrial liquid waste and radioactive waste begins extensive application because absorption ability was higher than other ion-exchange resins and low cost for treating them after out of using.

In content of “Application of Biosorption in Radioactive Liquid Waste Treatment”, project CS 04/03-03 researched items below:

- Researching factors which effected to biosorption process as temperature, pH, absorption rate, and media.
- Biosorption parameters
- Elution methods

The research object was imitation solution which had U, Th lowest concentration 0.5mg/l and highest concentration 400mg/l.

### **Results and discussion**

#### **I. Biomass preparation:**

Biomasses were collected and investigated from Hanoi Beer Company, Saigon Beer Company, and Mushroom Field of Bacninh Agriculture Company. Samples were analysed at Biotechnology Center, Hochiminh City.

**Tab 1.** Rhizopus arrhizus Biosorption Ingredient in waste of Hanoi Beer Company, Saigon Beer Company, and Bacninh Agriculture Company

No	Analytical date	Rhizopus arrhizus ingredient(%)		
		Hanoi	Saigon	Bacninh
1	03/10/2004	5	3	3
2	03/17/2004	5	3	3
3	03/25/2004	5	3	3
4	04/10/2004	4	3	2,5
5	04/17/2004	3,5	2,8	2,5
6	04/25/2004	3,5	2,5	2
7	05/05/2004	3	2	1,9
8	05/12/2004	3	2	1,7
9	05/21/2004	2,9	2	1,5
10	05/31/2004	2,5	2	1,5

As Biotechnology Center results, the content of biomass in samples have been changed because of market demand and effect of weather depend on seasons. Project suggested Biotechnology Center multiplication Rhizopus arrhizus biosorption to get purebred source for research.

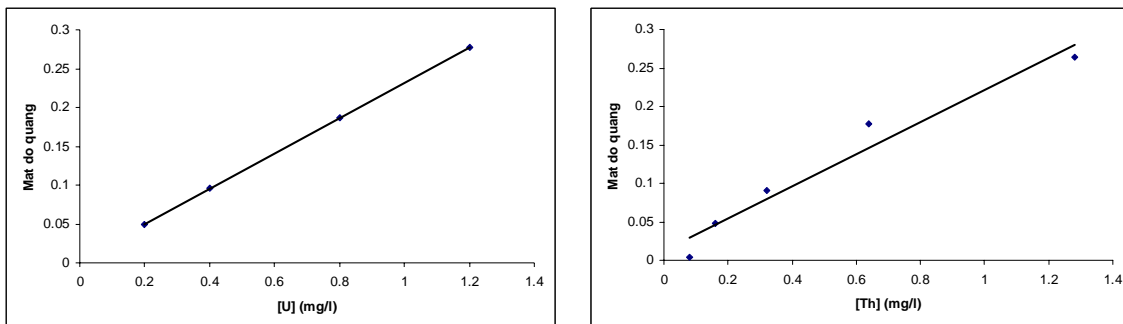
## II. Establishing directrix [1], [4]:

Uranium and thorium directrix have been established as table below:

**Tab 2.** Directrix of uranium and thorium concentration

STT	[U] (mg/l)	[Th] (mg/l)
1	0,2	0,08
2	0,4	0,16
3	0,8	0,32
4	1,2	0,64
5		1,28





**Fig. 1.** Uranium and thorium directrix at wavelength 662 nm and 666nm, respectively, are measured by UV-1601

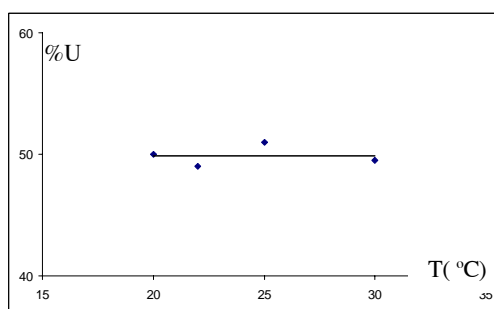
**III. Researching factors effect to absorption process in stable condition [1], [2], [4], [5], [6], [7]:**

**1. Study for dependence of temperature to biosorption process:**

The temperature range was studied from 20°C to 30°C. Samples were measured by UV-Visible Spectrophotometer UV-1601 at wavelength 660 nm.

**Tab 3.** The dependence of biosorption on temperature

Temperature	Sample 1	Sample 2	Sample 3	Sample 4
20°C	50	-	-	-
22°C	-	49	-	-
25°C	-	-	51	-
30°C	-	-	-	49,5



**Fig. 3.** The dependence of biosorption on temperature

Table 3 and Figure3 showed that uranium biosorption was not depended on temperature of solution.

**2. Studying for effect of pH and media to biosorption process [2], [7]:**

The media have been studied as HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>. pH were studied from pH=1.5 to pH=3. Input uranium solution concentration was 180 mg/l, and input thorium solution concentration was 150 mg/l, respectively. Uranium and thorium efficiency of biosorption is calculated as below:

$$K_d^A = \frac{[A] - [A]_n}{[A]} \times 100\%$$

$K_d^A$ : Biosorption efficiency

A: Symbol of uranium or thorium

[A]: Input uranium or thorium solution concentration

$[A]_n$ : Output uranium or thorium solution concentration

Concentration of U, Th which absorbed in biomass is calculated as below:

$$[A]_{sk} = [A] - [A]_n$$

#### a. HCl media:

**Tab 4.** The dependence of uranium and thorium biosorption on pH in HCl medium

pH	$[U]_n$ (mg/l)	$[U]_{sk}$ (mg/l)	$K_d^U$	$[Th]_n$ (mg/l)	$[Th]_{sk}$ (mg/l)	$K_d^{Th}$
1,5	4,98	175,02	97,23	4,52	145,48	96,98
2,0	7,5	172,5	95,83	6,81	143,19	95,46
2,5	3,699	176,301	<b>97,945</b>	3,47	146,53	<b>97,68</b>
3,0	5,18	174,82	97,12	5,02	144,98	96,65

#### b. HNO<sub>3</sub> media:

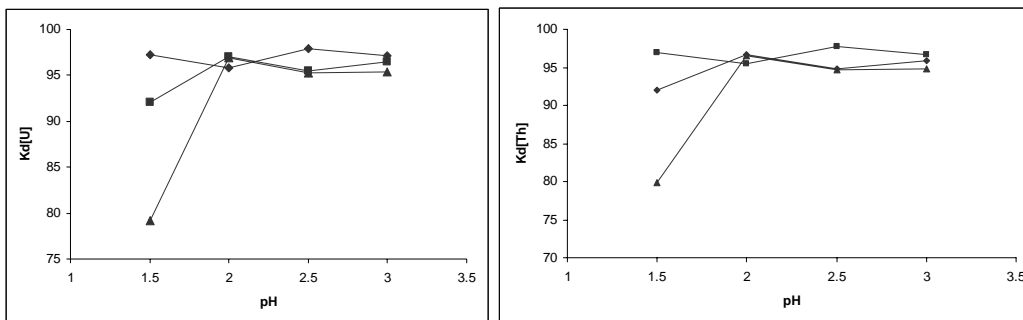
**Tab 5.** The dependence of uranium and thorium absorption on pH in HNO<sub>3</sub> media

pH	$[U]_n$ (mg/l)	$[U]_{sk}$ (mg/l)	$K_d^U$	$[Th]_n$ (mg/l)	$[Th]_{sk}$ (mg/l)	$K_d^{Th}$
1,5	14,3	165,7	92,05	12,1	137,9	91,93
2,0	5,34	174,66	97,03	5,02	144,98	96,65
2,5	8,2	171,8	95,44	7,83	142,17	94,78
3,0	6,28	173,72	96,51	6,18	143,82	95,88

#### c. H<sub>2</sub>SO<sub>4</sub> media:

**Tab 6.** The dependence of uranium and thorium absorption on pH in H<sub>2</sub>SO<sub>4</sub> media

pH	$[U]_n$ (mg/l)	$[U]_{sk}$ (mg/l)	$K_d^U$	$[Th]_n$ (mg/l)	$[Th]_{sk}$ (mg/l)	$K_d^{Th}$
1,5	37,37	142,63	79,24	30,21	119,79	79,86
2,0	5,55	174,45	96,92	5,25	144,75	96,5
2,5	8,55	171,45	95,25	7,95	142,05	94,7
3,0	8,24	171,76	95,42	7,84	142,16	94,77



**Fig 4.** The dependence of uranium and thorium absorption on pH in acid media

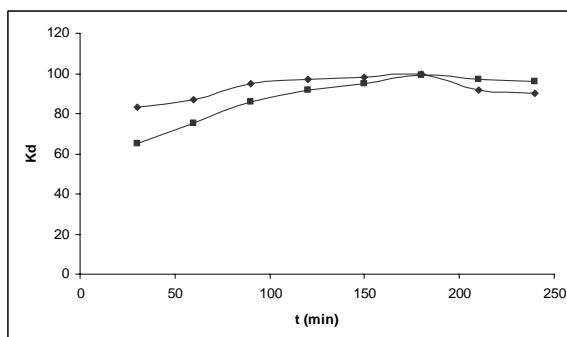
- HCl media
- ▲ H<sub>2</sub>SO<sub>4</sub> media
- HNO<sub>3</sub> media

**3. Studying for effect of time to biosorption process:**

Input uranium and thorium solution concentration are 180 mg/l and 150mg/l, respectively, pH = 2,5, HCl medium, room temperature.

**Tab 7.** The dependence of uranium and thorium efficiency on time

Time (min)	[U] <sub>n</sub> (mg/l)	[U] <sub>sk</sub> (mg/l)	K <sub>d</sub> <sup>U</sup>	[Th] <sub>n</sub> (mg/l)	[Th] <sub>sk</sub> (mg/l)	K <sub>d</sub> <sup>Th</sup>
30	0,306	1,494	83	0,525	0,975	65
60	0,234	1,566	87	0,375	1,125	75
90	0,090	1,710	95	0,210	1,290	86
120	0,054	1,746	97	0,120	1380	92
150	0,036	1,764	98	0,075	1,425	95
180	0,0018	1,7982	<b>99,9</b>	0,015	1,485	<b>99</b>
210	0,144	1,656	92	0,045	1,455	97
240	0,180	1620	90	0,060	1,440	96



**Fig. 5.** The dependence of U, Th efficiency on time

Table 7 and Figure 5 show that at  $t = 180\text{min}$ , the maximum capacity biosorption of biomass can be reached 99.9% U and 99% Th, respectively. Over this time, the biosorption capacity reduce because biomass cell wall networks have been broken by acid media so uranium and thorium solved to aqueous phase.

#### IV. Study for elution conditions and factors [1], [2], [4], [5], [6], [7]:

##### 1. $\text{NH}_4\text{HCO}_3$ media:

10 ml input uranium and thorium solution which has concentration of 180mg/l and 150 mg/l, respectively, was added to biomass at room temperature, stirred and kept stable in 180min. After biomass saturated of uranium and thorium, it was filtered, washed by distilled water and re-feed to triangular pot. Add 100ml of  $\text{NaHCO}_3$  solution which have concentration of 0.01, 0.05, and 0.1M, respectively, and kept in 15min. The solution after elution process were filtered and chemical treated. Samples were measured at wavelength 660 and 666nm by UV-Spectrometer. Elution performance is determined as below:

$$K_d^A = \frac{[A] - [A]_n}{[A]} \times 100\%$$

$K_d^A$ : U, Th elution performance (%)

[A]: Input solution concentration (mg/l)

$[A]_n$ : Concentration of U, Th in elution solution

**Tab 8.** Parameters of U, Th elution process in  $\text{NH}_4\text{HCO}_3$  media

Conc.(M)	pH	$[\text{U}]_n$ (mg/l)	$[\text{U}]_{sk}$ (mg/l)	$K_d^U$ (%)	$[\text{Th}]_n$ (mg/l)	$[\text{Th}]_{sk}$ (mg/l)	$K_d^{Th}$ (%)
0,01	7,85	126,7	53,3	70,38	60,12	89,88	59,92
0,05	7,92	132,5	47,5	73,61	59,07	90,93	60,62
0,1	7,94	134,4	45,6	74,67	57,88	92,12	61,41

##### 2. $\text{NaHCO}_3$ media:

**Tab 9.** Parameters of U, Th elution process in  $\text{NaHCO}_3$  media

Conc. (M)	pH	$[\text{U}]_n$ (mg/l)	$[\text{U}]_{sk}$ (mg/l)	$K_d^U$ (%)	$[\text{Th}]_n$ (mg/l)	$[\text{Th}]_{sk}$ (mg/l)	$K_d^{Th}$ (%)
0,01	8,1	170,3	9,7	94,61	117,33	32,67	78,22
0,05	8,2	174,67	5,33	97,04	126,78	23,22	84,52
0,1	8,3	179,9	0,1	99,94	135,12	14,88	90,08

### 3. $\text{Na}_2\text{CO}_3$ media:

**Tab 10.** Parameters of U, Th elution process in  $\text{Na}_2\text{CO}_3$  media

Conc.(M)	pH	[U] <sub>n</sub> (mg/l)	[U] <sub>sk</sub> (mg/l)	$K_d^U$ (%)	[Th] <sub>n</sub> (mg/l)	[Th] <sub>sk</sub> (mg/l)	$K_d^{Th}$ (%)
0,01	9,8	6,29	173,71	3,49	5,85	144,15	3,9
0,05	10,75	21,22	158,78	11,78	17,17	132,83	11,45
0,1	11,15	22,6	157,4	12,55	19,33	130,67	12,88

The results showed that in  $\text{NaHCO}_3$  0.1M medium, at pH = 8.3 almost of U (99.94%) and Th (90%) have been eluted.

#### V. Application of stable phase parameters to moving phase [3]:

Experiments were carried out in condition parameters as below:

- Room temperature.
- Input solution concentration: [U] 50mg/l , [Th] 50mg/l.
- Column volume (not including dead volume) was fed biomass: 27 ml (5g sinh khối), column height as 50 cm.
- pH: 2.5 in HCl medium.
- Eluent:  $\text{NaHCO}_3$  0,1M solution
- Speed rate: 20 ml/min

During absorption process, output solution was sampled every 3hrs and measured by UV-Spectrometer and ICP-MS. After 21hrs, concentration of thorium in output solution equal to input solution concentration, and after 30hrs, uranium concentration of output solution equal concentration of uranium in input solution concentration which mean biomass was saturated. Biomass was washed by distilled water and eluted by  $\text{NaHCO}_3$  0.1M solution. After finished elution process, solutions were measured by UV-spectrometer.

Maximum uranium absorption capacity	Maximum thorium absorption capacity
□ 350 mg U/g biomass	□ 150mg Th/g biomass

Biomass was regenerated by NaOH 0,1N solution and washed by distilled water until neutralize. Biosorption process was repeated. Concentration of uranium and thorium in output solution were measured by ICP-MS as below:

**Tab 11.** U, Th concentration of output solution

No	Sample	Conc. U (ppm)	Conc. Th (ppm)
1	M 1-3	0,024	0,012
2	M 1-4	0,020	0,011
3	M 2-4	0,007	0,003
4	M 2-3	0,011	0,015

The ICP-MS results showed that U, Th concentration of output solution are lower than Nuclear Safety Regulation of Vietnam (TCVN4379-87) to uranium are 1.8mgU/l and 0.15mgTh/l, respectively.

### Conclusion

1. Vietnamese biomass contents are corresponding to application researches.
2. Biosorption process was not depended on temperature.
3. Biosorption process depend on time. Biosorption efficiency can be reached 99.9%U and 99%TH at t=180min then reduce because the cell wall networks have been broken by media acid.
4. At pH = 2.5 in HCl medium, 97.95% U and 97.68%Th can be absorbed.
5. At pH = 8.3; NaHCO<sub>3</sub> eluent, 99.94%U và 90.08%Th can be eluted.
6. Biomass as active in moving phase condition. The maximum absorption capacity can be reached 350mgU/g and 150mgTh/g. Output solution concentration of U, Th are under Nuclear Safety Regulation.

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## **ANALYSIS & EVALUATION OF ACTIVITY LEVEL OF $^{134}\text{Cs}$ , $^{137}\text{Cs}$ , $^{232}\text{Th}$ , $^{238}\text{U}$ , $^{40}\text{K}$ IN AQUATIC PRODUCTS (FISH, SHRIMP, CUTTLE-FISH, ...) OF THE SOUTH OF VIET NAM**

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**Abstract:** *In recent decades, applications of improved techniques for increasing the quantity and the quality of aquatic products have shown good results but we also have experienced some unwilling influences which are decreased the quality of these products. Furthermore, impacts of using of nuclear energy in the world for peaceful purposes, nuclear accidents and nuclear weapon testings have increasing radioactive background level in the environment and in food – foodstuff, etc. So, we need to know about radioactivity level in environment to protect our health.*

*The main goal of this study was to monitor and evaluate the activity levels of  $^{134}\text{Cs}$ ,  $^{137}\text{Cs}$ ,  $^{40}\text{K}$ ,  $^{232}\text{Th}$ ,  $^{238}\text{U}$  in aquatic products of the south of Vietnam.*

### **I. Introduction**

To analyse radioactivity level of  $^{134}\text{Cs}$ ,  $^{137}\text{Cs}$ ,  $^{40}\text{K}$ ,  $^{232}\text{Th}$ ,  $^{238}\text{U}$  in aquatic products,

We used:

- The low background gamma spectrometer at our laboratory with relative efficiency of 17.3%, energy resolution of 1.8 keV at peak of 1332 keV ( $^{60}\text{Co}$ ), the ratio of peak and Compton of 45/1 at 1332 keV ( $^{60}\text{Co}$ ) and decreasing background of lead container of 160 times comparing between the counts taken outside and inside the lead container. Total count inside lead container is 0.961 counts per second.
- Sample containers are  $2\pi$  plastic ones containing about 10 gram of ash of about 1000 gram of fresh fish flesh.
- Standard sample is the ash of 250g powder containing 6.15Bq of  $^{134}\text{Cs}$ , 1.695Bq of  $^{137}\text{Cs}$ , 1.29 Bq of  $^{232}\text{Th}$ , 4.05 Bq of  $^{40}\text{K}$  and 1.2 Bq of  $^{238}\text{U}$  produced by level II standard laboratory – Institute for nuclear science and technology (INST), Ha Noi – Viet Nam.
- Time for measuring of every aquatic ash sample in the gamma spectrometer is 24 hours.
- Detection limits in 10g of ash of about 1000 gram of fresh fish flesh were determined by theory guided by Canberra Company. The results are as follows:

No.	Nuclide	Detection limit (Bq/kg)
1	$^{137}\text{Cs}$	0.002
2	$^{134}\text{Cs}$	0.002
3	$^{40}\text{K}$	0.150

4	$^{232}\text{Th}$	0.005
5	$^{238}\text{U}$	0.005

## II. Experimental

### II.1 Sample preparation

\* *Fishes having large size (Basa, Scad, Tuna, blue fish,...)*

- Fresh fishes collected from main markets, were primary cleaned (removed gills, intestines, fins, scales,...).
- Fishes were freezed by refrigerator until sampling to measure.
- Recording the weight of the fishes, taking 1 kg.
- Heating the sample in the oven at 100°C during 4 hours.
- Separating bones from flesh fishes.
- Weighting the bones and determining the weight of the flesh fishes.
- Heating the fish flesh at 200°C during 6 hours.
- Still heating the sample at 400°C during 16 hours.
- Collecting ash in the oven, storing in the container and measuring by the low background gamma spectrometer.

\* *Fishes having small size (Anchovy, Goby,...)*

- Fresh fishes collected from main markets, were primary cleaned (removed heads, adiantums, cover, legs...).
- Fishes were freezed by refrigerator until sampling to measure.
- Recording the weight of the fishes, taking 1 kg.
- Heating the sample in the oven at 100°C during 4 hours.
- Heating the fish flesh at 200°C during 6 hours.
- Still heating the sample at 400°C during 16 hours.
- Collecting ash in the oven, storing in the container and measuring by the low background gamma spectrometer.

\* *Shrimps, Cuttle-fishes, ...*

- Fresh shrimps (cuttle-fishes,... ) collected from main markets, were primary cleaned (removed heads, adiantums,...).
- Shrimps (Cuttle-fishes,...) were freezed by refrigerator until sampling to measure.
- Recording the weight of the shrimp flesh , taking 1 kg.
- Heating the sample in the oven at 100°C during 4 hours.
- Heating the flesh shrimps (cuttle-fishes,...) at 200°C during 6 hours.
- Still heating the sample at 400°C during 16 hours.



- Collecting ash in the oven, storing in the container and measuring by the low background gamma spectrometer.

### ***II.2 Verification of the accuracy of results***

Interpolation methods were used to calculate the activity level of each nuclide in aquatic-products sample. At first, the counts of peak areas for 4 samples of known activity were measured and approximation curves were drawn. Finally the activity of each nuclide was measured using the drawn curves. The results are given in the table 1/ below.

**Tab 1.** Verification of the accuracy of results

No	Nuclide	Estimation values	Values analyzed by Dalat Nuclear Research Institute (DNRI)	Values analyzed by present study
1	<sup>238</sup> U	0.10	0.07	0.13
2	<sup>232</sup> Th	0.29	0.13	0.12
3	K-40	95.53	133.06	89.72
4	<sup>134</sup> Cs	-	-	-
5	<sup>137</sup> Cs	0.06	0.08	0.11

*Note: samples used here were blue fish collected at Phan Thiet and Basa collected at An Giang.*

### **III. Results**

- Activity level of <sup>134</sup>Cs, <sup>137</sup>Cs, <sup>238</sup>U, <sup>232</sup>Th, <sup>40</sup>K in aquatic products at the South of Viet Nam were presented in table 1.
- Activity maximum levels of <sup>137</sup>Cs in aquatic products collected at Viet Nam were compared to the results of activity maximum levels of <sup>137</sup>Cs in aquatic products of some countries were presented in table 2.

### **IV. Conclusion**

- Activity levels of <sup>134</sup>Cs, <sup>137</sup>Cs, <sup>238</sup>U, <sup>232</sup>Th, <sup>40</sup>K in aquatic products of south areas of Viet Nam are well below comparing with these activity levels in aquatic products of European countries.
- From the results presented in table 1, we can conclude that quality of aquatic products of Viet Nam is good in aspect of radioactive contamination
- Our laboratory – Radiation Protection and Environmental Monitoring Department – is able to carry out this analysis with enough accuracy.

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**Tab 2.** Radio-activity of Cs-137 in marine fish flesh of Barent sea areas before and after happening Kursh accident were comparing to radio-activity of Cs-137 in marine fish flesh of European sea areas

Barent sea areas		European Sea	Man Island (2001)	Viet Nam sea areas
Before Kursh accident 12/08/2000	After Kursh accident 12/08/2000			
< 1 Bq/kg fresh fish flesh	Max. 0.27 Bq/Kg fresh fish flesh	0.3 – 21.0 Bq/Kg fresh fish flesh	1.3 – 7.3 Bq/Kg fresh fish flesh	Max. 0.2 Bq/kg fresh fish flesh

**Tab 3.** Radioactivity of Cs-137, Cs-134, Th-232, K-40 in aquatic products of the south areas of Viet nam

No	Sample	Place	Radioactivity (Bq/kg)									
			U-238		Th-232		K-40		Cs-137		Cs-134	
			Activity	Error	Activity	Error	Activity	Error	Activity	Error	Activity	Error
1	Anchovy	Nha Trang	0.11	0.01	0.06	0.02	31.04	7.76	0.04	0.01	-	
2		Can Tho	0.03	0.01	0.02	0.01	24.81	6.69	0.03	0.01	-	
3		Ho Chi Minh City	0.08	0.02	0.03	0.01	28.17	7.43	0.03	0.01	-	
4	Scad	Phan Thiet	0.11	0.06	0.12	0.04	84.14	18.69	0.11	0.01	-	
5		Vung Tau	0.15	0.04	0.07	0.03	60.85	12.75	0.10	0.01	-	
6		Ho Chi Minh City	0.09	0.03	-		89.72	22.86	0.15	0.03	-	
7	Tuna	Phan Thiet	0.12	0.03	0.13	0.06	77.22	18.05	0.14	0.05	-	
8		Kien Giang	0.12	0.03	0.11	0.04	75.44	15.27	0.12	0.03	-	
9		Ho Chi Minh City	0.07	0.02	0.10	0.03	58.30	15.70	0.08	0.02	-	
10	Fly fish	Nha Trang	0.15	0.04	0.13	0.06	59.63	16.32	0.08	0.03	-	

11		Ho Chi Minh City	0.10	0.06	0.07	0.04	58.58	15.84	0.15	0.04	-	
12	Blue fish	Phan Thiet	0.05	0.02	0.15	0.05	48.82	11.53	0.04	0.02	-	
13		Ho Chi Minh City	0.08	0.03	0.08	0.03	50.28	12.17	0.06	0.03	-	
14	Carp	Vung Tau	0.14	0.06	0.11	0.04	43.84	11.37	0.07	0.03	-	
15		Ho Chi minh City	0.14	0.04	0.02	0.01	45.63	12.13	0.06	0.02	-	
16	Basa	Can Tho	0.07	0.02	0.06	0.02	43.97	11.39	0.04	0.02	-	
17		An Giang	0.07	0.02	0.01	0.01	32.08	9.15	0.07	0.02	-	
18	Codfish	Vung Tau	0.08	0.03	0.15	0.06	45.30	12.50	0.03	0.02	-	
19		Ho Chi Minh City	0.10	0.06	0.11	0.05	70.23	16.20	0.02	0.01	-	
		Result intervals	0.03 – 0.15		0.02 – 0.15		24.81 – 89.72		0.02 – 0.15		< 0.02	
No	Sample	Place	Radioactivity (Bq/kg)									
			U-238		Th-232		K-40		Cs-137		Cs-134	
			Activity	Error	Activity	Error	Activity	Error	Activity	Error	Activity	Error
20	Bone	Tuna – Kien Giang	0.08	0.05	0.09	0.03	76.78	13.88	0.12	0.05	-	
21		Tuna – Phan Thiet	0.06	0.04	0.09	0.05	76.58	13.90	0.12	0.05		
22		Tuna – HCM City	0.21	0.08	0.06	0.02	59.99	12.47	0.25	0.06	-	
23		Scad – Phan Thiet	0.09	0.02	0.18	0.12	61.65	13.29	0.20	0.06	-	
24		Blue fish –HCM City	0.24	0.13	0.16	0.09	60.86	13.02	0.16	0.05	-	
25		Carp – HCM City	0.20	0.06	0.12	0.04	24.28	7.82	0.05	0.04	-	
		Result intervals	0.06 – 0.24		0.06 – 0.18		24.28 – 76.78		0.05 – 0.25		< 0.02	
26	Sugpo prawn	Kien Giang	0.06	0.02	0.07	0.03	22.87	7.09	0.02	0.01	-	
27		Vung Tau	0.09	0.03	0.17	0.07	44.30	12.56	0.03	0.02	-	

28		Ho Chi Minh City	0.12	0.03	0.09	0.03	25.75	9.37	0.02	0.01	-	
29	White shrimp	Nha Trang	0.04	0.01	0.11	0.04	45.80	11.20	0.04	0.02	-	
30		Ho Chi Minh City	0.08	0.03	0.07	0.03	55.75	14.58	-	-	-	
		Result intervals	0.04 – 0.12		0.07 – 0.17		22.87 – 55.75		0.02 – 0.04		< 0.02	
31	Squid	Kien Giang	0.05	0.02	0.03	0.01	3.26	0.92	0.02	0.02	-	
32		Can Tho	0.13	0.04	0.04	0.01	1.52	0.27	-		-	
33		Ho Chi Minh City	0.04	0.01	0.07	0.04	2.01	0.79	-		-	
34	Squid	Kien Giang	0.06	0.04	0.08	0.03	4.18	1.14	0.03	0.01	-	
35		Can Tho	0.06	0.03	0.07	0.04	2.47	0.62	0.02	0.01	-	
36		Ho Chi Minh City	0.02	0.01	0.07	0.03	3.72	0.87	0.02	0.01	-	
		Result intervals	0.02 – 0.13		0.03 – 0.08		1.52 – 4.18		0.02 – 0.03		< 0.02	
No	Sample	Place	Radioactivity (Bq/kg)									
			U-238		Th-232		K-40		Cs-137		Cs-134	
			Activity	Error	Activity	Error	Activity	Error	Activity	Error	Activity	Error
37	Shell	Can Tho	0.05	0.03	0.18	0.09	35.75	9.16	0.03	0.02	-	
38		Ho Chi Minh City	0.11	0.05	0.27	0.12	36.62	9.57	0.04	0.02	-	
		Result intervals	0.05 – 0.11		0.18 – 0.27		35.75 – 36.62		0.03 – 0.04		< 0.02	
39	Seaweed	Nha Trang	1.04	0.23	3.98	0.87	993.10	211.08	0.21	0.08	-	
40	Small gut	Basa –An Giang	0.02	0.01	0.06	0.03	19.39	6.56	-		-	
41	Cover of Sugpo prawn	Ho Chi Minh City	2.93	0.33	0.51	0.12	15.07	4.68	0.03	0.02	-	

## 1.7 - Biotechnology and Agriculture

## **STUDY THE EFFECT OF MICRO-RARE EARTH FERTILIZER ON THE PRODUCTIVITY, QUALITY AND PHYSIOLOGY OF TEA PLANT**

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**Abstract:** *To affirm advantages of the rare earth fertilizer on tea tree, the effect of micro-rare earth fertilizer on the productivity, quality and physiology of tea plant, had tested on young tea plants and tea plants on harvest at Tea Song Lo Company and Tea Research Institute. the compare of the remain of rare earth elements on product have been carried out at Institute of Technology for Radioactive and Rare Elements. The results showed that: the application of rare earth fertilizer can increase the yield from 10 -24.8%. increase the weigh of tea plant roots to 38 - 40%. decrease ratio of new shoots without youngest leaf from 10% to 7.8%. decrease processing coefficient K from 4.57 to 4.2 kg of new shoots/kg of dry tea. decrease the tannin content. increases the content of deoxidize glucose. These factors contributed to increase the yield and the quality of tea.*

**Key words:** *fertilizer, rare earth, physiology, tea tree.*

### **Introduction**

It has been known that Rare Earth Elements widely exist in the earth crust at the average content of 0.0153 %  $R_2O_3$ . The content of Rare Earth Elements in the soil is in the range of 0.015-0.02 %  $R_2O_3$ . Rare Earth Element content in plants and in the lake-water have been found to be approximately 0.003% and <0.001 ppm  $R_2O_3$ , respectively. Thus, it seems that plants absorb rare earth elements from the soil for their growing up. Based on the practice of tea plantation, it could be realized that the crop yield of tea in Tam Duong, Phong Tho, Lai Chau was higher than in many other areas in North Vietnam and the quality of tea products in those areas was also better. It was noticed that Tam Duong tea farm is located very closely to a rare earths mine in Phong Tho. Therefore, a question that whether rare earth elements have a good influence on the crop yield of tea has been taken into consideration.

The study on the application of micronutrients containing very low contents of Rare Earth Elements have been conducted in China, Australia, etc. The experimental data showed that in proper conditions, the use of rare earths micronutrients could give much higher crop yield and better quality of the products. During two years 2001-2002, under the frame work of the Ministry Project namely "Study on the preparation for some Rare earth products for increasing tea crop yield", Purification Technology Division, Institute for Technology of Radioactive and Rare Elements produced several kinds of rare earth micronutrients. These kinds of micronutrients (PBD1 and DH1) have been first experimentally applied to germinating and planting tea-trees in some places in the North of Vietnam such as the Song Lo Tea Company (Tuyen Quang province) and the

Cuu Long Farm (Hoa Binh province). The preliminary studies showed that the application micro-rare earth fertilizer with different on quantity and the way of use the young tea plants grow very well, the crop yield of tea plant increased from 10 – 38,3%, the quantity of new shoots with A quality level increased. It is advantage of micro-rare earth fertilizer over other fertilizers.

## Contents

### 1. Experiments

To affirm these advantages of a new fertilizer, the productivity, the quality and physiology of tea plant had been studied under the frame work of the Ministry Project namely “**Study the effect of micro-rare earth fertilizer on the productivity, quality and physiology of tea plant**”. The tests had been carried out at Tea Song Lo Company and Tea Research Institute.

To study the effect of micro-rare earth fertilizer on the productivity, quality and physiology of tea plant, the different ways of put down fertilizer had tested on young tea plants and tea plants on harvest. The tested factor of the effect concluded

- For young tea plant: The high of the tree, the diameter of the tree-trunk, the number of really leaves, the weight of roots.
- For tea plant on harvest: the density of new shoots, productivity of new shoots, the ratio of new shoots without the youngest leaf per all of new shoots, mechanical components of new soot, chemical components of new soot, tea quality and the ability to protect disease of the tree...

Besides, the application of micronutrient rare earth fertilizer had been carried on other food plants and vegetables, such as: rice, maize, cabbage, sweet-cabbage, tomato, rau muong, strawberry, daisy.

The remained content of rare earth elements on food after application of rare earth fertilizer had been tested to affirm the safe and the advantage of these new

### 2. Results

#### 2.1. Results of experiment on young tea plants

The results of the studying the effect of micronutrients rare earth fertilizer on the growing of young tea plants were showed in the flowing tables:

**Tab 1.** The growing of young tea plants 40 days after spraying RE fertilizer (Song Lo Tea Company, Tuyen Quang Prov)

Factor	CT1 (Control)	CT2 (Spray100 ml “Thuy Tien”/360 m <sup>2</sup> )	Comparison (%)
The high of the tree (cm)	23,5	25	106,4
The diameter of tree-trunk (mm)	3	3,1	103
The number of real leaves	8	8	100
The weight of tree-root ( g)	1,5	2,1	140

**Tab 2.** The effect of RE fertilizer on the growing of young tea plants  
(Phu Ho Tea Research Institute, Phu Tho Prov)

No	Sample	The high of the tree		The diameter of tree-trunk		The number of real leaves	
		cm	%	cm	%	Amount	%
1	Control	28,33	100,0	0,23	100,0	10,0	100,0
2	Spraying 50ml/180 m <sup>2</sup>	35,00	123,6	0,27	117,4	13,0	130,0
3	Spraying 75ml/180 m <sup>2</sup>	36,5	128,8	0,28	121,7	12,5	125,0

**Tab 3.** The effect of RE fertilizer on the growing of young tea plants  
(Phu Ho Tea Research Institute, Phu Tho Prov.)

No	Sample	The weight of tree-trunk		The weight of leaves		The weight of roots	
		g	%	g	%	g	%
1	Control	0,49	100,0	0,6	100,0	0,18	100,0
2	Spraying 50ml/180 m <sup>2</sup>	0,58	118,4	0,8	133,3	0,22	122,2
3	Spraying 75ml/180 m <sup>2</sup>	0,72	146,9	0,75	125,0	0,25	138,8

## 2.2. Results of experiment on the tree planting on harvest

**Tab 4.** The results of the growing of tea tree on harvest  
(Song Lo Tea Company)

Factor	Spraying			Control			Comparison %
	1 <sup>st</sup> pick tea leaves	2 <sup>nd</sup> pick tea leaves	average	1 <sup>st</sup> pick tea leaves	2 <sup>nd</sup> pick tea leaves	average	
Density of tea tender leaves /m <sup>2</sup>	100	76	88	85.7	70	77.8	113.1
Weight of tea tender leaves (g)	0.516	0.561	0.538	0.515	0.54	0.526	102.28
The thick of tea leaf (mm)	0.186	0.18	0.183	0.18	0.177	0.178	102.8
The color of tea leaves	Dark green	Dark green		Yellow green	Yellow green		



**Tab 5.** The effect of RE fertilizer on growing of tea tree  
(Tea Research Institute)

No	Sample	The high of trees		The wide of leaf canopy		The thick of leaf canopy	
		cm	%	cm	%	cm	%
1	Control	86.54	100.0	104.0	100.0	42.0	100.0
2	Spray 2.8 l/ha	88.67	102.5	109.0	104.9	45.0	107.1
3	Spray 4.2 l/ha	90.33	104.4	113.3	108.9	47.3	112.6
4	Put down ferti. 5.6 kg/ha	89.32	103.2	105.0	100.9	44.0	104.8
5	Put down 5.6 kg + spray 2.8 l/ha	93.00	107.5	112.7	108.4	48.6	115.7

**Tab 6.** The effect of spraying “Thuy Tien” and put down PBD1 on productivity  
of tea tender leaves (Song Lo Tea Company, Tuyen Quang Prov.)

No	Sample	Square of spray m <sup>2</sup>	The results of pick of tea tender leaves					
			1 <sup>st</sup> pick 22/7	2 <sup>nd</sup> pick 22/7	3 <sup>rd</sup> pick 7/8	sum	Compari- -son	Compari- -son
1	Control (without spraying)	360	9.8	9.4	10	29.2	100	
2	Spraying 100ml/360 m <sup>2</sup>	360	11.5	9.5	14	35	119.8	
3	Spraying 150ml/360 m <sup>2</sup>	360	8.5	9.8	13	31.3	107.2	
4	Control (without put down 5 kg PBD1)	360	9.5	9.9	10	29.4		100
5	Put down PBD1	180	5	5.8	4.4	15.2		110.9
6	Spraying 50ml/180 m <sup>2</sup> and put down 5 kg PBD1	180	5.5	6	5.6	17.1		124.8

**Tab 7.** The effect of RE fertilizer on factors relating to productivity of tea (Phu Ho Tea Research Institute. Phu Tho Prov.)

TT	Sample	The length of tea tender leaves		The weight of tea tender leaves		The density of tea tender leaves	
		cm	%	g/shoot	%	shoot/m <sup>2</sup>	%
1	Control	3.95	100.00	0.57	100.00	87.1	100.00
2	spray 2.8 l/ha	3.90	98.73	0.57	100.00	91.5	105.00
3	spray 4.2 l/ha	4.08	103.29	0.58	101.7	100.6	115.5
4	Put down 5.6 kg/ha	3.88	98.23	0.57	100.00	93.5	107.3
5	spray 2.8 l/ha and put down 5.6 kg/ha	4.09	103.54	0.58	101.7	105.9	121.6

**Tab 8.** The effect of RE fertilizer on mechanical component of tea shoots (Phu Ho Tea Research Institute. Phu Tho Prov.)

STT	Sample	The weight of bud (%)	The weight of 1st leaf (%)	The weight of 2nd leaf (%)	The weight of 3rd leaf (%)	The weight of stem (%)
1	Control	5.25	9.06	19.66	32.46	33.50
2	Spray 2.8 l/ha	5.36	9.03	19.86	33.72	32.00
3	Spray 4.2 l/ha	5.24	8.62	19.64	34.67	31.80
4	Put down 5.6 kg/ha	5.20	8.70	20.56	32.76	32.90
5	Spray 2.8 l/ha and put down 5.6 kg/ha	5.93	8.22	20.31	32.59	33.23

**Tab 9.** The effect of RE fertilizer on productivity of tea shoots (Phu Ho Tea Research Institute. Phu Tho Prov.)

STT	Sample	Productivity		Ratio of shoots without bud %
		Kg/ha	%	
1	Control	4140	100.00	10.08
2	Spray 2.8 l/ha	4493	108.53	8.37
3	Spray 4.2 l/ha	4695	113.41	7.86
4	Put down 5.6 kg/ha	4500	108.69	9.94
5	Spray 2.8 l/ha and put down 5.6 kg/ha	4763	115.04	7.66

**Tab 10.** The effect of RE fertilizer on chemical contents of tea tender leaves  
(Phu Ho Tea Research Institute. Phu Tho Prov.)

No	Sample	Tannin (%)	Soluble components (%)	Deoxidize glucose (%)
1	Control	29.45	36.79	2.18
2	Spray 2.8 l/ha	28.11	36.26	2.31
3	Spray 4.2 l/ha	27.89	35.98	2.36
4	Put down 5.6 kg/ha	27.22	34.46	2.55
5	Spray 2.8 l/ha and put down 5.6 kg/ha	27.93	34.02	2.75

**Tab 11.** The effect of RE fertilizer on tea quality  
(Phu Ho Tea Research Institute. Phu Tho Prov.)

Factor Sample	Appearance		The color of tea liquid		Perfume		Tasted		Final remark	
	Remark	Mark	Remark	Mark	Remark	Mark	Remark	Mark	Mark	Remark
1	Regular curly, slightly snow	4.08	Yellow green. Slightly diluted	2.35	Fragrant	5.2	Soft acrid	5.0	16.63	Rather good
2	Slightly crude, slightly snow	3.92	Yellow green. Slightly diluted	2.4	Light fragrant	4.8	Soft acrid	4.9	16.02	Rather good
3	Slightly crude, slightly snow	3.92	Yellow green. Thick	2.6	Light fragrant	4.8	Soft acrid	4.9	16.22	Rather good
4	Regular curly, young	4.25	Yellow green. Slightly diluted	2.4	Light fragrant	4.9	Soft acrid	4.8	16.35	Rather good
5	Regular curly, young	4.42	Yellow green. Thick	2.55	Special fragrant	5.1	Soft acrid	4.8	16.87	Rather good

**Tab 12.** The results of tea taste (Song Lo tea Company, Tuyen Quang prov.)

Factor	Pick on PM 21/10/03		Pick on AM 22/10/03	
	<i>Spray "Thuy Tien"</i>	<i>Control</i>	<i>Spray "Thuy Tien"</i>	<i>Control</i>
The color of tea liquid	Light-green	Diluted light-green	Thick- green	Diluted light-green
Perfume	Light fragrant	Light fragrant	Fragrant	Light fragrant
Tasted	Light bitter	Bitter	Light bitter	Bitter
K coefficient	4.14	4.39	4.2	4.57

### Conclusions

The results of experimentations showed that the application of rare earth fertilizer can increase the yield from 10% to 24.8%, increase the weigh of tea plant roots 38-40%, decrease ratio of new shoots without youngest leaf from 10% to 7.8%, decrease processing coefficient K from 4.57kg to 4.2 kg of new shoots per 1kg of dry tea, decrease the tannin content, increases the content of deoxidize glucose. These factors contributed to increase the yield and the quality of tea.

The application of RE fertilizer not only gives better crop yield and quality of tea products but also strengthen the resistibility/resistance to pets and diseases of tea trees. As a result, the use of pesticides/insecticides can be obviously reduced, giving the considerably lower cost of tea products. So far analytical data have showed only trivially small remaining/residual contents of RE in tender tea leaves that we could believe in the safety of tea products.

However, in order to affirm the effects of rare earth micronutrient application on tea production and crop yield as well as the quality and safety of tea products, the remained content of RE on dry tea had been determined and compared with the imported tea products that are being used in Vietnam.

It is hoped that the preliminary results of this project will be more widely applied in our agriculture, so that they can partly contribute to the poverty-alleviation movement in the midland and mountainous regions and effectively exploit rare earth resources in Vietnam.

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## **ISOLATION AND SELECTION OF SOME *TRICHODERMA* STRAINS POSSESSING ANTAGONISTIC ABILITIES AGAINST PLANT PATHOGENIC FUNGI**

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Tran Thanh Han, Le Viet Ngoc and Doan Nam Sinh**

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**Abstract:** *In our works, twenty four strains of Trichoderma were isolated. All of these Trichoderma spp. were tested in vitro for antagonistic ability against Rhizoctonia spp.- causing “Sheath Blight” on rice, and Botrytis spp.- causing “Gray Mold” on strawberry. The experiments showed that isolate T-8 directly attack and effectively control Rhizoctonia spp. in Petri dishes, similarly, isolate T-6 effectively control Botrytis spp.. The isolate T-12 showed inhibition effect on mycelial growth of both Rhizoctonia spp. and Botrytis spp.. Also, in a nylon house experiment screened against “Clubroot” (Plasmodiophora brassicae) on cabbage, two of the 21 isolates tested significantly reduced disease severity compared to the untreated control.*

**Key words:** *Trichoderma, antagonistic abilities*

### **Introduction**

The antagonistic abilities of some species of *Trichoderma* genus against plant disease-causing fungi was first recognized in 1930s. Antagonism of these species is based on different mechanisms like the competition for space and nutrients, the production of antifungal metabolites and mycoparasitism. Up to now, a lot of studies applying *Trichoderma* as biocontrol agents have been developed in the world.

In Vietnam, during a long period before, crop productivity was considered as the most important factor of agricultural production. To increase yield, farmers used and abused chemical pesticides without giving any care to undesirable environmental and ecological impacts. In the present economic background, the needs of being clearer in production activities and of improving the quality level of agriculture products do exist. The measure of biological control, however, is still so new and hasn't been paid adequate attention yet because using chemicals had already become a habit.

The aim of our project is to approach the above requirements and go towards preparing biocontrol products that may be used for local cultivation practice. Products derived from the project were strains of *Trichoderma* isolated from agricultural areas where they're expected to function in disease control. These native strains can then be screened *in vitro* with native fungal pathogens to evaluate the antagonistic abilities. Potential biocontrol strains of *Trichoderma* obtained in this manner might be more compatible with pathogens and ecological conditions of the area than those isolated from other places.

### **Content**

- Isolation and identification of *Trichoderma*.
- Isolation of plant disease-causing fungi.

- Evaluation of the *in vitro* antagonistic abilities of *Trichoderma* strains against fungi pathogens.
- Preservation of selected strains of *Trichoderma*.

**Results**

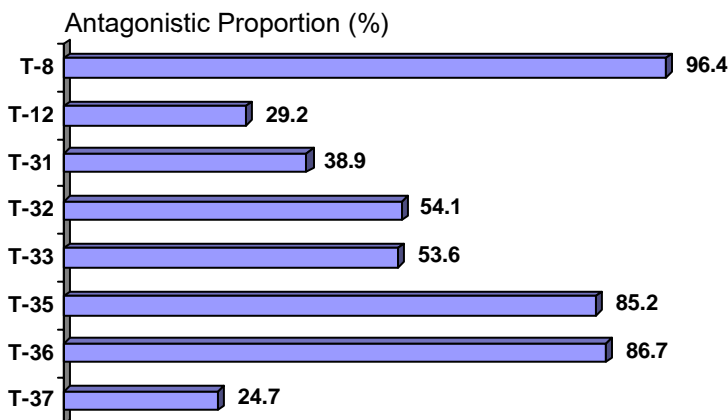
**Isolation and identification of *Trichoderma***

Twenty four strains of *Trichoderma* have been isolated. Most of them were from compost for cultivated mushroom and organic wastes.

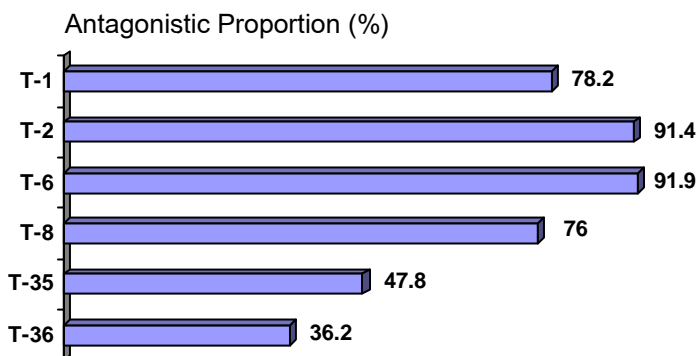
**Isolation of plant disease-causing fungi**

Two isolates of plant pathogen fungi have been isolated including *Rhizoctonia* spp.- causing “Sheath Blight” on rice, and *Botrytis* spp.- causing “Gray Mold” on strawberry.

**Evaluation of the *in vitro* antagonistic abilities of *Trichoderma* strains against fungi pathogens**



**Fig. 1.** Antagonistic abilities of *Trichoderma* strains against *Rhizoctonia* spp.

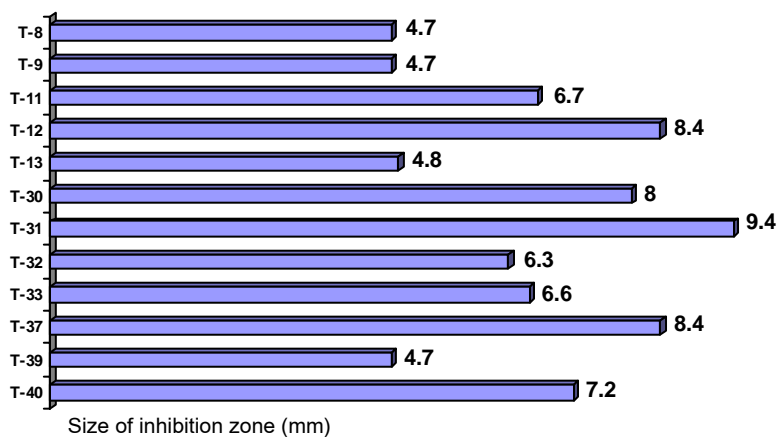


**Fig. 2.** Antagonistic abilities of *Trichoderma* strains against *Botrytis* spp.

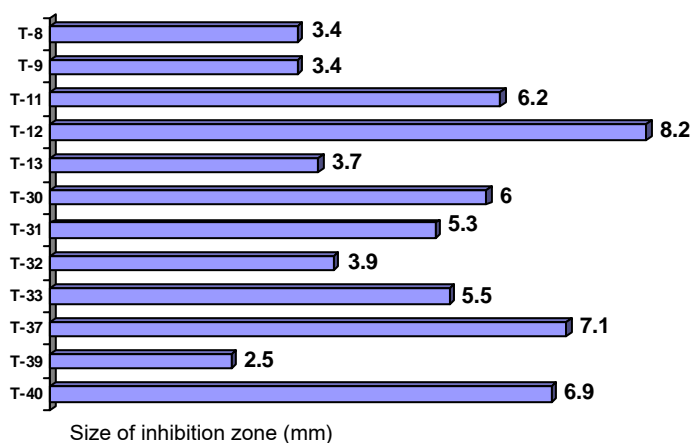
*Trichoderma* strains including in our test showed the biological specificity in antagonistic activity against different pathogen fungi. None of them was multipurpose,



i.e. having good antagonistic abilities against both *Rhizoctonia* spp. and *Botrytis* spp. (Fig. 1, Fig. 2). Although there seemed have not had very strict specificity in activity of growth inhibition of pathogen fungi by *Trichoderma* (Fig. 3, Fig. 4).



**Fig. 3.** Inhibition of mycelial growth of *Rhizoctonia* spp. by *Trichoderma* strains



**Fig. 4.** Inhibition of mycelial growth of *Botrytis* spp. by *Trichoderma* strains

Screening for potential biocontrol of clubroot caused by *Plasmodiophora brassicae*

**Tab 1.** Summary of trial results

Treatment	Clubroot (0 – 5)	LSD (P = 0,05)	Significant
T-1	4,30	0,385	-
T-2	3,89	0,205	-
T-6	4,13	0,569	-
T-8	0,33	0,316	**
T-10	4,00	0,361	-
T-11	4,75	0,304	-

T-12	4,30	0,275	-
T-13	4,00	0,427	-
T-14	3,10	0,641	*
T-20	4,10	0,213	-
T-26	3,44	0,335	-
T-30	4,75	0,588	-
T-31	4,78	0,279	-
T-32	0,75	0,931	**
T-33	4,40	0,403	-
T-35	3,89	0,651	-
T-36	4,10	0,403	-
T-37	4,63	0,494	-
T-38	4,44	0,335	-
T-39	4,22	0,279	-
T-40	4,30	0,275	-
Untreated	4,50	0,550	-

(-): Not significant; (\*):  $0,001 < p < 0,01$ ; (\*\*):  $p < 0,001$ .

The results of rapid screening test for “Clubroot” on cabbage in nylon house experiment showed that two strains T-8 and T-32 significantly reduced disease severity compared to the untreated control ( $p < 0,001$ ).

### Conclusion

- Because of the biological specificity of *Trichoderma* strains in antagonistic activity against different pathogen fungi, *in vitro* screening tests are necessary to evaluate and select potential strains for *in vivo* testing.

- Basing on our experimental results, following strains had been selected for further studies:

T-6: Possessing antagonistic ability against *Botrytis* spp. (91,9 %)

T-8: Possessing antagonistic ability against *Rhizoctonia* spp. and *Botrytis* spp. (96,4 % and 76 % respectively). Significant reducing disease severity of clubroot on cabbage ( $p < 0,001$ ).

T-12: Inhibition of mycelial growth of *Rhizoctonia* spp. and *Botrytis* spp.

T-32: Significant reducing disease severity of clubroot on cabbage ( $p < 0,001$ ).

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## **STIMULATION OF GROWTH OF POTATO EXPLANTS (*SOLANUM TUBEROSUM* L.) CULTURED *IN VITRO* BY LOW DOSES OF GAMMA RAYS**

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**Abstract:** *Low doses of gamma-rays (50, 100, 200 and 300 Rad) enhanced growth of potato plantlets and frequency of tuberization (from 60 to 80%) from isolated nodes cultured in vitro. The low doses of 50, 100 and 200 Rad also speeded up the sprouting of the irradiated microtubers, and induced higher yields of marketable tubers derived from these micro ones (17-25% higher yield than the controls).*

**Key words:** *Explants, Low doses of gamma-rays.*

### **Introduction**

Enhancement of plant growth by low doses of ionizing radiation has been proven and exploited for practical cultivation of different seed raising species like cabbage, cauliflower, spinach, corn, rice... (3). In potato, a plant crop grown from tubers, this positive effect of radiation has not been well investigated yet. The large size of potato tubers (ave. 4-7cm in diameter) appears to be responsible for such a limitation. Consequently, tiny potato explants derived from *in vitro* cultures, like the *in vitro* plantlets and micro tubers, could be of great potent to study the mentioned advantage of radiation. We summarize below our preliminary investigation on the effect of low doses of gamma rays on *in vitro* plantlets and micro tubers of two common potato cultivars in Vietnam: Diamond and O7.

### **Materials and methods**

*In vitro* plantlets of two common potato cultivars in Vietnam, namely O7 and Diamond, were established and rapidly cloned via the culture of single nodes on a plain medium (hereafter PM) of Murashige and Skoog formula (2). For microtuberization, nodes isolated from the *in vitro* plantlets were grown on modified PM supplemented with 8% sucrose and with 2mg/l BAP (6-benzylaminopurin). To investigate the effects of low doses of gamma-rays, the nodes and micro tubers were irradiated in sterile condition with absorbed doses of 0, 50, 100, 200 and 300 Rad, at a dose rate of 3.475 rad/sec. Irradiated nodes then were recultured *in vitro* to evaluate the radiation effects on plantlet growth and microtuberization frequency, while irradiated micro tubers were let to sprout, serving for further field planting.

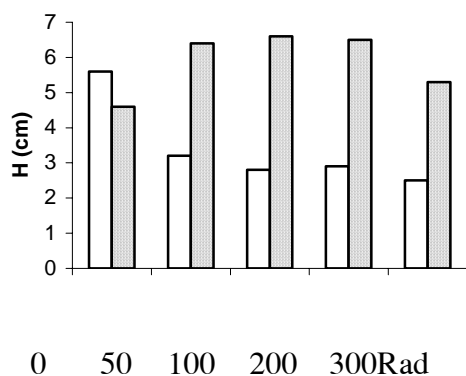
### **Results and discussion**

Gamma rays of 50-200 Rad (dose rate: 3.475 Rad/sec) were observed to enhance growth (plant height and number of formed adventitious roots) of plantlets reproduced from under-apex nodes cultured *in vitro*. Growth of the apex explants, however, was slightly retarded by the applied radiation (Fig. 1 and 2). Upon microtuberization, gamma rays of 50-300 Rad enhanced the average percentage of tuber-bearing nodes from 60% to 80%. This increment in tuber forming caused by gamma-rays, in contrast to the above

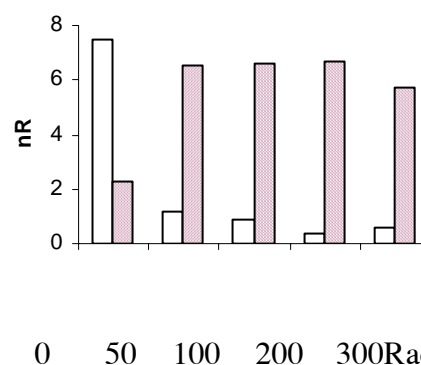
case of *in vitro* plantlets, was found mainly in apical explants (Table 1 and Fig. 3). Similarly, Al-Safadi *et al.* (2001) reported an enhancement of microtuberization frequency up to 38% higher than control by 250 Rad of gamma-rays in potato cv. Burbank (1). Interestingly, micro tubers directly treated with gamma-rays of 50-200 Rad possessed higher percentages of tuber sprouting (80% vs 60% of the control), and gave rise to meaningfully better yield of marketable tubers (17-25% higher in tuber yield) (Table 2 and Fig. 4).

### Conclusion

It is concluded that low doses (50-300Rad) of gamma-rays can stimulate growth of *in vitro*-derived explants of potato vs. Diamond and O7. A procedure to produce potentially high-yielding seed-tubers then can be set up as followings: i/ cloning of *in vitro* plantlets, ii/ mass production of *in vitro* micro tubers from these cloned plants, iii/ treatment of micro tubers with 100 Rad of gamma-rays, and iv/ direct use of radiation-treated micro tubers for commercial cultivation or treated micro tubers can be exploited as stock seed tubers for production of further high-quality miniatures.



**Fig. 1.** Effects of gamma-rays on height of apex-(white bars) and under-apex single nodes (dotted bars) of potato cv O7. Note the better growth of the under-apex nodes.



**Fig. 2.** Effects of gamma-rays on the formation of adventitious roots of apex - (white bars) and under- apex (stripped bars) nodes.

**Tab 1.** Microtuberization frequency recorded after 45 days of *in vitro* culture of single nodes irradiated with 0-300Rad of gamma-rays in potato cv Diamond.

Type of node	Tuber formation frequency (%) and tuber weight (mg) *				
	0 Rad	50 Rad	100 Rad	200 rad	300 Rad
Apex	10,5± 3,3 (46,4)	62,4± 8,2 (25,1)	87,5± 8,8 (21,3)	65,8± 7,3 (21,2)	70,6± 11 (21,4)
Under-apex	100± 0,0 (107,3)	93,7± 3,5 (57,8)	95,5± 3,3 (40,1)	100± 0,0 (39,8)	95,5± 3,3 (45,9)

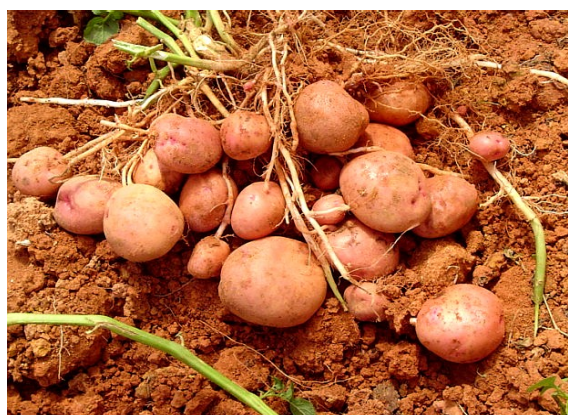
\*: Data are average results of three independent experiments, each with 16-18 nodes. Within each column, the above data are microtuberization frequencies and the below in brackets ones are tuber weights in mg. Numbers followed ± are the standard deviations.

**Tab 2.** Effects of low doses of gamma-rays on sprouting frequency and induced tuber yield of microtubers of potato cv O7.

Dose (Rad)	No. observed micro tubers	% of sprouting micro tubers	Average yield of induced tuber (Kg)	Estimated tuber yield increase (%)
0	200	66	0,92	0
50	200	88	1,08	17
100	200	86	1,15	25
200	200	72	1,12	21
300	200	58	0,90	0



**Fig. 3.** Photo presenting the *in vitro* micro tubers of potato cv Diamond (left) and cv O7 (right). Note the typically different tuber colors of the two cultivars.



**Fig. 4.** Photo showing high tuber yield of a cv O7 plant derived from a micro tuber which had been irradiated with 100Rad of gamma-rays.

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## **STUDY OF PROPAGATION OF HEAVY YIELD TEA CLONES (CAMELLIA SINENSIS L. O KUNTZE) IN LAM DONG PROVINCE BY *IN VITRO* CULTURE TECHNIQUE**

**Vo Thi Thu Ha, Nguyen Tien Thinh, Vo Thi Thu Ha, Dang Thi Dien,  
Nguyen Dinh Nhan and Tran Thanh Han**

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**Abstract:** *The initiation culture for in vitro clonal propagation has been established in tea plant. The primary explants were axillary buds of mature field – grown plants of TB14, LD 97, LDP1 cultivars. Axillary buds were culture on ½ strength MS medium supplemented with various concentrations of growth regulator including BAP, NAA, 2,4D, GA<sub>3</sub>, TDZ, Kinetin. Induction of multiple shoots growth of axillary buds dependent on concentrations of growth regulator. A high cytokinin ratio promotes shoot production. Rooting was achieved in 62% micro – shoots by liquid and shaken culture. Rooted plants were transferred to soil under glasshouse condition after hardening phase of 4 weeks*

### **Introduction**

Tea (*Camellia sinensis* [L] O. Kuntze) is a industrial perennial crop. It is being cultured in many countries on the world. It is cross -pollination and highly heterozygous. It has traditionally been propagated from seed so the crops usually are degenerated, the crops capacity is not high and requiring many years of selection to incorporate favorable traits. Asexual propagation of heavy yield tea clone is very necessary.

There are a number of reports on the micropropagation of tea on the world (Arulpragasam & Hatiff 1986; Kato 1985, 1986; Seneviratne et al 1988) – So far no reports on the micropropagation have been reported in Vietnam. Thus, the aim of this work was to develop for micropropagation the cultivars TB14, LDP1, LD 97 the most important commercial cultivars in Lam Dong province.

### **Materials and methods**

Explants were axillary bud segments (about 1-1,5cm) from the first 3-4 nodes of actively growing shoots from field-grown plants and the young leaves of cultivars TB14, LDP1, LD 97. The explants were washed in running tap water for 30 min followed by detergent. The axillary bud segments and leaves were disinfested with 0,1% mercuric chloride (w/v) for 5-20 min. Then, washed with sterile distilled water 6 times before use.

To decrease effect of tannin, before culture we dipped explants in Na<sub>2</sub>SO<sub>3</sub> solution 50mg/l for 1/4 sec.

The medium for initiation of culture is 1/2 strength MS mineral nutrients along with MS vitamin, saccharose 30g/l, agar 8g/l. Dependence on purpose of each experiment, we supplemented various growth regulator including BAP, NAA, 2,4D, GA<sub>3</sub>, TDZ, Kinetin.

Unless otherwise stated, all media were adjusted to pH 5,2-5,3 and sterile at 121°C under 1,2 atm pressure for 15 min. Each experiment consisted of 50 explants and results were confirmed after repeating at 3 times. The explants were put into agar medium and maintained at room temperature, under fluorescent light 16 h/day.

## Results

Like many other woody species, tea is a difficult plant for application of tissue culture due to interference from phenolics and microbial contamination. With the above-mentioned technique, the primary explants were contaminated and died about 20-22% after 2 weeks inoculation.

### *1. Effect of growth regulators on the induction of multiple shoots of axillary buds*

Initiation of growth of primary explants depended on growth regulator

- On ½ MS medium without GA<sub>3</sub> and BAP, shoot didn't grow.
- On ½ MS medium supplemented only BAP, frequency of explants response is low.

A combinations of BAP and GA<sub>3</sub> were found to be best for growth of the primary axillary bud. Frequency of explants response was decreased when concentrations of BAP ranging from 1mg/l to 3mg/l.

Effect of different cytokinin on shoot proliferation in tea was established. The combination of different cytokinin promoted the stimulation of axillary buds.

The combinations of BAP, IBA and kinetin were found to be best for both growth of the explants and multiple shoot formation (table 1). The induction of multiplication shoots and growth of axillary buds was best obtained on medium along with 4mg/l BAP, 2mg/l Kinetin, 0,2mg/l IBA.

**Tab 1.** Effect of BAP, IBA, Kinetin to in duction of multiple shoot of TB14 cultivars

Growth regulator(mg/l)			Frequency of shoot response (±)	No shoots per explant
BAP	IBA	Kin		
4	0,2	0,2	65 ± 2,3	2 - 4
4	0,2	0,5	67,4 ± 3,4	2 - 4
4	0,2	1,0	76 ± 3,1	3 - 5
4	0,2	1,5	79 ± 2,2	3 - 5
<b>4</b>	0,2	<b>2</b>	<b>87,4 ± 4,3</b>	<b>8 - 10</b>
4	0,2	3	89 ± 2,1	8 - 10

### *2. Rooting of micro- shoots and it's growth in soil*

Micro shoot about 3 – 5 cm were cultured in medium 1/2 MS supplemented with various concentrations of IBA for different periods of time for induction of roots. No rooting was induced in the medium was gelled with agar. But rooting were formed in



shaken culture without agar ( table 2) after 6 weeks cultured. The medium containing 3 mg/l IBA was found to be best for induction of rooting of micro shoots.

**Tab 2.** Effect of IBA to inducton of rooting of micro shoots after 6 weeks cultured

No	Concentration IBA (mg/l)	Frequency of shoot response ( $\pm$ )	No of roots per shoot ( $\pm$ )	High of root (cm)
1	1	0 $\pm$ 0,0	0 $\pm$ 0,0	
2	2	21,4 $\pm$ 3,5	6,5 $\pm$ 2,7	0,5 - 1
3	3	63,2 $\pm$ 7,8	13,8 $\pm$ 4,5	0,5 - 1,5
4	4	47 $\pm$ 6,0	7,2 $\pm$ 2,5	1 - 3
5	5	12,5 $\pm$ 1,2	3,7 $\pm$ 1,2	2 - 4

After shaken culture, rooted shoots were transferred to ½ MS medium supplemented agar for 4 weeks for growth of shoots and roots.

The rooted plants (3 –5 cm, 4 – 6 leaves, 8 – 15 roots) were transfer to small plastic pots containing a mixture of peat and soil ( 3 : 1 ), pH 5,1 and placed them in greenhous on pre- conditions at low temperature, low light intensity and kept high humidity. After 4 weeks, nearly 50% of plants survived and grow up.

### Conclusions

The present study proved that axillary bud can be used for initiation of culture. Primary shoots can be obtained on medium supplemented growth regulator as: BAP, NAA and GA<sub>3</sub>. Optimum concentration of BAP/IBA/Kinetin for induction of multiplication shoots and growth of shoot were different for each cultivar. Liquid and shaken culture can increase induction of rooting in tea. IBA is the most commonly used auxin for root induction in in vitro shoots.

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## 1.8 - Radiation Technology

## APPLICATION OF RADIATION PROCESSING TO PRODUCE BIOTIC ELICITOR FOR SUGARCANE

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**Abstract:** Sugarcane is the main raw material for production of sugar and ethanol. In Vietnam, it was reported in 1998 that the area for sugar cane growth was about 257,000ha. Up to now, the biotic elicitor, oligosaccharide has not been used for sugarcane yet. This study has been carried out to investigate the elicitation and the growth promotion effect of irradiated chitosan (oligochitosan) for sugarcane. The field test results indicated that alpha chitosan (shrimp shell) and beta chitosan (squid pen) samples with the content of water soluble oligomer of about 75% and 70% respectively were the most effective. The disease ratio of sugar cane tree-trunk treated with irradiated chitosan before harvesting time decreased to 30-40% compared to non-treated one. In addition, the productivity of sugarcane increased to about 20%. The combination of metal ion ( $Zn^{++}$ ,  $Cu^{++}$ ) with oligochitosan did not show the synergic elicitation effect. The results revealed that biotic elicitor made from chitosan by radiation degradation method is very promising for field application not only for protection of disease infection but also for growth promotion of plants. It is believed that this biotic elicitor could be used for safe and sustainable development of agriculture.

### I. Introduction

Sugarcane is the main raw material for production of sugar and ethanol. In Vietnam, it was reported in 1998 that the area for sugarcane growth was about 257,000ha [1]. Up to present time, the biotic elicitor namely oligosaccharide has not been used for sugarcane yet. In 1985, a new plant regulator namely oligosaccharide was reported which also exhibits elicitation effect for plants [2]. After that many research works were carried out [3-8], however up to now the product, oligosaccharide as elicitor, has been produced and commercialized only in some countries for instance “Enerplant”, Biotec, Mexico and “Iodus 40”, Goemar, France. In Vietnam, since 1996 research on radiation degradation of natural polysaccharides was carried out for preparation of growth-promoter and protector for plants [9]. In 2003, a product named Goldride (Permit No. 49/035RN) from irradiated chitosan to treat *Pyricularia Oryzae* for rice crop was commercialized by Research and Development center for Radiation Technology and Phuoc Hung Co. Ltd. However, the above products were not completely as elicitor.

This research subject is to investigate the elicitation effect of oligochitosan (oligoCTS) from radiation degraded of chitosan particularly for sugarcane. The combination of ion  $Zn^{++}$ ,  $Cu^{++}$  with oligoCTS for elicitation effect is also investigated.

## II. Experimental

### II. 1. Materials

Alpha chitosan (aCTS) with degree of deacetylation (DD) 70%, viscosity average molecular weight (Mv)  $216.10^3$  and beta chitosan (bCTS) with DD 90%, Mv  $96.10^3$  were used for preparation of elicitor.

### II. 2. Methods

**II. 2.1. Measurement of Mv:** Mv was measured by viscosity method and calculated as follows [10]:  $\eta = k \times M^\alpha$  - aCTS, DD70%:  $k = 0,104 \times 10^{-3}$  mg/g,  $\alpha = 1,12$  - bCTS, DD90%:  $k = 6,589 \times 10^{-3}$  mg/g,  $\alpha = 0,80$

**II. 2.2. Preparation of chitosan solution and irradiation:** Chitosan was dissolved in lactic acid solution 3% with the concentration of 40g/l. Chitosan solutions were irradiated by gamma irradiator SV-ST Co-60/B at VINAGAMMA Center with doses of 0, 30 and 50kGy.

**II. 2.3. Determination of water-soluble content of oligoCTS:** The content of water-soluble oligoCTS was gravimetrically determined by neutralization of irradiated chitosan solution by NaOH 2M to pH7.

### II. 2.4. Preparation of samples for elicitation effect test:

Samples and method of treatment were described in table 1.

**Tab 1.** Samples and method of treatment

No.	Sample	Method of treatment
1	A(0)	<i>aCTS solution, 0kGy</i>
2	A(30)	aCTS solution, 30kGy
3	A(50)	aCTS solution, 50kGy
4	B(0)	bCTS solution, 30kGy
5	B(M <sup>++</sup> )	B(0)+40g/LZn(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O
6	B(2M <sup>++</sup> )	B(0)+20g/LZn(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O+20g/LCu(NO <sub>3</sub> ) <sub>2</sub> .3H <sub>2</sub> O
7	Control	Water

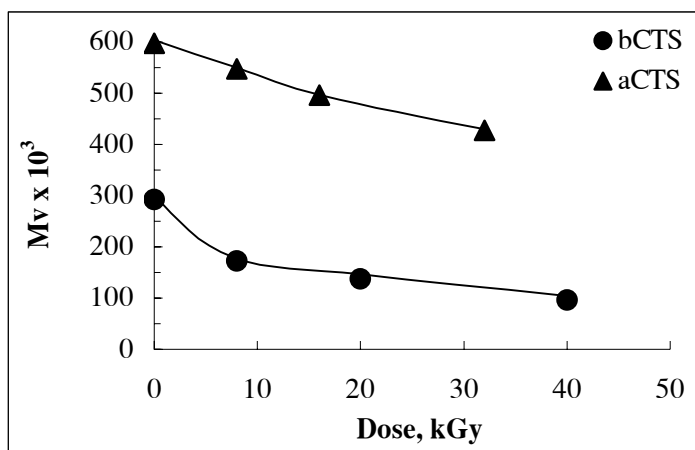
**II. 2.5. Field test of elicitation effect for sugarcane:** Field test of elicitation effect was carried out in the experimental field of the Institute of Sugarcane Research, Binh duong province.

Field test was designed by random block for 7 treatments with triplicate. The area of block was 100m<sup>2</sup> and spraying concentration was of 40ppm (dilution 1/1000). Sugarcane was sprayed three times as following. The first was carried out after 30days of sugarcane growing, the second was 15days after the first and the third was 15days after the second. Disease index (DI) was counted after 1 and 2 months after the third spraying and before harvest. The productivity was also investigated. Data were processed by analysis of variation method.

### III. Results and discussion

#### III. 1. Radiation degradation of chitosan

The decrease of Mv by irradiation was described in Fig. 1. Based on the results in Fig.1, radiation degradation yield  $G_d$  was calculated to be 0,203 and 1,76 for aCTS 70 and bCTS 90 respectively.  $G_d$  of bCTS was higher compared to that of aCTS.



**Fig. 1.** The relationship between Mv and dose

The contents of water soluble oligoCTS were of 43,39; 74,89 and 69,12 for A(30); A(50) and B(0) respectively. At the same dose of 30kGy, the content of water soluble oligoCTS of bCTS was higher compared to that of aCTS.

#### III. 2. Elicitation effect

**Tab 2.** Elicitation effect for sugarcane (variety VN85-1427)

No.	Sample	Leaf DI, % (1 month)	Leaf DI, % (2 months)	Trunk DI, % (at harvest)	For control %
1	A (0)	8.10 b	9.36 b	6.16 bc	56.9
2	A (30)	6.17 c	7.82 b	7.43 b	68.7
3	A (50)	6.06 c	8.01 b	3.98 cd	36.8
4	B (0)	6.21 c	8.84 b	3.32 bcd	30.7
5	B(M <sup>++</sup> )	7.94 b	9.00 b	3.67 d	33.9
6	B(2M <sup>++</sup> )	7.22 bc	8.80 b	4.19 cd	37.7
7	Control	11,95 a	14,12 a	10,82 a	100,0

Results in Table 2 indicated that CTS, oligoCTS and oligoCTS combined with metal ion all exhibit the elicitation effect for decreasing disease index. The samples A(50) and B(0) with high content of water-soluble oligoCTS (~70%) were the most effective. Metal ion (Zn<sup>++</sup>, Cu<sup>++</sup>) combined with oligoCTS did not show synergic elicitation effect.

### III. 3. Productivity and quality of sugarcane

**Tab 3.** Productivity and quality of sugarcane (variety VN85-1427)

No.	Sample	Ton/ha	Increase, ton/ha	Increase, %	CCS%
1	A (0)	53.65 c	4.54	9.3	11.65
2	A (30)	55.29 abc	6.33	12.9	11.71
3	A (50)	59.63 ab	10.67	21.8	11.54
4	B (0)	58.18 bc	9.22	18.8	11.96
5	B(M <sup>++</sup> )	55.06 bc	6.16	12.5	12.00
6	B(2M <sup>++</sup> )	56.12 abc	7.16	14.6	11.85
7	Control	48.96 d			11.36

CCS%: commercial content of sugar, %

Results in Table 3 indicated that the productivity increased from 4.74 to 10.67ton/ha (equiv. 9.3 to 21.8%) for all treatment compared to control. The highest productivity attained for two samples A(50) and B(0).

#### IV. Conclusion

- Two kinds of starting material namely aCTS with DD 70%, Mv 216.10<sup>3</sup> and bCTS with DD 90%, Mv 96.10<sup>3</sup> were selected for preparation of elicitor.
- Results of field test of elicitation effect indicated that two samples namely aCTS 50kGy and bCTS 30kGy with high content of water-soluble oligoCTS (70%) were the most effective.
- Besides elicitation effect oligoCTS has also growth-promotion by increasing productivity of sugarcane significantly (~20%).
- Biotic elicitor from irradiated chitosan is very promising for field application not only for defense of disease but also for growth promotion of plants. It is believed that this biotic elicitor could be largely used for safe and sustainable development of agriculture.

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## **STUDYING RADIATION-INDUCED MODIFICATION OF POLYMER TO MAKE WATER-SUPERABSORBER AS A SOIL MOISTURE CONDITIONER**

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**Abstract:** *Water superabsorbent polymer has been applied widely in healthcare, personal care and agriculture. The research and development of the material have been grown rapidly for their special benefits. The similar products that exist in different categories such as Terra-Sorb, Moist-Soil, Bioplex, SAP, Sky Gel, Aqua-Sorb, Horta-Sorb, Stockosorb in USA, England, South Africa, Australia, Japan, and so on are now commercializing throughout the world. Some alike are present in Vietnam such as coloured soil granular, Bioplex gel, and etc. An identical product named H<sub>2</sub>O super gel resulted in a study work of Chemical Institute, Hanoi. A project “Studying radiation – induced modification of polymer to make water – superabsorber as a soil moisture conditioner” was carried out at VINAGAMMA in 2003. The results of the project are very promising to expand a new study phase aimed to fulfilling a perfect process of irradiation and of production of the gel. The further study has been going on for determination of residual components of degraded Tb-g-AAc samples in soil, analysis of retained AAC monomer in the sample after irradiation, estimation of physical chemistry characteristics of Tb-g-AAc product, analysis of technical economy studies of the product on small-scale production, study of field trials using the gel on no-soil planting matrix (sand, bagasse, saw-dust, agrowaste, rice husk, etc.) for growing strawberry transplanting tree, green tree of red-pine, water morning-glory, Chinese cabbage.*

*It is expected that the study results of the project will be the milestone for the permitted gel production in Vietnam.*

### **I. General introduction**

Results of the project “Studying Radiation-Induced Modification of Polymer to Make Water-Superabsorber as a Soil Moisture Conditioner” (CS/03/07-01) were shown that the following affected factors are determined for the ratio of AAC/starch on percent of homopoly(acrylic acid) (HPAAc), swelling ratio, pH; cation ions, absorbed dose, absorbed dose rate, temperature on swelling ratio. Besides influence of enzym, soil media on degradation of the gel is investigated. Care of swollen gel on ability of conditioning soil moisture for grown plants is taken. There is a study of graft of acrylic acid (AAC)/acrylamide (AAm) on cassava starch to increase water uptake in Thailand. A product called Horta-Sorb originated from polyacrylamide (PAAm) is commercially available like a superabsorbent gel for many applications for plants such as annual beds, turf, vegetables, landscapings, bare root seedlings in USA. The product “Sky Gel” or SAP from crosslinking polyacrylic acid (PAAc) has been commercializing in use for planting under different cultivated conditions in Japan. The evaluation of WHO on AAC reported that released into water or air, AAC readily biodegrades; AAC has an atmospheric lifetime of less than one month. Separate guidance values are recommended for oral and inhalation exposure, 9.9 mg/litre for drinking-water and 54 µg/m<sup>3</sup> for ambient air for the general population are proposed. In other published documents,



water-hold polymer gels from PAAm or PAAc are widely used in agriculture, horticulture with scarce toxicity for human, creative and their environment.

## **II. Experiments**

### **II. 1. Raw materials-chemicals**

Cassava starch (Vietnam), acrylic acid (South Korea), KOH, acetic acid and perchloric acid (China).

### **II. 2. Equipment**

Irradiator (SV-ST Co-60/B, Hungary), oven (Shellab, USA) in VINAGAMMA.

### **II. 3. Methods**

*II.3.1. Preparation of samples:* Pasting completely 100 g of starch in 780 ml of 14% KOH solution is carried out at room temperature for 30 minutes. Cooling the mixture to ambient temperature, concentrated AAc is added into the mixture with the ratio of AAc to starch being 3/1, 2/1, 1/1 ( volume of AAc : 95, 190, 285 ml, respectively) and stirred to make the paste-like mixture homogeneous at room temperature for 30 minutes. The mixture is packed in double layer packs.

*II.3.2. Irradiation of samples:* The samples are irradiated in the Gamma irradiator at 5-8<sup>0</sup>C, with 4 kGy and 1.6 kGy/hr in the presence of air oxygen.

*II.3.3. Formation of samples:* The irradiated samples are cut, dried at 65<sup>0</sup>C. The samples are ground to make translucent granule with the size of 0.3-0.7 mm.

*II.3.4. Measurement and analysis:* Extract of HPAAc: 0.5 g of sample is weighed, wrapped in stainless steel net and extracted in Soxhlet set using methanol solvent at 70<sup>0</sup>C for 24 hrs. And then the sample is taken out, washed out in the deionized water, dried at 65<sup>0</sup>C being attainable a constant weight of the sample. The percent of PAAc is expressed  $[(m_1-m_2) \times 100] / m_s$  and the percent of graft is presented  $[m_2-m_s) \times 100] / m_s$ ,

Where  $m_1$ : Dry weight of irradiated sample (g),  $m_2$ : dry weight of extracted sample (g),  $m_s$ : Initial dry weight of starch (g).

- Swelling ratio: 0.5 g of sample is weighed and put in a beaker containing 500 ml of deionized water to swell a maximum for 48 hrs. The swollen sample is taken out and weighed. Swelling ratio is calculated by weight of maximum absorbed water for 1 g of extracted sample expressed a gram of water per gram of dried sample.

- Weight loss in soil: 5 g of sample is weighed, wrapped in stainless steel net, buried in the soil at depth of 3 cm. The sample is taken out for 3, 6, 9 months, washed out, dried at 65<sup>0</sup>C to constant weight.

- Residue of sample after 9 months buried in soil: Sample is analyzed according to the method of Dennenberg and Abbott.

- Residue of AAc in grafted sample: the sample is extracted in methanol solvent and shaken for 24, 48 hrs. Residual AAc monomer is analysed by method of high pressured liquid chromatography in the Centre for Experimental Analysis Service.

- Ash content: sample is analysed according to Vietnam Pharmacopoeia PL 7.6 in the Centre for Experimental Analysis Service (CEAS).

- Content of soluble component: 0.5 g of dried sample is immersed in 500 ml of deionized water in 48 hrs. The sample is removed, dried at 65<sup>0</sup>C to constant weight.

- Kali content: sample is analyzed according to BS EN 1122:2001 in CEAS.
- Content of toxic metal: Analysis of Hg, Pb, Cd, as is based on method TK. AOAC and TK. TCVN in the Centre for Experimental Analysis Service.
- Test of acute toxicity by the oral route on mice: According to method of Vietnam Pharmacopoeia III in Analytical Subinstitute, Department of Health, Vietnam.

*II.3.5. Irradiation process:* 78 litres of 14% KOH solution is added gradually and stirred concurrently into 10 kg of starch for 30 minutes. 20 kg of concentrated AAc is mixed with the prepared mixture for 30 minutes. The mixture is heat-emitted with temperature of 45-50°C and pH = 6.5-6.8. The finished mixture is packed by PE packs with an amount of 20 kg/pack. The sample-containing packs are cooled for 1 hr and irradiated in the gamma irradiator at 4 kGy having the absorbed dose rate of 1.6 kGy/ hr. After irradiation, the paste-like mixture becomes thick, translucent and heat-emitted (75 °C).

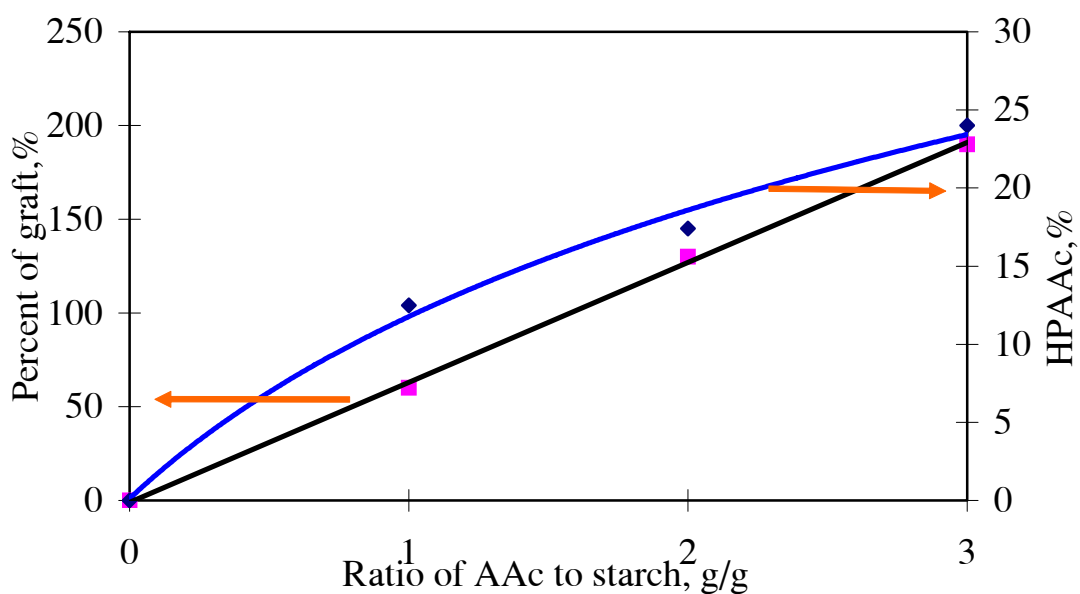
*II.3.6. Product formed process:* The paste-like mixture is extruded into vermicelli threads with a diameter of 2-3 mm. The threads are cut into short length pieces of 20-30 cm, spread on aluminum trays, dried at 65 °C in 8 hrs. The dried threads are granulated to make granules with the size of 0.3-0.7 mm. The final product is packed in PE packs in the quantity of 1, 2, 5, 10 kg/pack. The humidity of the product is about 2-3%.

### III. Results and discussion

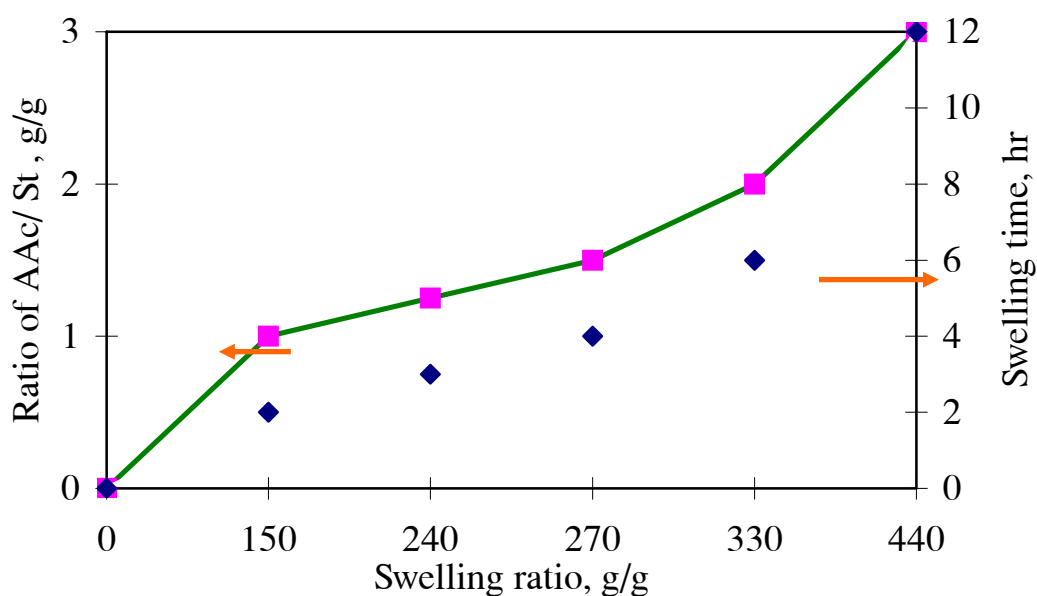
#### III. 1. Technical specifications of water superabsorbent gel (Tb-g-AAc)

**Tab 1.** Technical specifications of water superabsorbent gel

No.	Requirements	Values
01	Ratio of starch to AAc	1/2
02	Swelling ratio, g/g	300
03	Content of toxic metal: Hg, Pb, Cd, As	Permitted limitation
04	Acute toxicity test by the oral route on mice: 0.5 g/kg of weight	Non-detective in histopathological changes
05	Content of Kali, %	19.3
06	Content of ash, %	40.8
07	Weight loss in soil after 9 months, %	85.5
08	Residue odd AAc after irradiated, ppm	5.1
09	Content of soluble component, %	8.8
10	Residue after buried in soil 9 months, %	14.5
11	Colour	Translucent
12	Granular size, mm	0.3-0.7
13	Humidity, %	3



**Fig. 1.** Correlation between AAC/starch and percent of HPAAC, percent of graft



**Fig. 2.** Correlation between swelling ratio and swelling time, ratio of AAC to starch

**Tab 2.** Results of field test

1. Transplanting strawberry tree ( substrate: compost from saw-dust of rubber tree and coffee seed peel) after 30 days			
Experimental lot	Irrigation regime	Fresh weight, g	Dry weight, g
Substrate	Daily, 500 ml/kg of Sub.	0.24	0.03

Substrate+1%gel	4 days/ watering time	1.27	0.8
Substrate+3%gel	4 days/ watering time	1.47	1.02
<b>2. Green red-pine tree (substrate: red soil) after 40 days</b>			
Substrate	Daily, 300 ml/kg of Sub.	1.35	0.64
Substrate+0.1%gel	5 days/ watering time	1.33	0.67
Substrate+0.3%ge	5 days/ watering time	1.48	0.72
Substrate+0.5%gel	5 days/ watering time	1.47	0.78
<b>3. Chinese cabbage (substrate: compost and coconut fibre at ratio of 8 to 2) after 30 days</b>			
Substrate	Daily, 500 ml/bed	4.6	0.4
Substrate+0.75%gel	2 days/ watering time	3.14	0.25
Substrate+1%gel	2 days/ watering time	2.22	0.23
Substrate+1.5%gel	2 days/ watering time	3.0	0.23
<b>4. Water morning-glory (substrate: sandy soil) after 25 days</b>			
Substrate	Daily, 6000 ml/bed	0.81	0.11
Substrate+0.01%gel	2 days/ watering time	1.09	0.16
Substrate+8.3% TRIBAT soil	2 days/ watering time	2.62	0.28
Substrate+ 0.05% gel +8.3% TRIBAT	2 days/ watering time	3.12	0.32

### ***III. 2. Economic analysis of the product (Tb-g-AAc)***

#### *III. 2.1. Capital*

- Equipment: VND 150,000,000
- Workshop: VND 150,000,000
- Total capital: VND 300,000,000

#### *III. 2.2. Operating costs*

- Total annual operating cost: VND 7,137,590,000

#### *III. 2.3. Processing costs*

- Operating costs: VND 7,137,590,000
- Total annual processing costs: VND 7,182,590,000

(Throughput: 330 tons/yr, absorbed dose:4 kGy)

- Unit processing cost: VND 21,765 per kg of product

#### IV. Conclusion

- The product of Tb-g-AAc with the ratio of Tb to AAc (1/2) is irradiated at 4 kGy for a absorbed dose rate of 1.6 kGy/hr, which has a maximum swelling ratio of 330 g/g equivalent to that of imported products such as Terra-Sorb, Bioplex, Aquasorb, PAM, etc...
- The results of the project revealed that the technical specifications like content of potassium (19.3%), ash content (40.8%), residue odd AAc (5.1 ppm), weight loss in soil after 9 months (85.5%) of the product Tb-g-AAc has met the requirement of practical applications in agriculture, for example, for plants such as transplanting strawberry tree, red-pine tree, Chinese cabbage, water morning-glory, and so on.
- The initial unit processing cost is about VND 21,765/kg, which is estimated on the basis of inputs of domestic parameters and of annual throughput of 330 tons/yr. The cost can be competed against similar products available in Vietnam.

# STUDY ON PREPARATION OF COMPOSITE FROM BIODEGRADABLE POLYMER (POLYBUTYLENE SUCCINATE) AND NATURAL FIBRES BY IRRADIATION

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**Abstract:** *A biodegradable composite was prepared from small particles of milled coir with the size less than 0.5mm and biodegradable polymer-poly (butylene succinate) (PBS) by melt blend method. Suitable composition proportion of the composite material was selected (70PBS/30XD). Some properties of material were changed by crosslinking irradiation in the presence of crosslinker - trimethylallyl isocyanurate (TMAIC) at concentration of 1% with absorbed dose of 65 kGy. At this dose, tensile strength, heat stability and water absorption of material were improved thank to formation of gel fraction. The crosslinked effects of material by electron beams via the obtained results of gel content, tensile strength and elongation at break of composites also were investigated and compared to effects of gamma radiation. Coir is used as a filler in this composite with aiming cost reduction and wide application of poly (butylene succinate) in practice.*

## I. Introduction

Biodegradable polymers including poly(3-hydroxybutyrate-co-hydroxyvalerate) (PHBV), polycaprolactone (PCL), polylactide acid (PLA), polybutylene succinate (PBS) have been used widely in medical, agriculture, drug release and packaging material fields depending on their properties [1-4]. Biocomposite consists of a biodegradable polymer as matrix material and a natural fibre as a reinforcing or filling element [4-6]. Both of these compositions in the bio-composite are easily degraded in the natural environment after waste. Therefore, it is so-called an environmentally friendly material. Because of available and cheap raw material resource, natural fiber fillers can be used to reduce the cost of the above-mentioned polymers and apply widely them in practice. These materials have poor properties, low heat stability and wet resistance. Irradiation method is a clean and effective one compared to the chemical in improving mechanical strengths, wet resistance and heat stability of materials, especially in the presence of radiation crosslinkers [7-12].

In these report, PBS as a matrix; jute and coir in different sizes as fillers were used to made a bio-composite. Its properties were improved by crosslinking irradiation in the presence of crosslinker-trimethylallyl isocyanurate.

## II. Experiment

### II.1 Material

PBS#3001 (Japan) with  $M_w=2.96 \times 10^5$ ,  $M_p=92^\circ\text{C}$ . Jute (HCM city). Coir (Ben Tre province). Trimethylallyl isocyanurate (TMAIC) (Japan). Chloroforms (China).

## **II.2 Methods**

*Preparation of composite samples:* Composite sheets with the thickness of 0.5mm were fabricated in hot press machine (Toyoseiki) at 150°C, 3 min., at a pressure of 150 kg/cm<sup>2</sup>. Samples were packaged in vacuum, irradiated by <sup>60</sup>Co source at VINAGAMMA, at the dose rate of 1.3 kGy/h and accelerator with energy of 2 MeV, beam current of 1mA, and the dose rate of 10 kGy/pass at various doses.

*Gel fraction measurement:* Gel fraction was determined by measuring the insoluble part of the sample in boiling chloroform at 50°C for 24hrs.

*Mechanical properties* were determined with a tensile tester (Strograph V10-C, Toyoseiki, Japan) at a crosshead speed of 50mm/min according to ASTM D638. Melt Index (MI) (g/10min) were determined according to ASTM D1238 under 2.16 kg static weight. Thermal stability of samples was evaluated by an autoclave (Modern Sturdy SA-232) at 127°C for 15 min. with a pressure of 1.5 kg/cm<sup>2</sup>.

## **III. Results and discussion**

### **III.1 Selection of mixing method and kind of natural fibre**

The experiment was carried out in the samples with the mixed composition of 90PBS/10SD (or XD) by % weight. Jute and coir were cut and ground into two sizes. The obtained results show that the sample mixed with milled coir in which has the smaller size of  $\leq 0.5$ mm having tensile strength of 152.7 kgf/cm<sup>2</sup> and elongation at break of 146%. The measured values are highest in all of experimental samples. This size of milled coir was chosen to mix with PBS by melt blend in preparation of composite.

### **III.2 Selecting composition of composite**

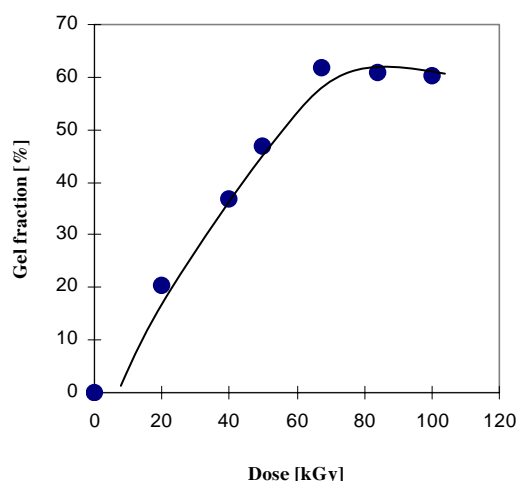
Tensile strength has not insignificant change between composite samples containing 10, 20, and 30% coir (XD). But the tensile strength and elongation at break decreased sharply in the sample mixed with 50%XD. Based on the obtained result, the PBS/30XD with the proportion of 70PBS and 30XD was chosen as a suitable sample to use in irradiation crosslinking experiments.

### **III.3 The effect of crosslinker (TMAIC) on PBS**

The gel fraction increased with increasing gamma irradiation dose in all of TMAIC concentrations (0.5-1.0-1.5%) and achieved the highest value at the dose of 65 kGy. The measured highest gel content in the sample containing 1% TMAIC (about 70.3%) compared to the samples adding 0.5% and 1.5% TMAIC in the same dose of 65 kGy. The gel formation concerned with mechanical properties of material. The obtained result showed that tensile strength achieved the highest value at the dose of 65 kGy and elongation at break decreased gradually with increasing dose. Therefore, 1% TMAIC concentration was chosen as a suitable concentration in crosslinking PBS by irradiation.

### **III.4 Crosslinking the PBS/XD/1%TMAIC composite by irradiation**

Figure 1 described that gel fraction increased with the increasing dose and also achieved highest content at the dose of 67 kGy (about 61.8%). After this dose, gel content almost did not change at the higher dose (about 60.2% at the dose of 100 kGy).



**Fig. 1.** The relationship between absorbed dose and gel fraction in PBS/30XD/1%TMAIC composite

Tensile strength and elongation at break of material were changed according to absorbed doses. This change corresponds to the gel formation in the experimental samples. Tensile strength also increased with the increasing dose and achieved the highest value at dose of 65 kGy ( $174 \text{ kgf/cm}^2$ ) and higher than that of un-irradiated samples ( $138 \text{ kgf/cm}^2$ ). Elongation at break decreased in inverse proportion with the increasing dose. It can be deduced that material was crosslinked by irradiation.

Figure 2 showed that crosslink affected to heat stability of material. PBS/30XD composite at dose of 0 kGy was deformed after steaming in autoclave, while the 65 kGy irradiated sample still kept its original shape (in dumbbell).

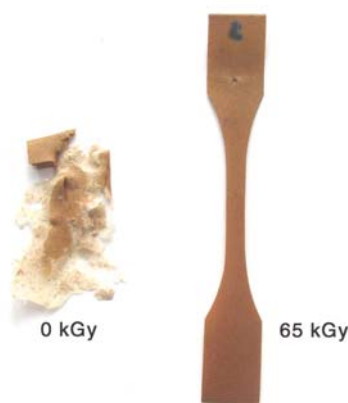
### ***III.5 Comparison of gamma and EB irradiation***

At all of EB irradiation doses, measured gel contents were higher than that of gamma irradiation. For example, gel content of EB treated samples at the dose of 40 kGy is 45.1%, while the gamma treated one at the same dose is 36.7%. It can be showed that electron radiation with the high dose rate affected certainly to crosslink of material.

### ***III.6 Investigation of processability of material***

Low MI of 65 kGy irradiated sample ( $2.1\text{g}/10\text{min}$ ) at the temperature of  $180^\circ\text{C}$  compared to unirradiated sample ( $5.9\text{g}/10\text{min}$ ). It showed that crosslinking irradiation improved heat resistance of material. Therefore, to facility in processing, the prepared composite needs to be processed before irradiation and then irradiated to improve its strength.





**Fig. 2.** The photograph comparing the heat stability of unirradiated and irradiated PBS/30XD samples

#### IV. Conclusions

1. Small particles of milled coir with the size of 0.5mm were filled in poly (butylene succinate) with the proportion of 70PBS/30XD to be prepared a composite by melt blend at the temperature of 150°C, mixing speed of 20 rpm in 10 minutes.
2. The 1% TMAIC concentration is suitable for using as a crosslinker to decrease crosslinking irradiation dose of PBS#3001.
3. The suitable crosslinking dose for PBS/30XD composite is about 65 kGy in the presence of 1% TMAIC. At this dose, the material improved of tensile strength, heat stability and water resistance. After irradiation, PBS/30XD composite has low MI at the high temperature.
4. Crosslinking effect in EB irradiation achieved higher than in gamma irradiation that expressed by measured insoluble gel content in experimental samples.

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## 1.9 - Radiochemistry and Materials Sciences

## STUDY ON THE TECHNOLOGY FOR THE TREATMENT OF VIETNAMESE MAIN RARE-EARTH MINERALS ON THE UPGRADED MONAZITE PILOT PLANT

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**Abstract:** *The research has been carried out in order to solve the problem of the exploitation of the India-given monazite processing pilot plant for full research and production of rare-earths, paving the way to the exploitation and utilization of Vietnamese rare-earth resources on an industrial scale.*

*The research involved the following contents:*

*1- Upgrading and additionally installing equipment for the monazite pilot line:*

*Some apparatuses of the monazite processing pilot has been upgraded and additionally installed to serve directly the treatment of Yen Phu rare-earth ore concentrate and Dong Pao rare-earth ore concentrate.*

*The apparatuses upgraded were: (i) a reaction tank lined with a composite-layer withstanding HCl, H<sub>2</sub>SO<sub>4</sub> acidic and alkaline environment at the temperature of under 120°C, and (ii) a press filter .*

*The apparatuses that have been additionally installed were: (i) a 250-litre stainless steel reaction tank; (ii) a concentrated H<sub>2</sub>SO<sub>4</sub> acid pump; and (iii) a lifting windlass for raw materials and chemicals.*

*2- Processing Yen Phu rare-earth ore concentrate:*

*The research results have allowed the improvement of technology for alkaline decomposition on a pressurized apparatus having a capacity of 30 litters. The new finding consists in that a multi-stage HCl leaching process can be employed in order to increase the ability to recover purified rare-earth chloride solution with no use of other agents, which is suitable to industrial scale with material recycling. Leaching yield for RE<sub>2</sub>O<sub>3</sub> was achieved at 85-90% and the rare earth solution obtained can be directly used to solvent extraction process.*

*3-Processing Dong Pao rare-earth ore concentrate:*

*The optimal conditions for leaching rare-earths from the concentrate after oxidizing calcination at 650°C for 4 hours were as follows: temperature - 80°C; H<sub>2</sub>SO<sub>4</sub> concentration - 3M; acid-to-ore ratio - 1:1; reaction time - 2 hours, giving a leaching yield of more than 95%.*

*Cerium was directly separated from other rare-earths in the leached solution by precipitation of rare-earths(III) disulphates. The optimal separating conditions were found as follows: C Ln<sup>3+</sup> - 80 g/L; temperature - 60°C; acid concentration - 1.2M; Na<sub>2</sub>SO<sub>4</sub>/Ln<sub>2</sub>O<sub>3</sub> ratio - 2; reaction time - 50 min.; additional HF amount was 0.01-0.045 mol per litter of leached solution. Leaching yield for Ce(IV) was achieved at ≥ 85% and the purity of Ce(IV) was obtained at more than 98%.*

*The obtained results allowed to set up a general process of recovering total rare-earths and high-grade cerium from Dong Pao rare-earth ore concentration.*

**Key words:** *Rare Earth, Dong Pao, Yen Phu, Monazite, Ore, Concentrate, Pilot, Apparatus, Upgrade.*

## **Introduction**

Rare-earth elements are a terminology referring to a group of 16 elements from lanthanum (ordering number of 57 on the Periodic Table) to lutecium (number of 71) together with yttrium (number of 39), possessing a continuous change in properties and behaving the same with each others. Rare-earth elements have been for a long time utilized in techno-economic branches, bringing important values which are not found from other elements. Rare-earth elements are found in the earth-crust at an average content of about 0.01% and exist in nine key mineral groups, of which fluoride, carbonate, fluoride carbonate, phosphate and oxide minerals are the most important. Three types of the most popular and exploitable valuable rare-earth bearing ores are bastnaesite in the form of fluoride carbonate ( $\text{LnFCO}_3$ ), monazite and xenotime in the form of phosphate.

In Vietnam rare-earth reserve in the bastnaesite-type accounts for more than 90% of the total rare-earth reserve, situating in ore-mines of Dong Pao, North Nam Xe, South Nam Xe in the region of North West. The Yen Phu rare-earth mine (also in the region of North West), although having a large reserve of minerals, possesses a high value because of containing the intermediate and heavy groups. Apart from that, there is a diverse source of coastal sand minerals, stretching along the country length, including monazite - a large resource of rare-earth ores that require a cautious treatment due to high content of thorium.

Technology for processing rare-earth ores in the world has been developed since early age and has recently achieved many outstanding progresses in order to create a competing ability in the production of rare-earth products. In our country all the three above-mentioned key ore mineral types have attracted much research, where Dong Pao bastnaesite ore has been studied the most, however there have still been limitations of technological measures to save the expenditure and to reduce the cost of the products so as to run the production on a large scale.

Monazite ore from beach sand mineral has experienced relatively basic technological researches, however at present monazite is essentially exported together with zircon, ilmenite and rutile without treatment at industrial scale due to the problem of generating radioactivity (thorium and radium)-bearing waste.

Since Yen Phu rare-earth ore has a small reserve, yet to become a exploitable mine, its treatment technology has been preliminarily studied, where the pressure-alkaline method hasn't been completely investigated.

In 1991 the Government of India offered the Vietnam Atomic Energy Commission a pilot-scale monazite processing line with alkaline method, having a capacity of 60 tons per year, which was installed at Phung establishment (Dan Phuong District, Ha Tay Province) of the Institute for Technology of Radioactive and Rare Elements. This is one of the two pilot plants that India has given to other countries (one to Vietnam, the other to Cuba) as an international aid. This is also a remarkably comprehensive technological line and has the largest scale over the country. Since its official operation, the pilot has served actively research and experimental production

activities on rare-earths from monazite. Because of the need for expanding studies on other types of Vietnamese rare-earth ore minerals, since 2002 the pilot has been used also for the research into processing Dong Pao bastnaesite ore and Yen Phu rare-earth ore.

Following the ministerial-rank research theme for 2001-2003 “Study of technology for the processing of rare-earth ore concentrates with alkaline method and for the purifying separation of some key heavy-group rare-earth elements from Yen Phu total rare-earths with extraction method”, the ministerial-rank research theme for 2003-3004 “Study on the technology for the treatment of Vietnamese main rare-earth minerals on the upgraded monazite pilot plant” has been carried out in order to solve the problem of the exploitation of the India-given monazite processing pilot plant for full research and experimental production of rare-earths, paving the way to the exploitation and utilization of Vietnamese rare-earth resource on an industrial scale.

**The research involved the following contents:**

1. Upgrading and additionally installing equipment for the monazite processing pilot plant.
2. Studying technology for processing Dong Pao rare-earth ore and experimentally producing on the pilot at a capacity of 100 kg per batch.
3. Improving the technology and implementing the treatment of Yen Phu rare-earth ore concentrate with pressure-alkaline method on a pilot scale.
4. Overview document on main sources of rare-earth minerals in Vietnam and the status of research and technological development on the treatment of rare-earth ores in the world as well as in Vietnam.

**Upgrading and additionally installing equipment for the monazite pilot line**

Some apparatuses of the monazite processing pilot line has been upgraded and additionally installed to serve directly the treatment of Yen Phu rare-earth ore concentrate and Dong Pao rare-earth ore concentrate. Utilizing capabilities of the pilot have been expanded to the treatment of main rare-earth mineral types in Vietnam such as monazite, Yen Phu xenotime and, particularly, Dong Pao bastnaesite.

The apparatuses upgraded were: (i) a reaction tank lined with a composite-layer withstanding HCl, H<sub>2</sub>SO<sub>4</sub> acidic and alkaline environment at the temperature of under 120°C, and (ii) a press filter.

The apparatuses that have been additionally installed were: (i) a 250-litre stainless steel reaction tank; (ii) a concentrated H<sub>2</sub>SO<sub>4</sub> acid pump; and (iii) a lifting windlass for raw materials and chemicals.

**Research and experimental development of processing Yen Phu rare-earth ore concentrate**

The research results have allowed the improvement of technology for alkaline decomposition on a pressurized apparatus having a capacity of 30 litters. Some solutions to the enhancement of decomposition efficiency as well as the maximum quantity of ore for each batch of decomposition have been recommended. With a loading of 5 kg of ore concentrate per batch of decomposition and by the way of gathering 5-10 decomposition batches to make material for one technological batch on the pilot scale, the treatment of Yen Phu rare-earth ore concentrate was carried out, enabling the recovery of a solution

of rare-earth chloride at a grade satisfactory to the followed purifying separation stage with solvent extraction. This is a reasonable solution to make full use of the monazite pilot plant to treat Yen Phu rare-earth ore in a mode of small-scale production when the fabrication of a decomposition apparatus with a larger capacity is still somehow difficult.

Moreover, the technology of phosphate leaching and HCl leaching as well as purification of the solution has been additionally studied. The new finding consists in that a multi-stage HCl leaching process can be employed in order to increase the ability to recover purified rare-earth chloride solution with no use of other agents, which is suitable to industrial scale with material recycling.

The results of pilot scale experimental production have allowed to implement some statistic calculations of the major costs for production of rare-earths from Yen Phu ore concentrate as follows: Yen Phu rare-earth ore concentrate 27,7% RE<sub>2</sub>O<sub>3</sub> - 10 kg; Caustic soda (industrial grade) - 20 kg; Hydrochloric acid (industrial grade) - 7 kg; Sodium sulfide - 0.5 kg; Disodium hydrophosphate - 0.1 kg; Water - 300 liters; Antraxite coal: 20 kg.

#### **Research and experimental development of processing Dong Pao rare-earth ore concentrate**

The results obtained when studying mineralogical and chemical compositions of Dong Pao rare-earth ore concentrate showed that the key mineralogical compositions in Dong Pao rare-earth ore concentrate were barite (BaSO<sub>4</sub>), bastnaesite-cerium (CeCO<sub>3</sub>F), cerianite (CeO<sub>2</sub>), bastnaesite-lanthanum (LaCO<sub>3</sub>F) and fluorocerite-lanthanum (LaF<sub>3</sub>). The main rare-earth composition of the ore concentrate was rare-earths of the light subgroup (with approx. 11.9% La<sub>2</sub>O<sub>3</sub>; 16.3% CeO<sub>2</sub>; 1.3% Pr<sub>6</sub>O<sub>11</sub>; 3.3% Nd<sub>2</sub>O<sub>3</sub>). The non-rare-earth compositions in the ore concentrate included Ba, Si, Al, Mn, Pb, Fe, Ca, F and S. The content of total rare-earths in the ore concentrate was 33.6%.

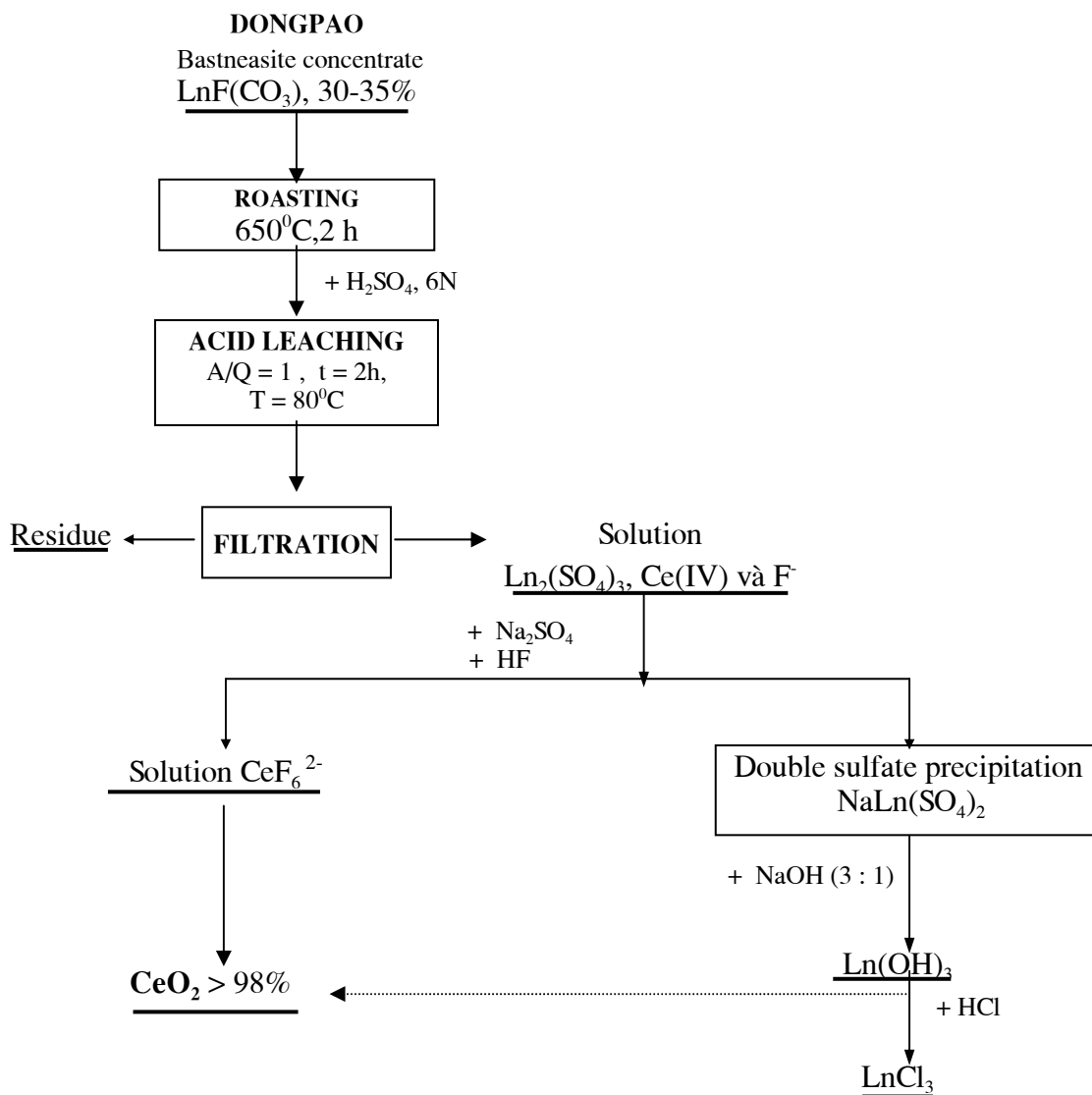
Under the condition of oxidizing calcination at 650°C for 4 hours, LnFCO<sub>3</sub> concentrate was transformed into LnOF type and facilitated the leaching at low acid concentration and low temperature. It was found that the optimal conditions for leaching rare-earths from the concentrate after oxidizing calcination were as follows: temperature - 80°C; H<sub>2</sub>SO<sub>4</sub> concentration - 3M; acid/ore ratio - 1:1; reaction time - 2 hours, giving a leaching yield of more than 95%.

Cerium was directly separated from other rare-earths in the leached solution by precipitation of rare-earths(III) disulphates. The optimal separating conditions were found as follows: CLn<sup>3+</sup> - 80 g/L; temperature - 60°C; acid concentration - 1.2M; Na<sub>2</sub>SO<sub>4</sub>/Ln<sub>2</sub>O<sub>3</sub> ratio - 2; reaction time - 50 min.; additional HF amount was 0.01-0.045 mol per liter of leached solution. Leaching yield for Ce(IV) was achieved at ≥ 85% and the purity of Ce(IV) was obtained at more than 98%.

Based on the results obtained from laboratory research, large amount treatment of Dong Pao rare-earth ore concentrate was experimentally carried out on the upgraded monazite pilot plant. The experimental scale was 500 kg per batch. Through the results obtained, technological conditions determined by lab-scale study were confirmed. The obtained product was used for the purpose of fabricating polishing powder and was separated into individual rare-earth elements. The amount of product obtained was beyond that envisaged and registered in the research application.

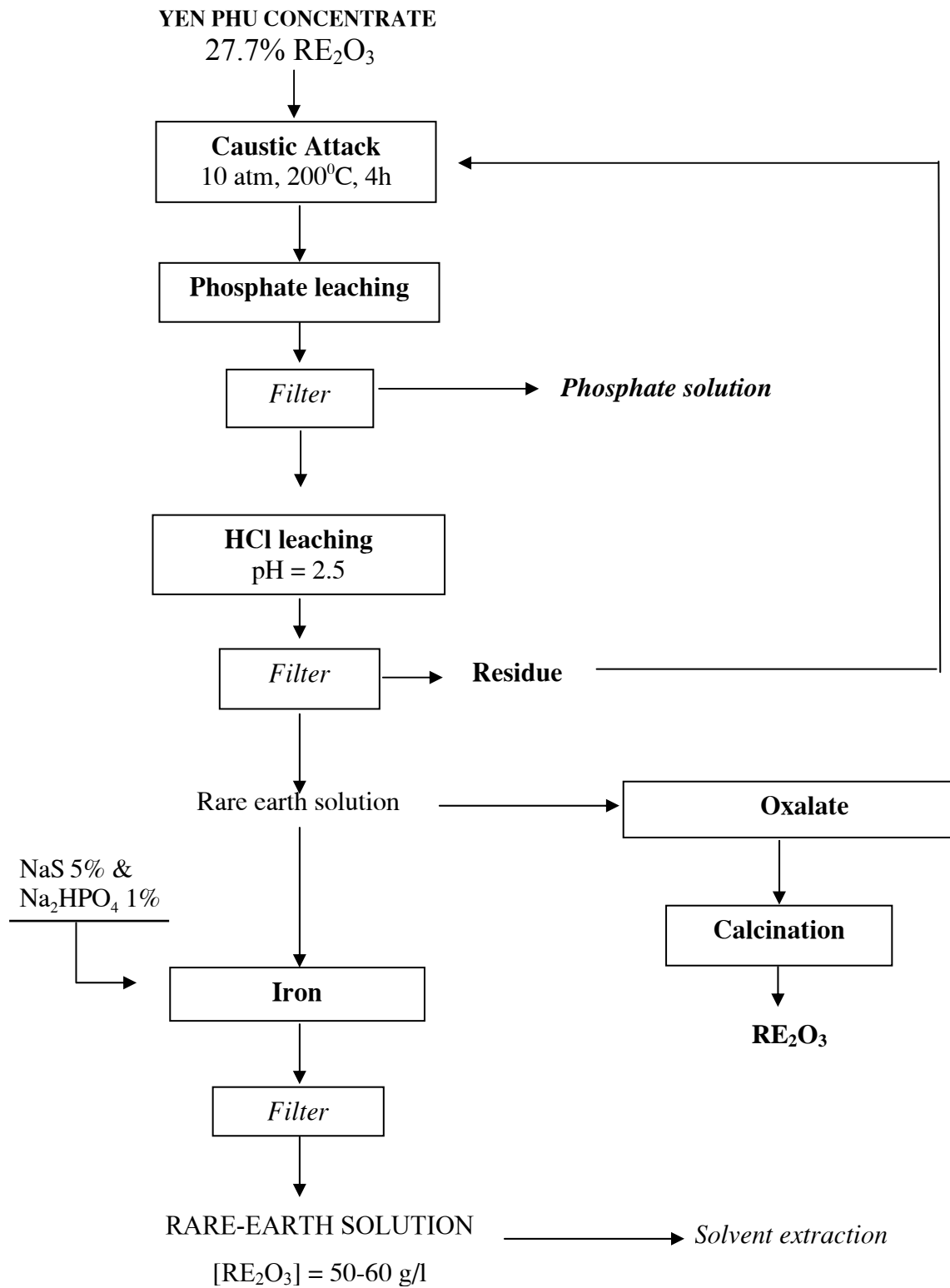
The obtained results allowed to set up a general process of recovering total rare-earths and high-grade cerium from Dong Pao rare-earth ore concentration. This process has been applied to the production of rare-earths from Dong Pao bastnaesite on a pilot scale at the Institute for Technology of Radioactive and Rare Elements.

### Technological schema for treatment of Dong Pao Rare Earth Concentrate





### Technological Schema for Treatment of Yen Phu Rare Earth Concentrate by Pressure-Caustic Process



## STUDY ON URANIUM DISTRIBUTION IN ORE SAMPLES OF NONG SON BASIN (VIET NAM)

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**Abstract:** *The study has conducted classification by radioactivity measurement for each ore particle (size of 25-200 mm) and determination of uranium content in respective ore sample of Nong Son Basin- Quang Nam (Vietnam). Result obtained from the study showed the possibility to use radiometric sorting to enrich ores from the above area.*

**Key words:** *urani ore, Nong Son Basin, radiometric sorting.*

### I. Rationale

Geological studies show that uranium ore bodies in Nong Son basin (Quang Nam province, Vietnam) are holes, lens, chain of lenses with uranium content of  $U_3O_8 \square 0.01\%$ . In one level, the uranium contents widely vary from 0.001 to 0.675%. Study on uranium distribution according to ore particle size makes it possible to assess possibility to classify ore contents in order to find measures to increase efficiency of further chemical treatment and to better meet technical-economic and environmental requirements.

### II. Method and experiment instruments

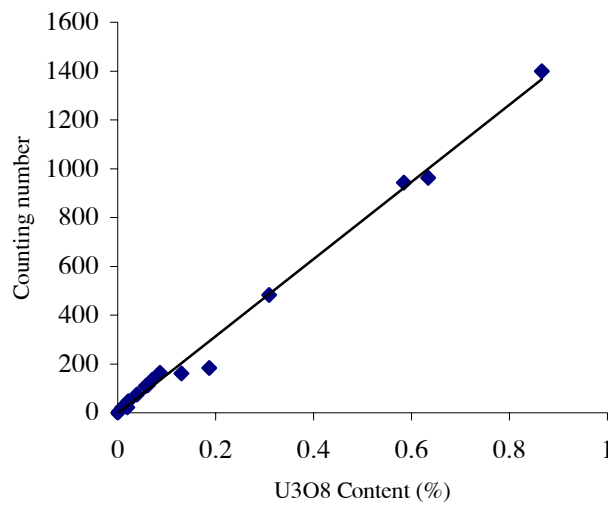
The study has conducted classification by radioactivity measurement for each ore particle (size of 25-200 mm) and determination of uranium content in respective ore sample.

To determine radioactivity, gamma spectrometer (thallium-activated sodium iodide crystals NaI(Tl) 80x80mm and multi-channel analytical system of model MCA-2003-001, VNEC) were used. Uranium contents were determined by color photometry (Spectronic 20 D+, USA).

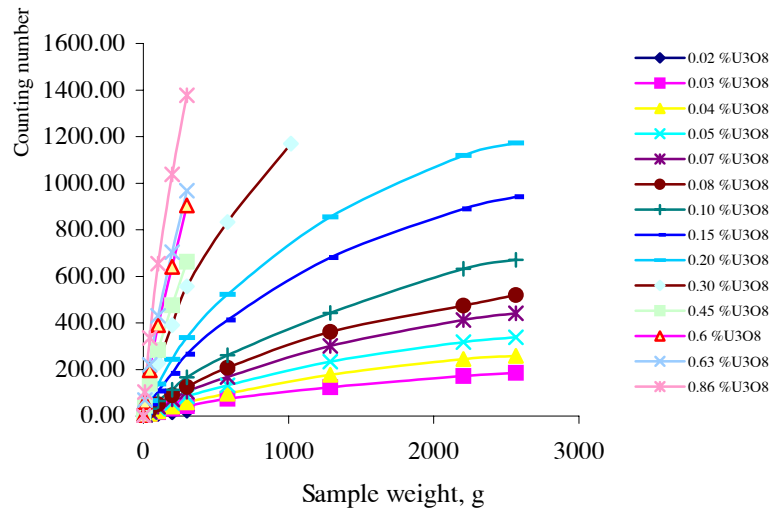
### III. Results and comments

The dependence of counting number on uranium content is a linear relation (Figure 1). Adjustment of the effect of particle size (weight) was determined based on the diagram in the Figure 2.

Uranium ore sample at the point 47 in the Dong Nam Giang has size composition shown in the Table 1. The sortability curves of respective particle sizes in the Figure 3 shows that uranium distribution levels are not even in the ores.



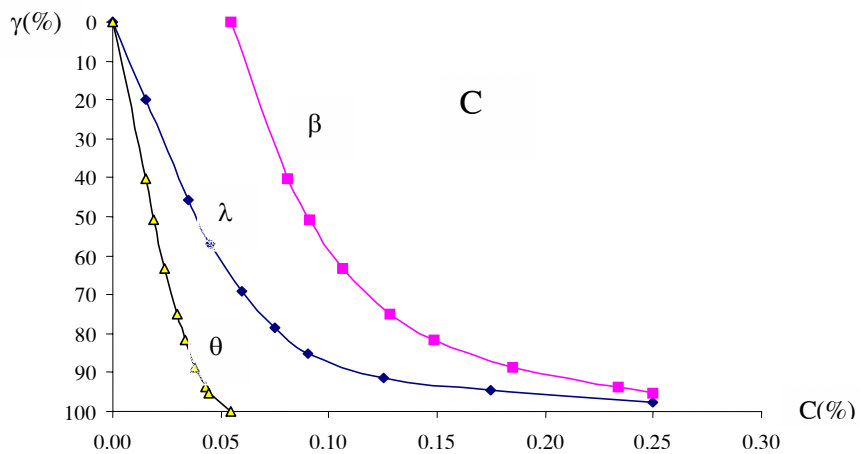
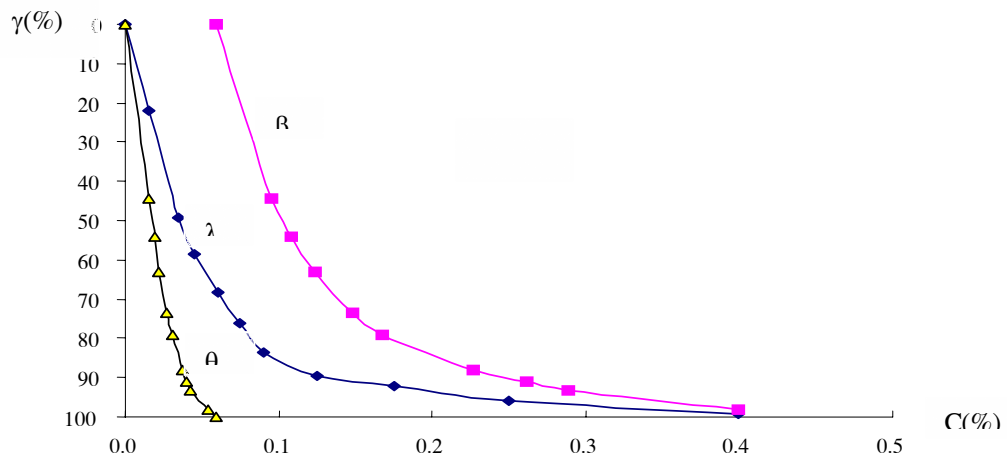
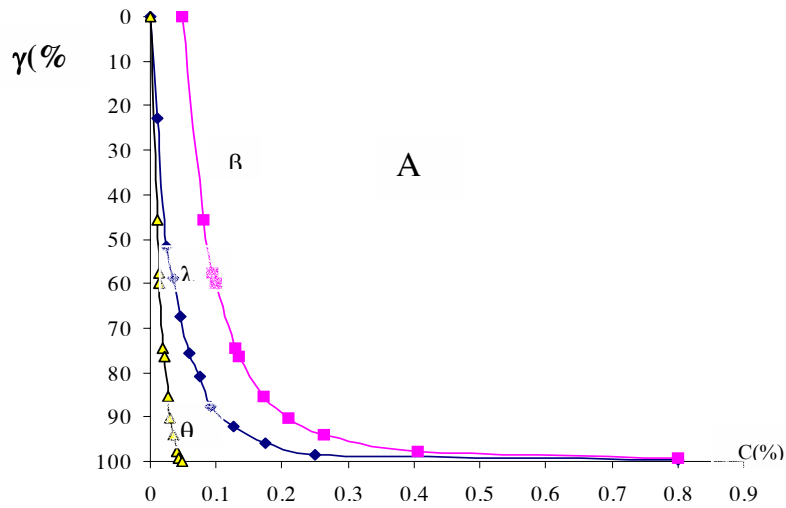
**Fig. 1.** Dependence of radioactivity on U<sub>3</sub>O<sub>8</sub> content in the ore samples



**Fig. 2.** Dependence of counting number on ore sample weight.

**Tab 1.** Distribution of particle size of the ore sample DT 47 in the Dong Nam Giang

	Particle size, mm		
	25-50	+ 50 - 100	+ 100 - 200
Weight, kg	5.989	42.657	195.018
Weight ratio, %	2.458	17.506	80.036
U <sub>3</sub> O <sub>8</sub> content, %	0.050	0.060	0.054



**Fig. 3.** Sortability curves for different particle sizes (A. 25-50 mm, B. +50-100 mm, C. +100-200 mm)

According to the data from relations in the Figure 3, it is possible to come up with the following comments:

- For particle size in the 25-50mm range, by radiometric sorting the reject (0.01%  $U_3O_8$  content) had 57.70% of the initial weight of sample and the accept

(42.30% of the initial sample weight) had content of 0.10%  $U_3O_8$ . The recovery rate reached 84.11%.

- For particle size in the +50-100mm range, the reject (0.02%  $U_3O_8$  content) had 54.26% of the initial weight of sample and the accept (with content of 0.11%  $U_3O_8$ ) had 45.74% of the initial sample weight. The recovery rate reached 83.01%.

- For particle size in the +100-200mm range, the tailings (0.02%  $U_3O_8$  content) had 50.97% of the initial weight of sample and the accept (49.03% of the initial sample weight) had content of 0.09%  $U_3O_8$ . The recovery rate reached 82.03%.

The study also has been conducted for samples from Pa Lua, Pa Rong and similar results were obtained.

#### **IV. Conclusion**

Results obtained from the study of uranium distribution in ore samples of the above area allow to come up with the following conclusion:

1. Uranium distribution in the studied samples is not even.
2. It is possible to use radiometric sorting to enrich ores from Nong Son basin.

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# STUDY ON PREPARATION OF HYDROXYAPATITE POWDERS AND FABRICATION OF POROUS HYDROXYAPATITE BIOCERAMICS

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**Abstract:** Apatite calcium phosphate powders- $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  with degrees of crystallinity ranging from 20% to 80% were preparing by wet method. Temperature, pH and precipitation rate were essential parameters for the control of precipitate composition. The precise determination of atomic Ca/P ratio and chemical composition was carried out by using several complementary techniques such as XRD, ICP and EDS. The hydroxyapatite (HA) powder with crystalline degree of 70-80% was used for preparing porous bioceramic bodies. Our porous bodies were tested as bone implants for several adult dogs. After 6 months, all of the implants have presented good characteristics of biocompatibility and bioadaptability.

**Keywords:** Hydroxyapatite; Porous bioceramics; In vivo tests.

## Introduction

Calcium phosphate based ceramics have proved to be attractive materials for biological applications. Among these bioceramics, particular attention have been given to hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  due to its bioactivity, and to tricalcium phosphate  $\beta\text{-Ca}_3(\text{PO}_4)_2$  due to its bioresorbability [1, 2].

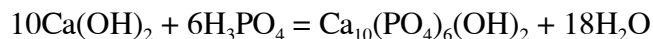
HA is the main inorganic compound of hard tissues such as bone and teeth of vertebrate animals and humans.

Our work is concerned with synthesis of HA powder, fabrication of porous HA bioceramics and preliminary in vivo tests with the fabricated HA bioceramics.

## Research Results

### 1. Synthesis of HA powder

The HA powder were prepared by precipitation between  $\text{Ca}(\text{OH})_2$  and  $\text{H}_3\text{PO}_4$  according to the following the reaction [3]:



An aqueous 10%  $\text{H}_3\text{PO}_4$  solution was added very slowly to a suspension of  $\text{Ca}(\text{OH})_2$ . During reaction, temperature of the suspension was maintained at following values for 3 degrees of crystallinity of HA powder:

- At 30°C for degrees of crystallinity of 30%
- At 60°C for degrees of crystallinity of 60%
- At 95°C for degrees of crystallinity of more than 70%

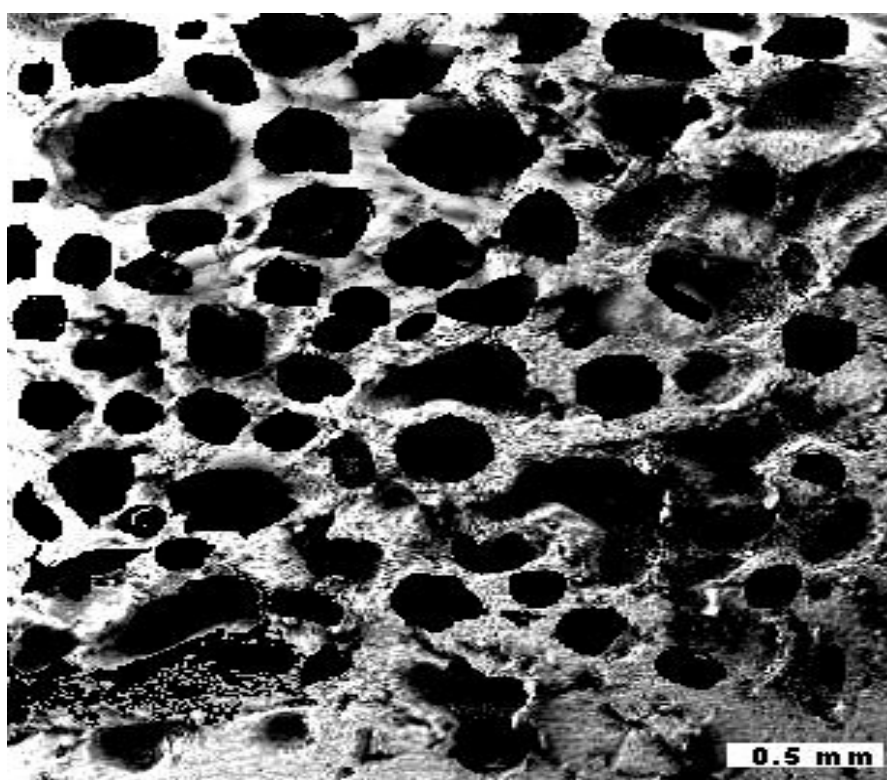
The suspension was continuously stirred and at the end of the reaction, the pH of the reaction was maintained at around 11 by adding  $\text{NH}_4\text{OH}$  solution. The ageing time for 3 degrees of crystallinity of HA powders was 2, 2 and 24 hours, respectively.

## ***2. Fabrication of porous Ceramics***

Cellulosic sponge was used as a supporting base for fabricating porous HA ceramics. Ceramic porous HA bodies were prepared by soaking cellulose sponge into slurry prepared from HA powder and water in a 1:3 volume ratio. The sample was dried and calcinated very slowly to 550°C for firing cellulose, then sintered up to 1250°C for 1h. The fabricated ceramics have porosity as follows:

- Closed porosity of 10%
- Open porosity of 54%
- Total porosity of 64%

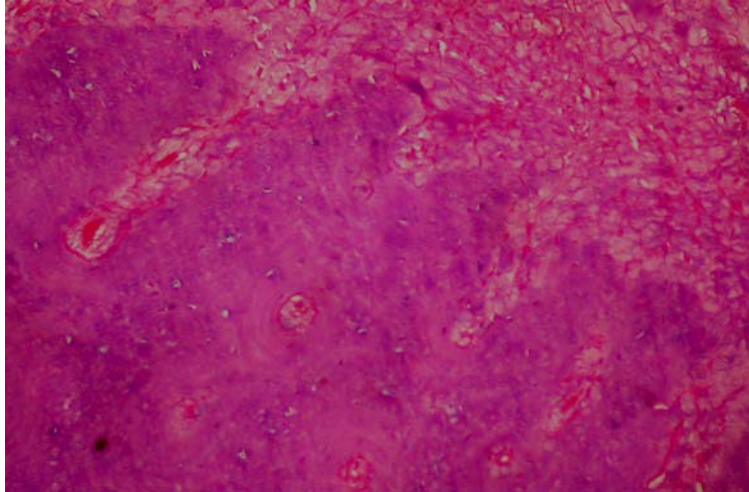
We can see the SEM micrograph of porous ceramics as shown in fig. 1.



**Fig. 1.** The SEM micrograph of the fabricated porous HA ceramics

## ***3. Use of the fabricated porous HA Ceramics for Testing bone Implant in adult Dogs***

Ten healthy adult dogs were used for this experiment. Before the operation, implants were  $\gamma$ -ray sterilized with  $\text{Co}^{60}$  isotope of dosage of 2.5 Mrad. The twenty porous artificial ceramic samples were used for bone implantation in 10 adult dogs. The in vivo study in dogs has revealed that the implant was well tolerated without showing extrusion and infection. It allowed the blood vessels and newly formed bone to grow into the implant. The figure 2 has presented the experimental results.



**Fig. 2.** The SEM micrograph showing bone tissue growing within porous ceramics

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## **RESEARCH ON DEFINING THE COMPOSITION OF MATERIALS IN THE URANIUM ORE AT PA LUA MINE AND ITS INFLUENCES ON TECHNOLOGICAL PROCESS**

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**Abstract:** *The uranium ore of the Pa Lua mine is a class of the sandstone ore with the ore bodies distributed unevenly and complicatedly. It is mostly existed in the two forms of unweathered ore and weathered one.*

*In the unweathered ore, the specific existing minerals include nasturan, coffinit, pyrites, marcasite, galena, sphalerite, siderite containing manganese, calcite and organic substances.*

*In weathered ore, the existing minerals are products of the oxygenation process altering the pre-existed minerals, that including major minerals such as uranofan, metauranoxiaxite, soddyite, bassetite, hematite, hydrogötite, piroluzite, ramsdellite, different clay minerals, etc. The average content of  $U_3O_8$  of the studied ore sample is 0.077%.*

*Uranium minerals are unevenly distributed and mainly in cement is soft hole structure. Minerals containing iron are the impurity component that receives the most attention and its distributive rule is closely related to uranium minerals. Commonly, the content of iron is high when that of uranium is high and vice versa.*

*The results of the study and exploration show that the uranium ore of the Pa Lua mine is possible separated and selected with traditional methods, in which the radioactive method and floating one are promising. The enrichment coefficient can be obtained at 1.5- 2.5.*

*Due to the fact that the extent of weathering, the hardness and the component of uranium minerals (the ratio of deoxidized form over the oxygenized form) of UW ore and W ore are greatly different, the absorbing speed of the agent dissolved and separated inside the ore particle and its back-to-surface absorbing speed are also different. The absorbing experiment is carried out for the four ore samples in accordance with the Darcy absorbing model. So as to acquire equal uranium dissolution and separation performances under the same conditions, the size of unweathered ore must be a quarter of semi-weathered ore's size.*

**Keywords:** *Uranium ore, sandstone, Pa Lua mine, Nongson Basin, unweathered ore, weathered ore, percolation leaching.*

### **Preface**

The Pa Lua uranium ore mine is one of the four uranium ore mines located in the Nong Son sunken basin area which its reserve forecasted in grade P1+P2 with 12,494 tons including 5,542 tons of first class and 6,952 tons of second class, among them 2,694 tons are of grade P1. Especially, there are 2,785 tons of  $U_3O_8$  with the content  $\geq 0.1\%$ .

Existed some projects on material composition of the uranium ore in Pa Lua Area [5]. However, the Theme: *"The research for defining the composition of materials in the uranium ore of Pa Lua mine uranium ore and its influences in regards to the technological process"* is carried out and studied in order to acquire a better insight on the above-mentioned ore and its influences in regards to the technological process; especially supplementary research on some its physical properties such as hardness, density, grinding resistance; as well as possibility in the application of some traditional physical selecting methods in order to enhance the uranium's content. Such is still carried out the research of absorbing process depending basically on the physical nature, the structure of ore one by one, the sponginess and the dimension of the spongy capillary.

## Method and experiment

### Method

1. Method for researching the material component of the ore specimen:

The analysis of mineral physiognomy, geochemistry and petrography on the polar-microscope, the inductive plasma spectrum mass; X-ray analysis, the gamma spectrum, X-ray fluorescence, the technique for measuring active aggregation of the gamma degree and microzond analysis.

2. Methods for researching and assessing the possibility for selecting uranium ore are gravity selection on the sifting table, dry-magnetic selection and floating one.

3. The steam-absorbing method in the laboratory of the Technological Center for Treating Environment (belongs to the Army's Chemical Headquarter) has been applied to define the parameters on the ore's sponginess, the specific surface area and the size of the spongy capillary hole in both weathered state and unweathered one to study the absorbing possibility. The research of absorbing process is carried out on an Italian device for measuring absorptivity with available ore specimens with dimensions of 150x150x150(mm) and 100x100x100(mm).

### Experiment

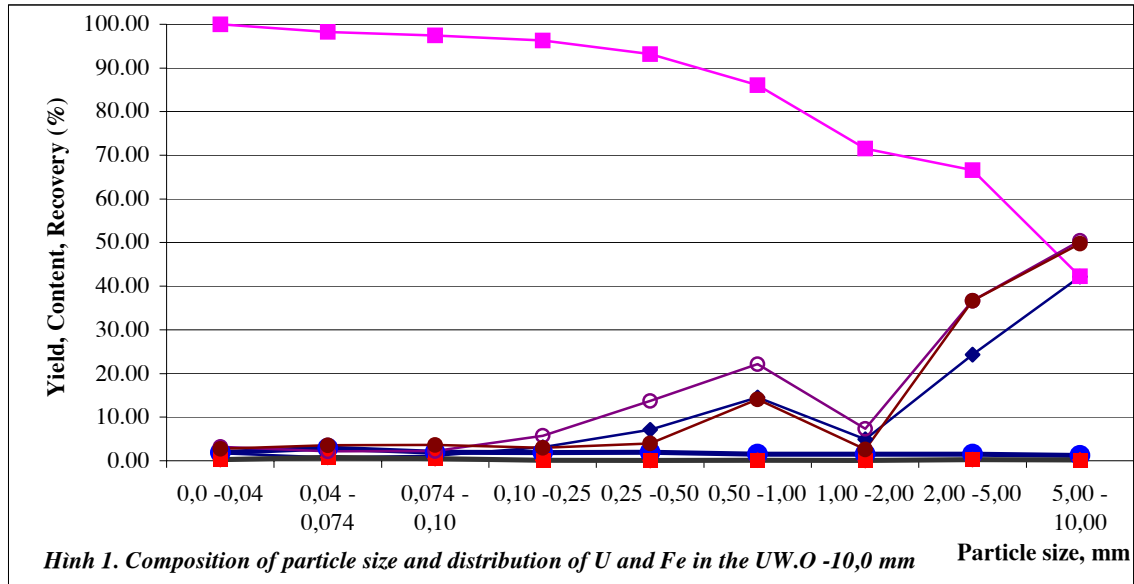
1. Particle size determination of the unweathered ore - 10,0 mm

Composition of Particle size is listed in Table 1 and picture 1.

**Tab 1.** Composition of Particle size of the unweathered ore -10,0 mm

Particle size, mm	yield, %		Content, %		Recovery, %	
	$\gamma$	by plus	Fe <sub>2</sub> O <sub>3</sub>	U <sub>3</sub> O <sub>8</sub>	Fe <sub>2</sub> O <sub>3</sub>	U <sub>3</sub> O <sub>8</sub>
0,0 - 0,04	1,75	100,00	1,81	0,273	2,15	2,77
0,040 - 0,074	0,78	98,25	2,88	0,783	1,55	3,53
0,074 - 0,10	1,19	97,47	1,94	0,525	1,61	3,61
0,10 - 0,25	3,10	96,28	1,88	0,166	3,99	2,98
0,25 - 0,50	7,14	93,18	1,96	0,096	9,55	3,96
0,50 - 1,00	14,50	86,04	1,56	0,168	15,35	14,08

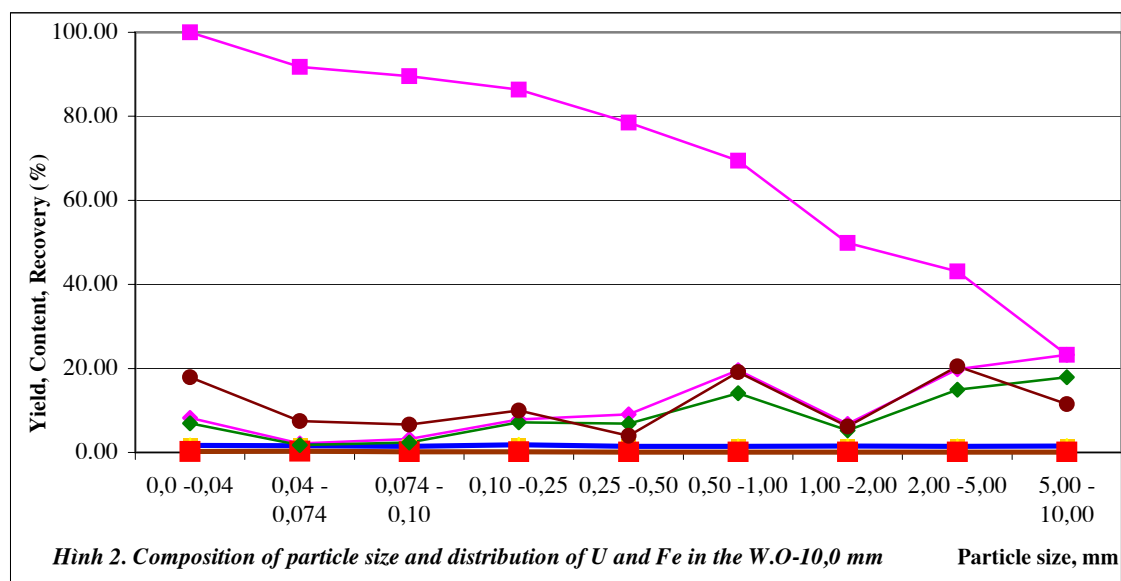
1,00 - 2,00	4,97	71,54	1,50	0,091	5,15	2,61
2,00 - 5,00	24,31	66,57	1,54	0,191	25,45	26,84
5,00 - 10,00	42,26	42,26	1,22	0,162	35,20	39,62
Feed	100,00	-	1,47	0,173	100,00	100,00



## 2. Particle size determination of the weathered ore - 10,0 mm

Tab 2. Composition of Particle size of the weathered ore -10,0 mm.

Particle size, mm	Yield, %		Content, %		Recovery, %	
	$\gamma$	by plus	$Fe_2O_3$	$U_3O_8$	$Fe_2O_3$	$U_3O_8$
0,0 - 0,04	8,26	100,00	1,66	0,197	9,0	17,3
0,040 - 0,074	2,17	91,74	1,58	0,313	2,3	7,2
0,074 - 0,10	3,20	89,57	1,46	0,188	3,1	6,4
0,10 - 0,25	7,85	86,37	1,80	0,116	9,3	9,7
0,25 - 0,50	9,10	78,52	1,48	0,040	8,9	3,9
0,50 - 1,00	19,56	69,42	1,42	0,089	18,3	18,5
1,00 - 2,00	6,80	49,86	1,52	0,083	6,8	6,0
2,00 - 5,00	19,84	43,06	1,48	0,094	19,3	19,9
5,00 - 10,00	23,22	23,22	1,52	0,045	23,1	11,1
Feed	100,00	-	1,52	0,094	100,0	100,0



### 3. Defining the chemical composition of the ore samples

**Tab 3.** Chemical analysis of the ore samples by X-ray fluorescence method

No	Constituent	Content, %	
		<i>unweathered ore</i>	<i>weathered ore</i>
1	SiO <sub>2</sub>	64,90	61,60
2	Fe <sub>2</sub> O <sub>3</sub>	2,67	2,90
3	MgO	5,59	4,08
4	TiO <sub>2</sub>	0,40	0,38
5	P <sub>2</sub> O <sub>5</sub>	0,011	0,004
6	K <sub>2</sub> O	2,71	3,29
7	CaO	3,54	1,05
8	Al <sub>2</sub> O <sub>3</sub>	14,32	13,73
9	V <sub>2</sub> O <sub>5</sub>	0,14	0,41
10	Th	0,0011	0,0006
11	U <sub>3</sub> O <sub>8</sub>	0,175	0,077
12	MnO <sub>2</sub>	0,13	0,048

**Tab 4.** The results of analysis by the technique measuring gamma active aggregation that is made by Hanoi Institute for Nuclear Techno-Science.

Item No.	Ore species	Content of U <sub>3</sub> O <sub>8</sub> (ppm)	Content of ThO <sub>2</sub> (ppm)	Content of Radium (ppm)
1	Weathered	839±18	33 ±7	(3.57± 0.05)10 <sup>-4</sup>
2	Unweathered	1964±37	49±8	(5.16±0.10)10 <sup>-4</sup>

**Tab 5.** Results of chemical analysis by ICP-MS

No	Element	Content of element in ore samples			
		Unweathered		Weathered	
		ppm ( $\mu\text{g/g}$ )	%	ppm ( $\mu\text{g/g}$ )	%
1	B	951,89	0,095189	872,09	0,08721
2	Na	20993,10	2,09931	14233,10	1,42331
3	Ca	13138,78	1,31388	4519,78	0,45198
4	Ni	17,59	0,00176	15,12	0,00151
5	Cu	20,97	0,0021	18,41	0,00184
6	Cu	21,02	0,0021	18,53	0,00185
7	Zn	1729,74	0,17297	472,14	0,04721
8	As	89,12	0,00891	153,76	0,01538
9	Y	26,25	0,00262	11,63	0,00116
10	Zr	278,50	0,02785	135,40	0,01354
11	Nb	8,93	0,00089	7,03	0,0007
12	Mo	2,32	0,00023	8,64	0,00086
13	Ag	11,40	0,00114	12,76	0,00128
14	Cd	30,55	0,00305	10,48	0,00105
15	La	148,13	0,01481	53,25	0,00533
16	Ce	250,24	0,02502	99,24	0,00992
17	Pr	23,75	0,00237	7,94	0,00079
18	Nd	71,34	0,00713	25,43	0,00254
19	Sm	10,10	0,00101	3,82	0,00038
20	Eu	2,10	0,00021	0,81	0,00008
21	Gd	7,99	0,0008	3,15	0,00032
22	Tb	0,96	0,0001	0,41	0,00004
23	Dy	4,70	0,00047	2,15	0,00022
24	Ho	0,82	0,00008	0,39	0,00004
25	Er	2,10	0,00021	1,06	0,00011
26	Tm	0,28	0,00003	0,15	0,00002
27	Yb	1,61	0,00016	0,93	0,00009
28	Lu	0,21	0,00002	0,13	0,00001
29	Ta	7,16	0,00072	5,15	0,00052
30	W	10,09	0,00101	7,41	0,00074
31	Au	0,04	0,00000	0,02	0,00000
32	Hg	13,19	0,00132	2,68	0,00027
33	Pb	213,85	0,02138	93,52	0,00935

#### 4. Determinating mineral, petrography, mineral graphic composition of ore samples

97 weathered and unweathered ore samples were analyzed by mineral, petrography, mineralgraphy facies methods and by the advanced Equipment at the Department for Geology of Radioactive and Rare Elements, at the Institute of Mineralogy and Petrography, the Zagreb University, of the Republic of Croatia, and the Vietnam Petrol-Oil Institute.

The results of studies, have discovered the presence of The nasturan, coffinit in unweathered ore and uranophan, autunit và meta-autunit in weathered one. Indicator is Vanadium. The main rocky soil minerals are quartz, feldspar and other minerals of the mica group (also known as the crushed particle component). The main cement component is minerals of mica group and hydro mica, chlorite, carbonate, etc.

**Tab 6.** Results of defining compound name and chemical formula of ore samples (the Institute of Mineralogy and Petrography, the Zagreb University, of the Republic of Croatia)

Ref. Code	Score	Compound name	Chemical Formula
39-1351	30	Metaautunite-9A	Ca(UO <sub>2</sub> ) <sub>2</sub> (P O <sub>4</sub> ) <sub>2</sub> !3 H <sub>2</sub> O
39-1351	69	Metaautunite-9A	Ca(UO <sub>2</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> !3 H <sub>2</sub> O
01-0649	44	Quartz	SiO <sub>2</sub>
39-1351	27	Metaautunite-9A	Ca(U O <sub>2</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> !3 H <sub>2</sub> O
08-0301	65	Uranophane-\$GB	Ca(UO <sub>2</sub> ) <sub>2</sub> ( Si O <sub>3</sub> OH) <sub>2</sub> !5 H <sub>2</sub> O
08-0442	61	Uranophane	Ca(H <sub>3</sub> O) <sub>2</sub> (UO <sub>2</sub> ) <sub>2</sub> (Si O <sub>4</sub> ) <sub>2</sub> !3 H <sub>2</sub> O
39-1351	26	Metaautunite-9A	Ca(U O <sub>2</sub> ) <sub>2</sub> (P O <sub>4</sub> ) <sub>2</sub> !3 H <sub>2</sub> O
39-1360	60	Uranophane	Ca(U O <sub>2</sub> ) <sub>2</sub> (Si O <sub>3</sub> O H) <sub>2</sub> !5 H <sub>2</sub> O
46-1045	33	Quartz, syn	Si O <sub>2</sub>
39-1351	34	Metaautunite-9A	Ca(U O <sub>2</sub> ) <sub>2</sub> (P O <sub>4</sub> ) <sub>2</sub> !3 H <sub>2</sub> O
46-1045	27	Quartz, syn	Si O <sub>2</sub>
15-0019	Unmatched Strong	Iron Niobium Oxide	FeNbO <sub>4</sub>
39-1351	28	Metaautunite-9A	Ca(U O <sub>2</sub> ) <sub>2</sub> (P O <sub>4</sub> ) <sub>2</sub> !3 H <sub>2</sub> O
33-1161	26	silica	Si O <sub>2</sub>

#### 5. Defining some physical properties of the ore specimen

*a. Defining the intensity of pressing-resistance, strain-resistance and anti-shock of the unweathered ore (by Institute for Research of Geology and Minerals)*

**Tab 7.** The results of measurement on intensity of pressing-resistance, strain-resistance and anti-shock of the unweathered specimen

Code of specimen	Kind of experimental ore	Pressing resistant intensity (KG/cm <sup>2</sup> )	Strain resistant intensity (KG/cm <sup>2</sup> )	Anti-shock (KG/cm <sup>2</sup> )	Ratio of weight (%)
XII-04CD2 (Unweathered)	Soft stone	65	15	2.0	38.0
	Hard stone	583	65	4.5	36.0
	Separable spongy ore	-	-	-	26.0

*b. Defining the density of the ore specimen*

Measuring the density of the ore specimen according to the method is measuring the density of the mixed ore powder [12]. Take the 100% pounding product grade - 0.10 for measure and calculation. With the unweathered ore, the density is 2.642g/cm<sup>3</sup> while that of the weathered ore is 2.453g/cm<sup>3</sup>.

### 6. Studying the selecting possibility

The Theme has been carried out to study the possibility for selecting ore specimen by some methods such as gravity selection on water panning table, dry magnetic selection and floating one. The results of experiment as follows:

**Tab 8.** Results of selection on the shaking table (Unweathered)

No	Product	Yield, %	Cont. U, %	Recovery U, %
N1	Heavy	20,83	0,14	21,44
N2	Middle 1	13,29	0,08	7,83
N3	Middle 2	43,05	0,08	25,32
N4	Fine particle	22,83	0,27	45,41
Total		100,00	0,136	100,00

**Tab 9.** Results of selection of magnetic separation (Unweathered), Particle size 0,1 - 2,0 mm

Particle size, mm	Product	Yield, %	Content, %		Recovery, %	
			Fe <sub>2</sub> O <sub>3</sub>	U <sub>3</sub> O <sub>8</sub>	Fe <sub>2</sub> O <sub>3</sub>	U <sub>3</sub> O <sub>8</sub>
- 0,10	-	20,89	0,88	0,432	18,03	52,12
0,10 - 0,25	Non magi	7,42	0,90	0,098	6,55	4,20
	Magi	3,02	1,64	0,163	4,86	2,85

0,25 - 0,50	Non magi	20,72	0,80	0,060	16,25	7,19
	Magi	1,77	3,46	0,218	6,00	2,23
0,50 - 1,00	Non magi	30,94	0,86	0,098	26,09	17,53
	Magi	4,84	1,62	0,16	7,69	4,48
1,00 - 2,00	Non magi	9,75	1,06	0,107	10,13	6,03
	Magi	0,65	1,58	0,900	1,01	3,38
Feed		100,00	1,02	0,173	100,00	100,00

As for the floating selecting method, the separation and selection is depended on many factors such as the collective substances, the selecting modes such as the R/L ratio, the grinded smoothness, the selective duration and other selective substances (such as stimulation, sunk oppressiveness, environmental adjustment), the selective duration and mode in regards to studied object.

The theme only studied at an explorative level the ability of applying the floating selecting method, so the selected specimen is pounded to 85 % of the particle's size-0.074 mm. The selecting substance used for study is a mixture of anion and is unpolarized.

**Tab 10.** The experiment results floating selection for exploring (Unweathered) specimen

No	Product	Yield, %	Content, %		Recovery, %	
			U	Fe <sub>2</sub> O <sub>3</sub>	U	Fe <sub>2</sub> O <sub>3</sub>
N1	Float	24,17	0,27	1,39	68,69	37,98
N2	Sink	75,83	0,039	0,72	31,31	62,02
Total		100,00	0,095	0,88	100,00	100,00

**Tab 11.** The experiment results floating selection for exploring (Weathered) specimen

No	Product	Yield, %	content U, %	Recovery U, %
N3	Float	27,20	0,33	60,64
N4	Sink	72,80	0,08	39,36
Total		100,00	0,148	100,00

## 7. Studying the permeating possibility

The permeation mainly depends on physical characteristics, material structure; porosity and dimension of porosity capillary of ore types. Sandstone ore in this area has been weathered differently: unweathered; semi-weathered and weathered ore. The



unweathered ore has dense; hard and solid structure and high density. The weathered ore usually is in scattered, porous state and low density. The semi-weathered ore is in intermediate state between above mentioned two types. Certainly, permeation possibility of three types of ore is different and possibility for uranium extraction will be verified. In order to elementary estimate influences of material structure of ore types on percolation leaching, we have conducted the determination of porosity and size of porous capillary for the unweathered and weathered ores. The results of water vapor absorption analysis are: porosity in range from 0.007 - 0.008 cm<sup>3</sup>/g for unweathered ore samples and 0.011 - 0.013 cm<sup>3</sup>/g for weathered ore samples. The capillaries of average size are about 65 % for unweathered ore and 70% for weathered one.

The rate of uranium percolation leaching has been decided by permeation rate of leaching agent into ore particles and reverse permeation of uranium solution to the surface of ore grains. So the investigation for determination of permeation possibility for ore types should be conducted.

The results have showed that permeation possibilities of unweathered ore and semi-weathered one are very low. So that there is orientation of ore grinding to adequate particle sizes for rate of leaching process of sandstone ore samples. These experiments are initial base for investigating uranium extraction from sandstone ore by percolation leaching.

## **Result and discussion**

### ***Results***

The following main results have been drawn from the theme's research:

1. The uranium ore of the Pa Lua mine is a class of sandstone one. It existed in the two forms of unweathered ore and weathered one. The indicator is vanadium.

2. For the unweathered specimen

- The main uranium minerals are nasturan, coffinit.
- The main rocky soil minerals are quartz, feldspar and other minerals of the mica group (also known as the crushed particle component)
- The main cement component is minerals of mica group and hydro mica, chlorite, carbonate, etc.
- The selectivity: The enrichment coefficients fluctuate from 1.5 to 2.5 times with the real uranium volume reaching 45-68% depending on the selecting method.

3. For the weathered ore

- The main uranium minerals are uranophan, meta-autunite and autunite.
- The main rocky soil minerals are quartz, feldspar and mica-group minerals (also known as the crushed particle component)
- The main cement component is mica-group minerals and hydro mica, chlorite and carbonate.
- The selectivity: The enrichment coefficient fluctuates from 1.5 to 2 times with the recovery reaching 40-60% depending on the selecting method. Generally

speaking, for weathered ore, it is harder to select and enhance the uranium content than for unweathered ore.

4. The physical properties of the two classes of ore are as follows:

5. The experiment result of grinding the particle in size from -2mm to 100%- 0.1 mm is as follows:

- For unweathered ore: The time for grinding is 45 minutes;
- For weathered ore: The time for grinding is 30 minutes;

6. The result of absorbing study has identified the fixed absorbing coefficients of the four specimens as follows:

Types of ore specimens	Absorbing coefficient ( $10^{-5}$ cm/s)
Unweathered ore (100x100x100 mm)	1.333
Semi-weathered ore (150x150x150 mm)	7.417
Weathered powdered ore mixed with tiny one	1,410.0
Weathered powdered ore	2,457.0

### Discussion

The experiment results of the material component of Pa Lua uranium mine's ore shows that: The sandstone component generally comprises two parts, which are crushed particles and cement. The main uranium minerals in the unweathered ore are nasturan and coffinit. The main uranium minerals in the weathered ore are uranophan, autunit and meta-autunit. The indicator is vanadium.

Because uranium minerals are distributed unevenly and are contained mostly in cement, the orientation for studying the ability of selecting to enhance the uranium content of the Pa Lua mine is well founded (radioactive selecting, floating selecting and gravity selecting).

The component of harmful element and constituent in the studied ore specimen causes little impact on the technological processes.

The results of petrography studies at the Institute of Mineralogy and Petrography, the Zagreb University, of the Republic of Croatia, have discovered the presence of minerals containing niobium ( $\text{FeNbO}_4$ ).

The unweathered ore has much greater hardness than weathered ore, which leads to the greater consumption of energy for grinding. The weathered ore can be over-pounded easily. The density of the two ore specimens Unweathered ore and weathered are virtually equal. The absorbing speed of Unweathered ore is only a quarter of that of weathered one.

### Conclusion and suggestion

The theme has basically completed the objectives set in the explanation and declaration. It has also made supplementary analysis on hundreds of petrography, mineralogical and chemical specimens (element and constituent) by several modern analyzing methods to ensure the accuracy and diversity of results. Based on the results of studying the material composition of ore specimens, the theme has studied its impact

on the absorbing process (of the agents integrated into the ore and the back-to-surface absorbing of the uranium-containing solution) and explored the ability of selecting for the enhancement of uranium content by some traditional mineral selecting methods.

In order to affirm the results of research and exploration on the possibility of selection for the enhancement of uranium content by the traditional mineral selective methods, the authors would like to suggest the authorities to permit continuing research deeply of this Theme in the above direction.

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## STUDY ON SINTERING PROCESS FOR FABRICATION OF $UO_2$ CERAMICS HAVING GRAIN SIZE REQUIRED FOR FUEL CERAMICS

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**Abstract:** A number of references of following matters were collected:

- Technology for  $UO_2$  ceramics production,
- New trend of studying fuel ceramics,
- Methods of ceramic pellet quality valuation.

1030 g of  $UO_2$  was prepared to produce  $UO_2$  ceramic pellet.

The obtained  $UO_2$  powder has high value of SSA (specific surface area), low bulk density, low tap density and a large/wide range of particle size distribution. The quality of green compacts/pellets, especially their density, was verified. It was observed that the density of green compact was low and the higher specific surface area of the powder used for preparing the green compact was, the lower density of the compact was.

The process of releasing the lubricant  $Zn(C_{17}H_{35}COO)_2$  from sintered pellet was studied. The result was that the lubricant was decomposed and got out of sintered pellet in gas form at  $800^\circ C$ . Data of XRD analysis showed that there was no Zn in the pellets at sintering temperature of  $1000^\circ C$ . This very well agreed with data reported in work of Balakrishna [16].

The sintering at temperature of 1500, 1550, 1600, 1650,  $1700^\circ C$  for different periods of time (2, 4 and 6 hours) was carried out. It was observed that the density and grain size of sintered pellets very much depended on sintering time and temperature. The density and the grain size of the sintered pellet increased with the enhancement of the temperature and the time of sintering. However, density of sintered pellet reached the value of 98% TD at  $1700^\circ C$  and was invariable when the sintering temperature increase up to  $1750^\circ C$  while the grain size continuously increased with the growth of/raising temperature.

The pellets that were sintered at  $1700^\circ C$  for 6 hours had the grain size of about  $12\mu m$  (intended grain size is  $10\mu m$ ).

The procedure and the sintering curve for  $UO_2$  production were made. The number of  $UO_2$  pellets that is enough for having quality test and storage was obtained. The products had norm of quality as follows: density of  $10.62 g/cm^3$  (97%TD); grain size of about  $12\mu m$ ; compress strength of more than  $4.5 kG/mm^2$ ; hardness of more than  $500 kG/mm^2$ .

**Key words:**  $UO_2$  sintering, microstructure.

### Introduction

Nuclear fuel in ceramic form, especially  $UO_2$  ceramics, have been used for most of nuclear reaction types in many countries in the world. Studies have been developed to improve their quality (to enhance burn-up and their life time).

In our country, studies on preparation of  $\text{UO}_2$  from ADU were started in 1998 in laboratories. Research works were carried out based on knowledge extracted from foreign references and experiences got from training courses abroad. Obtained  $\text{UO}_2$  ceramics have just some base characteristics that required for nuclear fuels ceramics. Our work has been developed to purpose having thorough grasp and mastering the technology of fabricating  $\text{UO}_2$  ceramic pellet having characteristics of a nuclear fuel ceramics.

## Experiments and results

Reagents used for preparing experimental specimens were  $\text{UO}_2$  powder, the lubricant of stearate zinc ( $\text{Zn}(\text{C}_{17}\text{H}_{35}\text{COO})_2$ ).

### 1. Study on sintering process

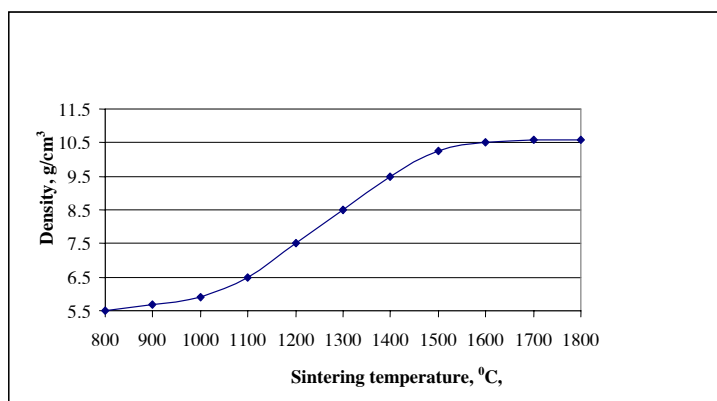
#### 1.1. The release of lubricant $\text{Zn}(\text{C}_{17}\text{H}_{35}\text{COO})_2$

$\text{Zn}(\text{C}_{17}\text{H}_{35}\text{COO})_2$  was used as a lubricants in the step of press forming green pellet. The presence and content of Zn in pellet specimens sintered at different temperature 300-1000°C were determined by XRD method. The lubricant comprising Zn started decompose at 500°C. Products of the decomposition completely/fully got out of ceramic specimens at 1000°C. This very well agreed with the result reported by Balakrishna [5].

#### 1.2. The relation of sintering temperature and density of $\text{UO}_2$ ceramics:

Determining dimension and density of ceramic specimens sintered at the range of 800-1700°C was carried out. Sintering time of 4 hours, rate of increasing temperature ( $V_T$ ) of 150°C/h, cooling rate ( $V_C$ ) of 200°C/h and sintering atmosphere of  $3\text{H}_2+1\text{N}_2$  mixture were applied to/used for all of experiments. (The result was shown in figure 1.) As shown in figure 1, the density of sintered specimen very much depended on sintering temperature. At 800°C density of sintered specimen was not much different from / did not much change in comparison with that of green specimen. The sintered density was rapidly enhanced from 53% TD to 93% TD (the value of 93% TD was obtained at 1500°C) when the sintering temperature increased from 1000°C to 1500°C. From 1550°C upwards, it continuously grew up; however, speed of growing density was getting slower and slower. This implies that

The density of specimens sintered at 1550, 1600, 1650, 1700°C were 10.38g/cm<sup>3</sup> (94%TD), 10.48 g/cm<sup>3</sup> (>94% TD), 10.56g/cm<sup>3</sup> (96% TD) and 10.58g/cm<sup>3</sup> respectively. The water absorption of sintered specimens was obviously/clearly realized during measuring density by Archimede method. This is considered due to existing of open porities. At the range of 1550-1600°C water-absorption ability of specimens degreased with the increase in sintering temperature, while their density was enhanced. From 1650°C up, the water absorption of sintered specimens was negligible. Density of specimen almost unchanged. A number of large grains appeared. (The sintered products reached stage of high condensation). This can be explained by that at such high sintering temperature, there were no open porities left, and the porities existing in specimens could not shrink any more. At sintering temperature of 1700°C, obtained ceramics really achieved high condensation.



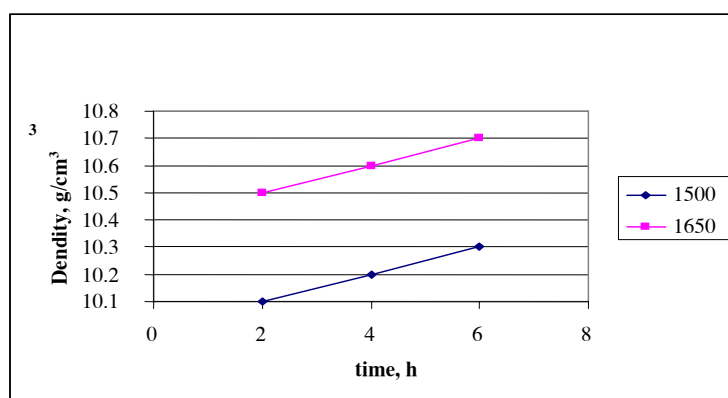
**Fig. 1** The independence of density on sintering time

### 1.3. Relation between density and sintering time:

Experiments were carried out under conditions as follows:

Sintering temperature: 1500, 1650, 1700°C. At each temperature, specimens were sintered for different periods of time, 2 hours, 4 hours and 6 hours. Result was shown in figure 2.

At each temperature, the longer sintering time, the higher density was. When sintering time was enhanced from 2 to 6 hours, density of specimens increased from 10.13 to 10.24 g/cm<sup>3</sup>, 10.49 to 10.58 g/cm<sup>3</sup>, 10.54 to 10.59 g/cm<sup>3</sup> at 1500°C, 1650°C and 1700°C respectively.

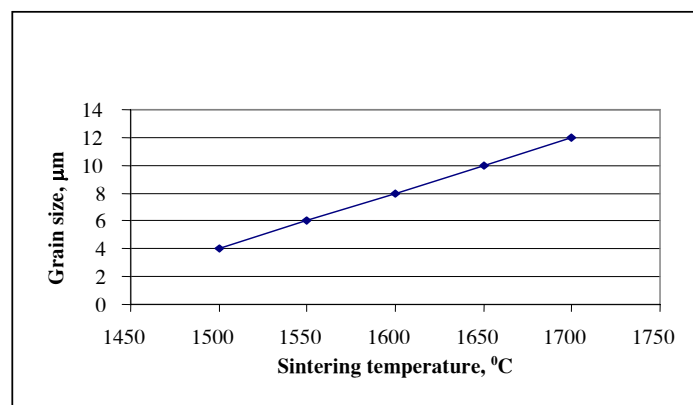


**Fig. 2.** The dependence of density on sintering time

### 1.4. Relation between grain size and sintering temperature:

The sintering process was conducted at different temperatures of 1500, 1550, 1600, 1650, 1700°C. Sintering time of 4 hour and atmosphere of 3H<sub>2</sub>+N<sub>2</sub> mixture were kept constant for all of experiments. Metallographic method was used to measuring grain size. Result was illustrated in figure 3.

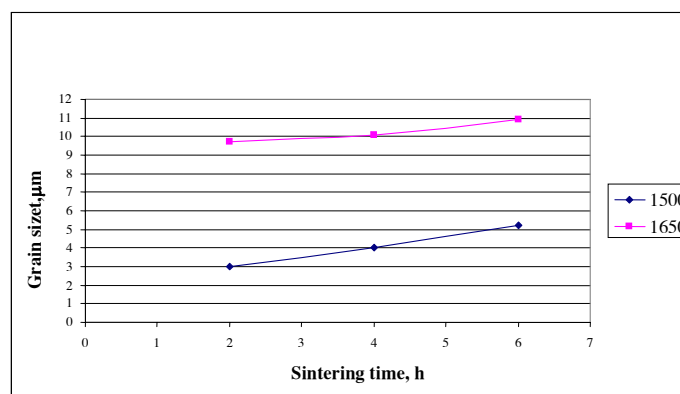
It was shown that sintering temperature very much influenced on grain size of obtained UO<sub>2</sub> ceramics. The higher sintering temperature, the larger grain size was. The grain size increased from 4μm to 11.4 μm when temperature was enhanced from 1500°C to 1700°C.



**Fig. 3.** The effect of sintering temperature on the grain size

### ***1.5 Relation between grain size and sintering time:***

Three values of time period, 2, 4 and 6 hours, were applied to sintering process at 1500°C and 1650°C.



**Fig. 4.** The relationship between sintering time and grain size of UO<sub>2</sub> ceramic specimen

As shown in figure 4, sintering time obviously affected grain size. The increase in sintering time resulted in the growing grain size, e.g. the enhancement of sintering time from 2 hours to 6 hours resulted in the grain size growth of from 3 μm to 5 μm and from 9.5 to 11 μm at sintering temperature of 1500°C and 1650°C respectively. Compared with the results obtained at Pitesti, Romania, which were presented that grain sizes of 11 μm and 12 μm were obtained at 1700°C, with sintering time periods of 2 hours and 6 hours respectively.

### ***1.6 Relation between grain size and density:***

The maximum value of density required for fuel ceramic is in the range of 95-98% TD. It is unprofitable /unbeneficial to enhance the density over this value because there will not be space enough to keep fission gas released during working time of a fuel rod in nuclear reactors. This results in cracks of fuel pellet as well as swells of fuel rod. Conversely/On the contrary, the larger grain size of fuel ceramics, the better it is. It means that fuel ceramic will burn-up better. Thus, a certain condition under which ceramic product having largest size and an acceptable density can be received should be chosen. As result of it, the temperature of 1700°C and the time period of 6 hours were used to sinter UO<sub>2</sub> fuel ceramics.

## 2. Procedure of sintering and sintering curve

### 2.1. Procedure of sintering:

Based on knowledge of sintering theory extracted from numerous references and experimental results, a procedure of sintering  $UO_2$  ceramics was built up as follows:

- Preparing specimen: Put green pellets having adequate density and not having crack, chip into a tray made of corundum or molipdel
- Preparing oven and gas feeding system: check electric supply for oven, valves of controlling gas feeding, especially the unit of preventing from inverse combustion located in  $H_2$  feeding tube, thermometer and gas gauges/meter.
- Clean atmosphere for sintering: Place the tray with green pellets into the oven then it is shut tightly. Have argon gas passed the sample chamber and heating wire chamber of the oven for 2-3 hour at the gas flow of 3 liters per hour to clean sintering atmosphere and prevent the heating wires.
- Sintering:

Turn on the oven, set the program as follows:

+  $0^{\circ}C$  ()  $\rightarrow$   $1000^{\circ}C$  ( $V_n=150^{\circ}C/h$ , keeping/retaining time = 2 hours)

+  $1000^{\circ}C \rightarrow 1700^{\circ}C$  ( $V_n=150^{\circ}C/h$ , retaining time = 6 hours)

+  $1700^{\circ}C \rightarrow 60^{\circ}C$  ( $V_{cooling} = 200^{\circ}C/h$ )

Feed the sample chamber using gas mixture of  $3H_2+N_2$  at flow of 3-4 liters per hour instead of Ar. The feeding heating wire chamber and cooling water was retained over oven's working time.

After the program was completed, stop feeding gas and cooling water. Sintered products are cooled to the room temperature.

### 2.2. Sintering curve for $UO_2$ ceramics:

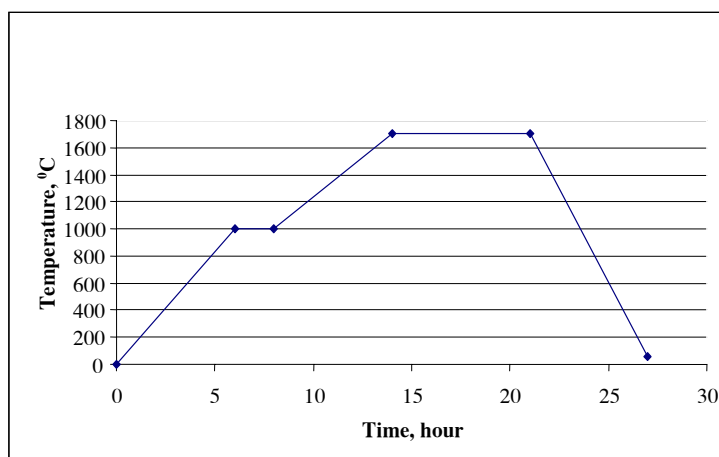


Fig. 5 Sintering curve for sintering  $UO_2$  ceramics

## 3. Obtained products and data of quality

The number of  $UO_2$  ceramic pellets was prepared following the above procedure. Obtained products have specifications as follows:



- Density of 10.60 g/cm<sup>3</sup> (97% TD)
- Mean value of grain size(μm): 12.08
- Compress strength (KG/mm<sup>2</sup>) of 12.0 (>4.5)
- Hardness Hv (KG/mm<sup>2</sup>) of 557 (>500)
- Horizontal shrinkage (%) of 21-22
- Vertical shrinkage (%) of 19-20

#### 4. Conclusion

- The process of releasing the lubricant Zn(C<sub>17</sub>H<sub>35</sub>COO)<sub>2</sub> from sintered pellet was studied. It was found that the lubricant was decomposed and completely got out of sintered pellet in gas form at 1000<sup>0</sup>C. Data of XRD analysis showed that there was no Zn in the pellets at this sintering temperature. This very well agreed with data reported in the work of Balakrishna [16].

- The sintering at temperature of 1500, 1550, 1600, 1650 and 1700<sup>0</sup>C for different periods of time (2, 4 and 6 hours) was carried out. It was observed that the density and grain size of sintered specimens very much depended on sintering time and temperature. The density and the grain size of the sintered specimens increased with the enhancement of the temperature and the time of sintering. However, density of sintered specimen reached the value of 98% TD at 1700<sup>0</sup>C and was invariable when the sintering temperature increased up to 1750<sup>0</sup>C while the grain size continuously increased with the growth of/raising temperature.

- The pellets that were sintered at 1700<sup>0</sup>C for 6 hours had the grain size of about 12μm (intended grain size is 10 μm).

- The procedure and the sintering curve for UO<sub>2</sub> production were made. The number of UO<sub>2</sub> pellets that is enough for having quality test and storage was obtained. The products had norm of quality as follows: density of 10.62g/cm<sup>3</sup> (97%TD); grain size of about 12μm; compress strength of more than 4.5 kG/mm<sup>2</sup>; hardness of more than 500 kG/mm<sup>2</sup>.

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**STUDY ON POSSIBILITY OF PRODUCING OF LIGHT-CONVERTING  
POLYETHYLENE MEMBRANE CONTAINING BIS-PHENTHROLINE  
EUROPI(III) NITRATE COMPLEX FOR AGRICULTURE**

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Nguyen Thi Thanh Thuy and Luu Xuan Dinh.**

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**Abstract:** *Eu-coordination compounds doped PE plastic has ability to convert light from violet into red increasing photosynthesis of plants. In this work, bis (1-10 phenantroline) Eu(III) nitrate complex is selected as a light converter for preparation of Eu doped PE plastic film.*

*Bis (1-10 phenantroline) Eu(III) nitrate complex was synthesized and characterization by various physical methods such as thermal analysis, IR spectroscopy, <sup>1</sup>H and <sup>13</sup>C - MNR and mass spectrum.*

*The Eu doped PE plastic film was prepared by dry mixing PE grains and powder of the complex. The optical properties of the film were characterized by absorption and emission spectra and show that the film converts light from violet into red range.*

*Preliminary tests for flower and vegetable show the good influence of the PE film on grow of the plants.*

**Key words:** *PE plastic film, Eu- coordination compounds*

## Content

### **1. Synthesis and construction of bis (1,10-phen)Eu(NO<sub>3</sub>)<sub>3</sub> complex**

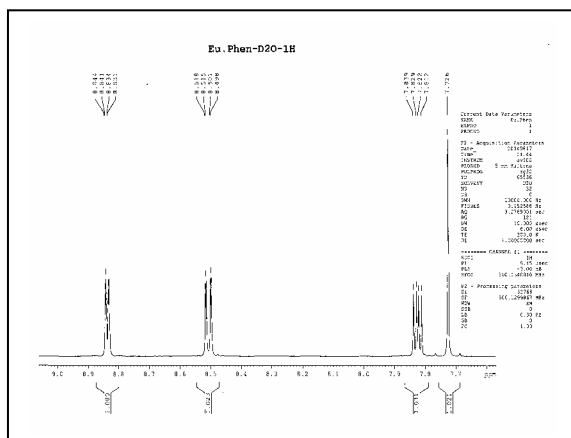
Synthesis of complex with mol ratio of ingredients and Eu(III) as a Phen/Eu = 1:1; 1:2 and 1:3, the results showed table 1

**Tab 1.** Synthesis efficiency between Eu(III) and ingredient1, 10-phenanthroline at other mol ratio

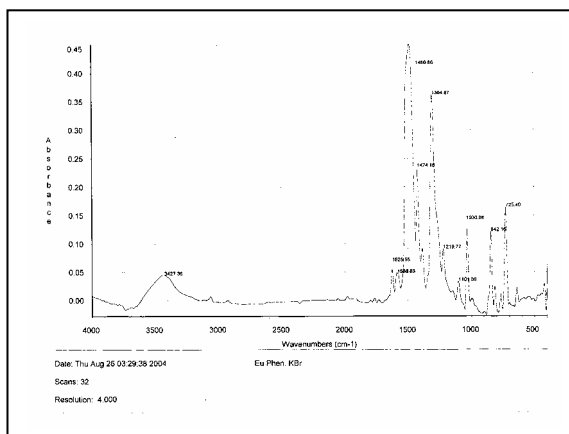
No	1,10-phen.	Eu(III)	$\frac{\text{phen}}{\text{Eu(III)}}$	Efficiency
1	2 mM	2 mM	1	47%
2	4 mM	2 mM	2	79%
3	6 mM	2 mM	3	36%

Table 1 showed that at mol ratio Phen/Eu = 1:2 synthesis efficiency highest achieved.

Bis(1,10-phen)Eu(NO<sub>3</sub>)<sub>3</sub> construction defined by modern physic methods such as Nuclear Magnetic Resonance (NMR-1H), NMR-13C, Mass Spectrum (MS), Temperature Analysis Schema and Infra-Red Spectrum.



**Fig. 1.** Nuclear Magnetic Resonance 1H of bis(1,10-phen)Eu(NO<sub>3</sub>)<sub>3</sub> complex



**Fig. 2.** Infra-Red Spectrum of bis(1,10-phen)Eu(NO<sub>3</sub>)<sub>3</sub> complex

**Tab 2.** Chemical movement and NMR-<sup>1</sup>H intensity of bis(1,10-phen)Eu(NO<sub>3</sub>)<sub>3</sub> complex

No	Frequency		Intensity	Position	σ of standard phen (ppm)
	[Hz]	[PPM]			
1	4423,085	8,8439	0,23	H <sub>5</sub> , H <sub>14</sub>	9,19 (phen) <sub>2</sub> Eu(NO <sub>3</sub> ) <sub>3</sub> (8,84)
2	4421,694	8,8411	0,27		
3	4418,110	8,8339	0,24		
4	4416,764	8,8312	0,27		
5	4259,873	8,5175	0,22	H <sub>7</sub> , H <sub>12</sub>	8,27 (phen) <sub>2</sub> Eu(NO <sub>3</sub> ) <sub>3</sub> (8,51)
6	4258,472	8,5147	0,27		
7	4251,635	8,5011	0,24		
8	4250,233	8,4938	0,28		
9	3920,412	7,8388	0,22	H <sub>6</sub> , H <sub>13</sub>	7,65 (phen) <sub>2</sub> Eu(NO <sub>3</sub> ) <sub>3</sub> (7,83)
10	3915,439	7,8288	0,23		
11	3912,178	7,8223	0,22		
12	3907,203	7,8124	0,21		
13	3863,909	7,7258	0,77	H <sub>9</sub> , H <sub>10</sub>	7,72 (7,72)

Fig 1: NMR-<sup>1</sup>H spectrum of bis(1,10-phen)Eu(NO<sub>3</sub>)<sub>3</sub> complex showed chemical movement (σ) between 1,10-phenanthroline and complex is quite difficult. Moving of electron from (14→1) to (5→4) position causes to σ decrease at this position, that proves the Eu<sup>3+</sup> center ion had connected ingredient with nitrogen atom into gamette.

Analyzing NMR-<sup>13</sup>C spectrum of bis(1,10-phen)Eu(NO<sub>3</sub>)<sub>3</sub> complex, we have seen chemical movement between standard phen and complex and chemical movement is listed at table 3

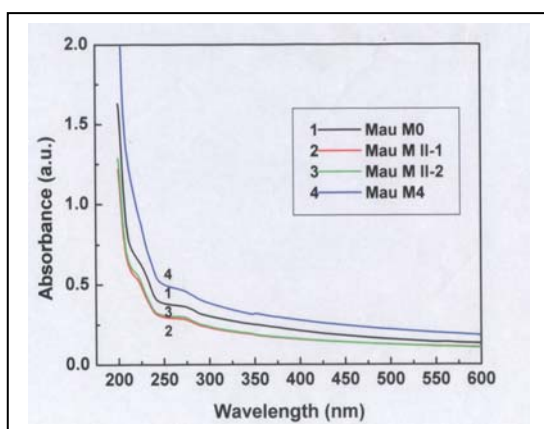
**Tab 3.** Chemical movement of Carbon in NMR-<sup>13</sup>C spectrum of Phen standard and complex

N°	Position	$\sigma$ standard Phen	$\sigma$ complex
1	C <sub>13</sub> và C <sub>6</sub>	123,4ppm	127,022ppm
2	C <sub>10</sub> và C <sub>9</sub>	126,8ppm	127,022ppm
3	C <sub>11</sub> và C <sub>8</sub>	129,0ppm	130,843ppm
4	C <sub>2</sub> và C <sub>3</sub>	137,887ppm	146,5ppm
5	C <sub>12</sub> và C <sub>7</sub>	143,387ppm	136,3ppm
6	C <sub>14</sub> và C <sub>5</sub>	148,356ppm	150,6ppm

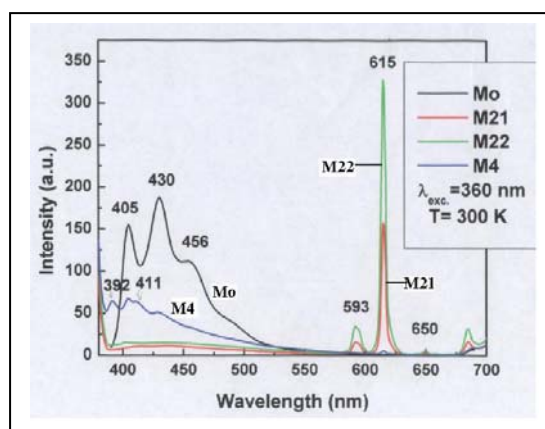
Analyzing Nuclear Magnetic Resonance (NMR-1H), NMR-13C, Mass Spectrum (MS), Temperature Analysis Schema and Infra-Red Spectrum showed bis(1,10-phen)Eu(NO<sub>3</sub>)<sub>3</sub> complex consists of NO<sub>3</sub><sup>-</sup> ion. May be construction of complex is octahedron.

## 2. Defining convert light property of PE film

PE membrane convert light property has defined by emission and fluorescence spectrum.



**Fig. 3.** Emission spectrum of PE membrane



**Fig. 4.** Fluorescence spectrum of PE membrane

*Mo:* The sample without complex

*M21:* The sample has 0,05% complex

*M22* The sample has 0,1% complex

*M4:* The standard sample (Made in Russia)

The obtained results showed that this membrane completely absorb light having wave length higher 200nm and wave length between 600 and 630nm.

Convert light efficiency of standard sample is 2%.

Convert light efficiency of M21 sample is 51%.

Convert light efficiency of M22 sample is 108%.

### Conclusion

1. Various conditions on synthesizing bis(1,10-phen)Eu(NO<sub>3</sub>)<sub>3</sub> complex such as mol ratio of ingredients, solvent content, temperature, etc... are carried out. The results showed that the best complex obtained at mol ratio phen/Eu = 2/1 and Temperature = 80°C. At this optimal condition, the synthesis efficiency is 79% with purity of 96,3%.

2. We have identified the bis(1,10-phen)Eu(NO<sub>3</sub>)<sub>3</sub> complex using modern physic methods such as Nuclear Magnetic Resonance (NMR-1H), NMR-13C, Mass Spectrum (MS), Temperature Analysis Schema and Infra-Red Spectrum. These spectra showed that the bis(1,10-phen)Eu(NO<sub>3</sub>)<sub>3</sub> complex has octogon structure with molecular form of 1-10phen)<sub>2</sub>Eu(NO<sub>3</sub>)<sub>3</sub>.

3. We have produced light converting membrane containing bis(1,10-phen)Eu(NO<sub>3</sub>)<sub>3</sub> complex with the contents of 0,05% and 0,1% and đã determined the light conversion using emission and absorption spectra. The obtained results showed that this membrane completely absorb light having wave length higher 200nm and wave length between 600 and 630nm. Therefore, this membrane can be considered as filter converting ultra light into infrared light, which is beneficial for plants.

4. The light converting membrane has been preliminarily tested on some plants.

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## **STUDY ON PREPARATION OF RUBBER ACTIVATOR CONTAINING LOW CONTENT OF ZINC OXIDE**

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**Abstract:** *The object of the present studies is to investigate the feasibility of the active zinc oxide and the activator containing low content of active zinc oxide preparation by hydrometallurgy method using ammonia- ammonium carbonate or ammonia ammonium sulfate systems.*

*The factors that effect on the active zinc oxide preparation process such as zinc basic carbonate obtaining procedure (stripping time and stripping conditions), calcination temperature, calcination time were investigated to determine the optimum processing parameters. Based on the obtained results, 98,5-99,3 % active zinc oxide having value of specific surface area equals 29–50 m<sup>2</sup>/g can be obtained by calcinating the basic zinc carbonate precursor.*

*The activator containing low content of active zinc oxide that can be obtained with high yield by co-precipitating zinc ammonium sulfate complex with lime milk (approximately 110g CaO/l) and subsequently calcinating obtained precipitate at 250°C in 2 hours, satisfied all requirements of rubber cure testing trial.*

**Key word:** *Zinc oxide, activator, vulcanization, rubber.*

### **Introduction**

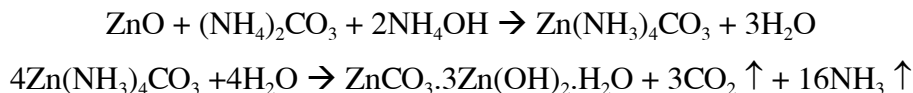
Recently, there is pressure on the rubber industry, especially in Developed Countries to reduce, or even remove, the zinc oxide used in rubber compound because of affects on the aquatic environment [1]. The use of active zinc oxide – high dispersion zinc oxide (surface area > 10m<sup>2</sup>/g) have reduced the zinc content in rubber cure process comparing with conventional zinc oxide products (>98.5%, surface area 3-5m<sup>2</sup>/g) [11, 12] while keeping or improving physico-mechanical properties of rubber products. [1-4]

Thermal decomposition of basic zinc carbonate obtaining from hydrometallurgy processes is of commercial interest in the production of active zinc oxide products. By means of this process, zinc oxide products have met two basic standards: high surface area and low content of harmful impurities (as Pb) [7-10, 14]. Besides, commercial rubber activator containing low content of zinc oxide (33-35% ZnO) required further investigations for establishing suitable flowsheet and adapting the new requirement of activator market.

### **Results and discussion**

Based on the easily conversion to other zinc compounds (including zinc oxide), basic zinc carbonate is most important zinc precursor. The decomposition at low temperature can permit obtaining high surface area zinc oxide because of minimizing agglomeration effects. [7, 10, 14]

The project coding CS/03/03-03 showed the efficiency of zinc leaching process by using ammonia – ammonium carbonate solution.



In zinc basic carbonate recovery step, the use of steam gas for stripping permits efficiently recovering uniform basic zinc carbonate with high yield (about 95%) and capacity in comparison with the use of air and external heating because of  $\text{NH}_3$ ,  $\text{CO}_2$  are efficiently separated from solution.

In calcination step, the dried powder becomes loose due to both the separation of internal molecular water and the formation of  $\text{CO}_2$  gas produced from the thermal decomposition reaction of basic zinc carbonate, giving zinc oxide powder. Calcination time and temperature strongly affected to the physico-mechanical properties of the oxide powder including the specific surface area – the important factor that determines “active” character and applicability of the product as rubber cure activator [5,6]. The influence of calcination temperature and calcination time on the specific surface area of product have been investigated.

Based on the obtained results, we can see strongly effect of calcination temperature and calcination time because of agglomeration effect at high temperature; and these data are agreeable with references [1-4]. After calcining at about 300 - 400 °C in 2 hours, active zinc oxide product with 98.5-99.3% content can be obtained and the specific surface area values have reached 29 – 50  $\text{m}^2/\text{g}$ .

In order to produce rubber cure activator containing low content zinc oxide, technological orientation, selection depend on the chemical physical tests of commercial samples as chemical analysis, XRD, DTA-TGA. The obtained results showed that the RA sample consists of  $\text{ZnO} \cdot x\text{H}_2\text{O}$  and calcium sulfates as  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ;  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$  with mol ratio between Zn and  $\text{CaSO}_4$  is equivalent 1:1. Based on these evaluation, This kind of activator can be produced by co-precipitation method using calcium compounds as precipitation agent from zinc complex solution (zinc-ammonium-ammonium sulfate system) and subsequent to drying and calcining obtained precipitate.

Problems must be solved in investigations is that

- High zinc recovery yield.
- Composition and specific surface area of powder must be equivalence to commercial sample (RA).

Considering the practical conditions, the co-precipitation can be carried out by using two precipitation agents as  $\text{CaCl}_2$  solution or lime milk with two mode:

- Dropping zinc complex solution to reactor containing  $\text{CaCl}_2$  solution or lime milk with agitation, heating and air stripping.
- Dropping zinc complex solution to reactor containing  $\text{CaCl}_2$  solution or lime milk with agitation and steam stripping.

Based on the obtained data, zinc can be recovered with high yield by coprecipitation method using lime milk as precipitation agent.

The co-precipitation with lime milk and steam stripping qualified all above requirements and precipitate can be used for the next investigation steps.

After filtered, washed, dried at about 70°C, the precipitate will be calcined in the range of 200 - 600°C in 2 hours. Zinc content and specific surface area are determined and the obtained product have qualified main standards as composition, specific surface area compared to commercial sample (RA – Thailand).

Test results for material standard and phisico-mechanical properties of rubber products using obtained product and RA sample are compared each other. The obtained results show that the quality of product are the same as RA sample.

### Conclusion

1. Basic zinc Carbonate can be recovered from zinc-ammonium-amonium carbonate system by steam stripping process with yield as about 95%.

2. Active zinc oxide (98.5-99.3 %) can be produced by calcination of basic zinc carbonate at about 300-400 °C in 2 hours. The specific surface area value can be reached 29 – 50 m<sup>2</sup>/g .

3. The rubber cure activator containing low content of zinc oxide (33-35% ZnO and base filler CaSO<sub>4</sub>) can be produced by using co-precipitation method with lime milk as precipitation agent from zinc-ammonium-ammonium sulfate system. The obtained product have qualified testing trial for material standard and phisico-mechanical properties of rubber products.

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# APPLICATION RESEARCH OF INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS) FOR EVALUATION OF ENVIRONMENTAL WATER AND INSPECTION OF NUCLEAR GRADE URANIUM PRODUCED IN INSTITUTE FOR TECHNOLOGY OF RADIOACTIVE AND RARE ELEMENTS

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**Abstract:** *Qualification assurance and qualification control protocol (QA/QC Protocol) was provided. Based on research and development, EPA method, ASTM, procedure for analysis of Cr, Ni, Cu, Zn, As, Cd, Pb, Th and U in surface water and impurities in nuclear-grade uranium is established.*

**Key word:** *QA/QC, Surface Water, Impurity, Nuclear-grade uranium, ICP-MS*

## Experimental and Results

### **1. Qualification Assurance and Qualification Control protocol (QA/QC Protocol)**

ICP-MS Qualification Assurance and Qualification Control protocol is a part of Laboratory QA/QC system. Based on references and specification of ICP-MS, ICP-MS QA/QC protocol is provided with section as following:

- 1.1. Warm up
- 1.2. Mass Calibration
- 1.3. Response Calibration- Mass Linearity
- 1.4. Detector Cross – Calibration
- 1.5. Resolution Check
- 1.6. Memory Check
- 1.7. Blank Acceptance
- 1.8. Calibration – Sensitivity
- 1.9. Stability
- 1.10. ICP-MS Operation Log

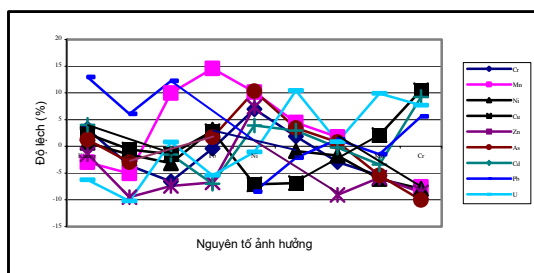
### **2. Research on the determination of As, Cd, Cr, Cu, Pb, Zn, Mn, Ni and U in surface water by ICP-MS**

ICP-MS technique is very wide linear range. Linearity of Cr, Ni, Cu, Zn, As, Cd, Pb, Th and U concentration within 0.5 ppb – 5000 ppb and 10 ppb – 10000 ppb were studied (table 1).

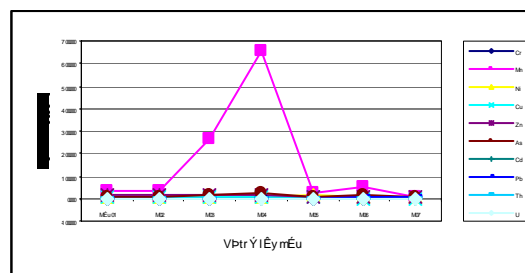
**Tab 1.** Linear equation of As, Cd, Cr, Cu, Pb, Zn, Mn, Ni and U

No	Element	Linear Equation	Correlation coefficient	Con. Range (µg/L)
1	As	$y = 1,479 \cdot 10^3 x + 6,947 \cdot 10^2$	0,9901	0,5-5000
2	Cd	$y = 4,937 \cdot 10^3 + 1,27110 \cdot 10^2$	1,000	0,5-5000
3	Cr	$y = 3,226 \cdot 10^3 x + 6,223 \cdot 10^2$	0,9980	10-10000
4	Cu	$y = 1,775 \cdot 10^4 x + 2,24 \cdot 10^4$	0,9990	10-10000
5	Pb	$y = 2,518 \cdot 10^4 x + 9,790 \cdot 10^3$	1,0000	0,5-5000
6	Zn	$y = 4,626 \cdot 10^3 x + 2,87 \cdot 10^4$	0,9998	10-10000
7	Mn	$y = 3,572 \cdot 10^4 x + 1,259 \cdot 10^4$	0,9999	10-10000
8	Ni	$y = 6,798 \cdot 10^3 x + 1,876 \cdot 10^3$	0,9996	10-10000
9	U	$y = 4,076 \cdot 10^4 x + 5,80 \cdot 10^2$	0,9998	0,5-5000

Results of research showed that analytical results of Cr, Ni, Cu, Zn, As, Cd, Pb, Th and U in surface water were not interfered by matrix. In the other hand, Cr, Ni, Cu, Zn, As, Cd, Pb, Th and U were not interfered one another when one concentration is 2500 times higher than others (Fig. 1).



**Fig. 1.** Influence of As, Cd, Cr, Cu, Pb, Zn, Mn, Ni and U one another when their determination by ICP-MS



**Fig. 2.** Analytical results of metals in water samples located in Hanoi

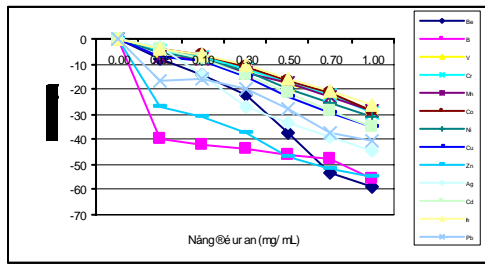
Based on research and development, EPA method, ASTM, procedure for analysis of Cr, Ni, Cu, Zn, As, Cd, Pb, Th and U in surface water is established.

Analysis of metals in water samples located in Hanoi by ICP-MS was carried out and the analytical results were showed in fig. 2.

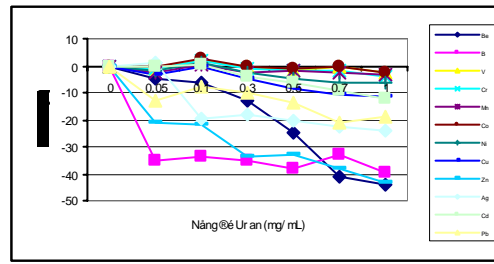
### 3. Determination of impurities in uranium produced in Institute for Technology of Radioactive and Rare Elements.

#### 3.1. Determination of metal impurities

Studies on the determination of metal impurities in the present of large amount uranium using and without using internal standard were carried out. Response was decreased when uranium concentration was increased (Fig.3 and 4), but metal impurities in nuclear grade uranium can be determined without any separation step of impurities from uranium matrix.



**Fig. 3.** Influence of uranium on bias of results of metal impurities determined by ICP-MS



**Fig. 4.** Influence of uranium on bias of results of metal impurities determined by ICP-MS using internal standard

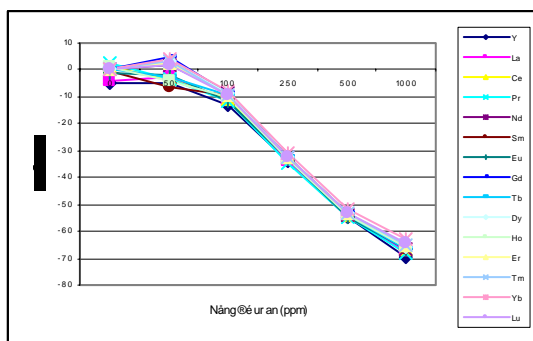
Based on research and development, Standard Test Method for uranium impurities (ASTM), procedure for analysis of metal impurities in nuclear grade uranium is established.

Determination of metal impurities in nuclear grade uranium produced in Institute for Technology of Radioactive and Rare Elements by ICP-MS using procedure provided was carried out.

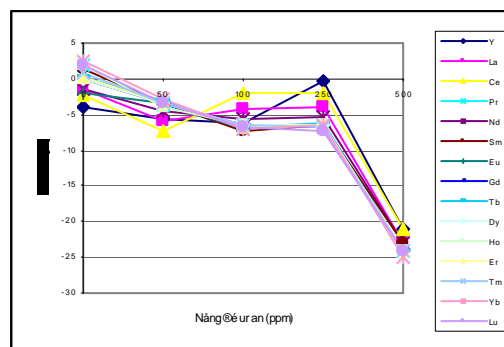
**3.2. Determination of rare earth elements (REs) impurities**

Studies on the determination of REs impurities in the present of large amount uranium using and without using internal standard were carried out. The results of studies showed that REs impurities can be determined by ICP-MS when uranium concentration of 150 ppm (250 ppm using internal standard) (Fig.4 and 5). In order to determine REs impurities in nuclear grade uranium, they must be separated from uranium by solvent extraction with TBP and CCl<sub>4</sub>, medium HNO<sub>3</sub> 4 N.

Response was decreased when uranium concentration was increased (Fig.4 and 5), but impurities in nuclear grade uranium can be determined without any separation step of impurities from uranium matrix.



**Fig. 4.** Influence of uranium on bias of results of REs impurities determined by ICP-MS



**Fig. 4.** Influence of uranium on bias of results of REs impurities determined by ICP-MS using internal standard

## Conclusion

Based on research and development, Standard Test Method for impurities in uranium (ASTM), procedure for analysis of REs impurities in nuclear grade uranium is established.

Determination of REs impurities in nuclear grade uranium produced in Institute for Technology of Radioactive and Rare Elements by ICP-MS using procedure provided was carried out.

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## **STUDY ON PREPARATION OF TUNDISH FOR CONTINUOUS STEEL CASTING**

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**Abstract:** *Some kinds of tundishes made in China, Austria, India, that have been used in the lines of continuous casting of steel in Vietnam, were collected. Their dimension, shape and composition have been verified. A kind of tundish, that has the outer layer of high alumina refractory and inner layer of zirconia ceramics, was prepared in our laboratory. The technological parameters (especially the shrinkage) of the two materials used for production of tundish inner and outer layers were investigated. It was found that high alumina refractory of more than 80%  $Al_2O_3$ , which has the shrinkage of 0-1% at 1600<sup>o</sup>C and zirconia ceramic material sintered at 1700 <sup>o</sup>C for 2 hours, which has volume density of 5.4 g/cm<sup>3</sup> and the shrinkage of 12-13 %, were adequate to fabricating the tundish outer layer and inner layer respectively.*

*The number of tundishes was made. The products were tested at the line of continuous casting of steel. These tundishes worked well for continuous 7 hours.*

**Keyword:** *Tundish, high alumina refractory, zirconia ceramics.*

### **Introduction**

Tundishes used for middle/pouring tank in system of continuous steel casting is a refractory device, which is required a resistance to wear caused by melting steel running by. In Vietnam tundishes used for steel casting (about 40 000 pieces per year and about 90 000 pieces for 2007) has been all imported.

Tundishes are made mainly of zirconia ceramics because this material has a good resistance to the abrasion of melting steel at high temperature (about 1600<sup>o</sup>C).

Some private and state enterprises are interested in study on fabricating (and testing) tundish. However, none of tundishes made in Vietnam has been used in practice of fabricating steel so far.

The main objectives are as follows:

1. Building up a technological procedure of preparing three-layer tundish used for continuous steel casting and
2. Preparing, testing and applying obtained products to enterprises of steel casting.

### **Theory**

During working time, tundishes have to sustain very severe conditions, such as high temperature (1530-1600<sup>o</sup>C), chemical attack and mechanical abrasion due to running by of melting steel. Materials used for fabricating tundish must have special, typical properties such as lasting resistance to high temperature, low degree of wear, absence from chemical reactions with melting steel, etc.

High alumina refractory material obtained from natural  $\text{Al}_2\text{O}_3$  rich minerals, which briefly comprised mullite and corundum, was used for preparing the outer layer of tundish.

Zirconia ceramics, which is made from pure  $\text{ZrO}_2$  and stabilizers of CaO, MgO by ceramic technology, was used for fabrication of inner layer of tundish.

## **Experiment and result**

### **1. Learning about tundishes of foreign countries**

Some kinds of tundishes that were imported from China, India and Austria were collected

The chemical compositions, shape, dimension and construction of the tundishes' layers were determined.

### **2. Study on preparation of materials**

#### ***2.1 Study on preparation of high alumina refractory:***

Start materials consist of high alumina refractory material in particle form, which have more than 80%  $\text{Al}_2\text{O}_3$ , less than 2%  $\text{Fe}_2\text{O}_3$ , particle size of 0,5 mm, glass and PVA (polyvinyl alcohol) used as kaolin's dopant.

The influences of kaolin content and temperature on shrinkage of material were verified. It was found that the effect of temperature was trivial while affect of kaolin content was evident. The higher content of kaolin was the higher shrinkage of materials was. However, the shrinkage caused by kaolin is considered as being not high (0-0.1%). At the dopant content of 10-15%, process of forming devices was done easily and dimension of obtained products well met the requirement for assembling devices of product.

#### ***2.2 Study on fabrication of zirconia refractory:***

The raw materials comprises zirconia powder of ZIRCOA ( $\text{ZrO}_2$ - ZIRCOA), which has 99,3%  $\text{ZrO}_2$ , particle size of less than  $10\mu\text{m}$  and zirconia of ITRRE ( $\text{ZrO}_2$ -CNXH), which contains about 96%  $\text{ZrO}_2$  and dopants of MgO, CaO, PVA.

The effect of sintering temperature was investigated. The result implied that  $\text{ZrO}_2$ - ZIRCOA and  $\text{ZrO}_2$ -CNXH both have rather good sinterability.

CaO and MgO were used as stabilizers. It was observed that condensation process in the presence of CaO is better than that in the presence of MgO. The pressure of around 1-1.5  $\text{T/cm}^2$  did not much effect on volume density and shrinkage of ceramic products.

### **3. Preparing tundish and testing obtained products**

#### ***3.1. Preparing tundish:***

Based on the technical parameters of materials, especially their shrinkage, the dies used for preparing outer and inner layers of the tundish were designed. More than 20 tundishes have been made.

#### ***3.2. Testing obtained products:***

Six tundishes were tested in the line of continuous steel casting of Luu Xa steel factory. They all worked well without any problems/breakdowns. The maximum period

of continuous working was 8.5 hours. The period of 7 hours was considered as safe working time for these tundishes.

### **Conclusion**

Some kinds of tundishes made in China, Austria, India, which have been used for the lines of continuous steel casting in Vietnam, were collected. Their dimension, construction and composition have been verified. A kind of tundish, that has outer layer of high alumina refractory and inner layer of zirconia ceramics, was prepared in our laboratory. The technological parameters (especially the shrinkage) of the two materials used for production of tundish inner and outer layers were investigated. It was found that high alumina refractory of more than 80%  $\text{Al}_2\text{O}_3$ , which has the shrinkage of 0-1% at  $1600^\circ\text{C}$  and zirconia ceramic material sintered at  $1700^\circ\text{C}$  for 2 hours, which has volume density of  $5.4 \text{ g/cm}^3$  and the shrinkage of 12-13 %, were adequate to fabricating the tundish outer layer and inner layer respectively.

The number of tundishes was made. The products were tested at the line of continuous steel casting. These tundishes worked well for continuous 7 hours.

The results of the work, especially the results of the test, implied that all the objectives of the theme were completed well.

It is necessary to have further studies to enhance product quality and to have equipping with hydraulic press and oven that have output capacity appropriate to production rank, so that stable supply enterprises of steel casting with tundish can be available.



## **RESEARCH ON ABILITY OF ENRICHING TIN ORE WITH HIGH IRON CONTENT AT THE QUY HOP, NGHE AN**

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Nguyen Duc Hung, Le Quan, Ta Vu Nguyet Anh, Tran Van Son and Nguyen Hoang Son**

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**Abstract:** *The researching ore sample of the theme is mother-tin middling ore with difficult washability and big reserve at Quy Hop tin mine in Nghe An province. At present, an optimum technology to treat this tin ore is not researched by any special organization.*

*The implementing group have researched and deployed for near one year, the results obtained as followings:*

*1. Tin in the ore sample exists in cassiterite category dispersed very fine from 0.01mm to 1.2mm for tin containing mineral.*

*Iron in the ore sample exists mainly in non-magnetic, weak-magnetic or mineral category such as limonite, mactic, gothite, and hematite, etc also dispersed from very fine 0.02mm to 0.6mm for iron containing mineral.*

*2. The ore treating technology is described as followings:*

*Raw ore is dissolved actively by HCL acid with solvent, and then mechanical separations such as classification, crushing, dry magnetic separator with high or low magnetic field strength are used for getting standard clean ore quality.*

*Ore sample is dissolved actively by HCL acid with solvent, washed cleanly, dried and screened by 0.5mm aperture screen. Under screen product is separated by high magnetic field strength separator that made from rare earth, the non-magnetic product is clean tin ore product. The over screen product is crushed 0.5mm minus particle and together magnetic product from magnetic separator is dissolved again. Clean tin ore quality exceeds proposed demand.*

- Content of tin Sn: > 68.0 %
- Content of iron: < 3.0 %
- Tin recovery: (89.0 ÷ 92.0) %

**Key words:** *Tin ore with high iron; Ore dressing chemical.*

### **Report**

The researching ore sample of the theme is mother-tin middling ore with difficult washability and big reserve at Quy Hop tin mine in Nghe An province. At present, an optimum technology to treat this tin ore is not researched by any special organization.

Mineral component of the ore sample is rather complicated with high tin and iron contents (Sn = 42.46 % and Fe = 17.87%); especially iron content is higher than permissible iron content in tin ore.

Tin containing mineral only exists in cassiterite category. Iron containing mineral mainly exists in non-magnetic, weak-magnetic or middling-magnetic category such as limonite, mactic, gothite, and hematite. Iron containing mineral exists in magnetite category consists of a little proportion.

Tin containing mineral and iron containing mineral are dispersed from very fine to fine from 0.01mm to 1.2mm for tin containing mineral and from 0.02mm to 0.6mm for iron containing mineral. Other side, there are some other minerals such as pyrite, covenlin, rutil, ilmenite, granite, etc in the ore sample.

In order to get tin ore with iron content lower than 2.5% - 3.0% obtaining permissible iron content for metallurgy, the ore-sample enriching technology is not a conventional technology (Mechanical method) but a chemical-treating technology.

Raw ore is dissolved by HCl acid for dissolving iron containing mineral. As of the result, almost tin containing mineral particles in different size are liberated. The implementing group has chosen an actively dissolved method by using solvent with efficient and fast dissolving time. After that, mechanical separation such as classification, crushing, dry magnetic separator with high or low magnetic field strength is used for getting clean ore with standard quality.

The technology diagram for treating ore sample is showed in the figure 1: Ore sample is dissolved actively by HCl acid with solvent, washed cleanly and screened by 0.5mm aperture screen. Under screen product is separated by high magnetic field strength separator that made from rare earth. The non-magnetic product is clean tin ore product. The over screen product is crushed into particle of <0.5mm for generating a new contacting surface between the particles and acid, then is dissolved again together with magnetic product from magnetic separator.

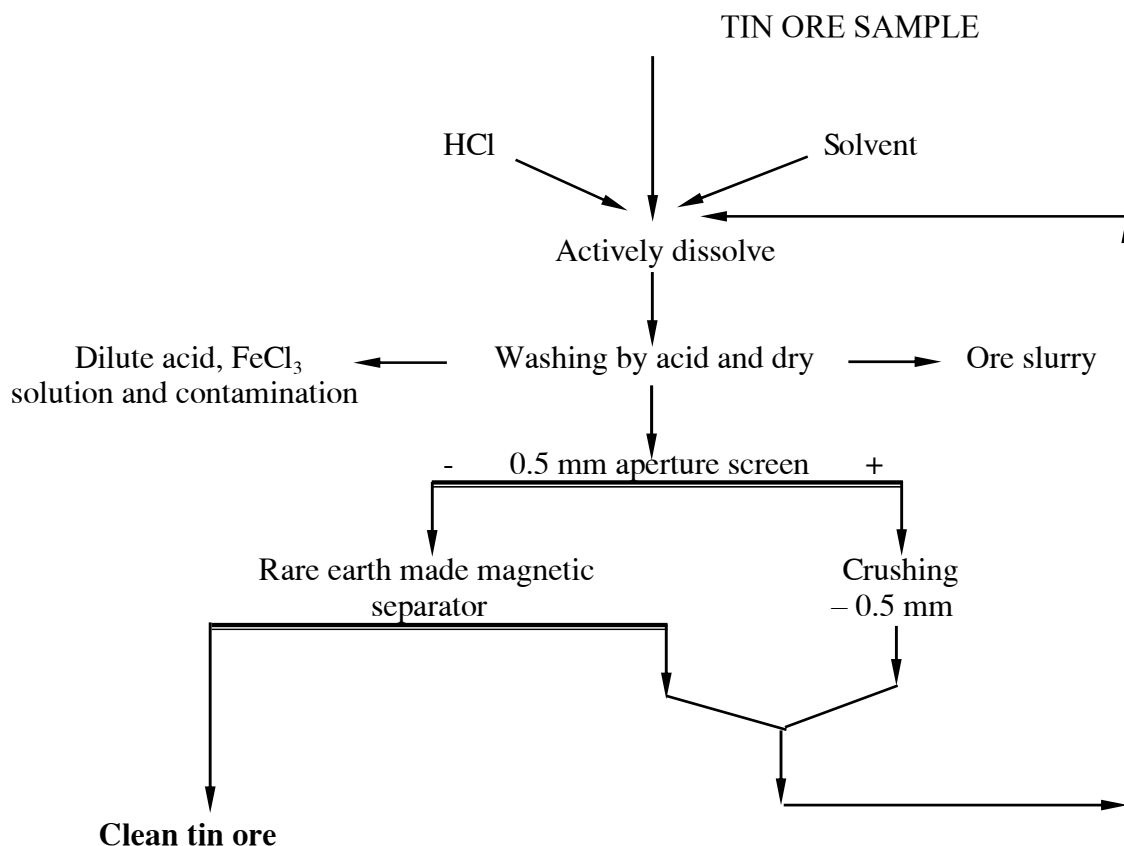


Fig. 1. Tin ore actively dissolving with solvent and enriching technology

The final result from ore treating procedure in the figure 1 is to obtain clean tin ore product with high quality (Supposing that, Cassiterite mineral is not dissolved by HCl acid in calculation).

- Content of tin: > 68.0 %
- Content of iron: < 3.0 %
- Tin recovery: (89.0 ÷ 92.0) %

According to researching results, the theme proposes some problems necessary for researching and deploying proceedingly such as:

1. Recovery of very fine tin from slurry overflow product in dissolved-tin ore washing process is necessary. It occupies from 7% to 9% in raw tin ore with high tin content from 43% to 56%.

2. In order to use effectively natural mineral resource, it is necessary to recovering solution  $\text{FeCl}_3$ , a sub product from dissolving process. The sub product with a large volume is quite clean and contains a little amount of contaminants (Raw ore is middling product). 1.2-1.3kg of the 30%  $\text{FeCl}_3$  solution of is obtained from 1kg of raw ore.

3. Experiments on proposed technology diagram and determination of enriching cost in semi-industry or production scale have been carried out.

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## STUDY ON VIETNAMESE ILMENITE ORE TREATMENT IN HIGH TEMPERATURE FURNACE USING $\text{CaC}_2$ IN ORDER TO GET REDUCED ILMENITE PRODUCTS FOR WELDING SUBSTANCE AND WELDING ELECTRODES

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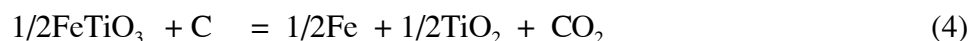
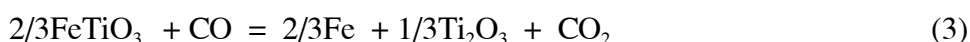
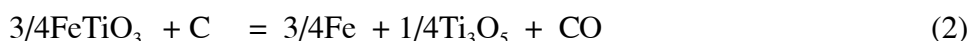
**Abstract:** *The selection of reagents for ilmenite ore treatment depends on the demand and purpose of application's products. The project aim is to study ilmenite ore treatment in high temperature furnace using reductant  $\text{CaC}_2$ . The treatment processes were carried out at various temperatures,  $\text{CaC}_2/\text{FeTiO}_3$  ratio, time of roasting process and based on these studied, optimum technological parameters of process have been determined, they are as following:  $T = 1150^\circ\text{C}$ ,  $t=3\text{h}$ ,  $\text{CaC}_2/\text{FeTiO}_3 = 0,15$ . The reduced ilmenite product has following characteristics: recovery efficiency = 85%, bulk density =  $1,45\text{g/cm}^3$ ; particle size of ore < 0,15 mm. The chemical compositions of reduced ilmenite product (%):  $\text{TiO}_2 > 50$ ;  $\text{Fe} > 24$ ;  $\text{FeO} < 6,5$ ;  $\text{CaO} < 0,75$ ;  $\text{C} < 0,2$ ;  $\text{P}$  and  $\text{S} < 0,015$ . This reduced ilmenite product is suitable for making of welding substance and welding electrodes. The study result may be used for ilmenite ore treatment on the pilot scale.*

*In comparison with other traditional methods, the roasting method has some things well in technology and can meet all environmental and technical objectives.*

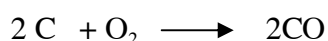
**Key words:** *Ilmenite, reduced ilmenite product.*

### Theory Base

The reducing reaction between the ilmenite ore and reagents C and CO at temperature  $950 - 1200^\circ\text{C}$  can be written as following:



The reaction between ilmenite concentrate and reductant  $\text{CaC}_2$  happens in two stages: The first, at temperature about  $1000^\circ\text{C}$ , cacbua canxi is converting into Ca and C:



and then C, CO reacts with ilmenite ore like reactions (1), (2), (3), (4).

The final product of these reactions is reduced ilmenite product. The reduced ilmenite product consists of Fe, FeO, TiO,  $\text{TiO}_2$ ,  $\text{Ti}_2\text{O}_3$ ,  $\text{Ti}_3\text{O}_5$ . This reduced ilmenite product may be separated by magnetic separation method.

## Experiments and results

### Starting materials:

Hatinh ilmenite concentrate, the mineralogical analysis (by weight) of which is shown in table 1.

- Reductant  $\text{CaC}_2$  ;
- Other additives.

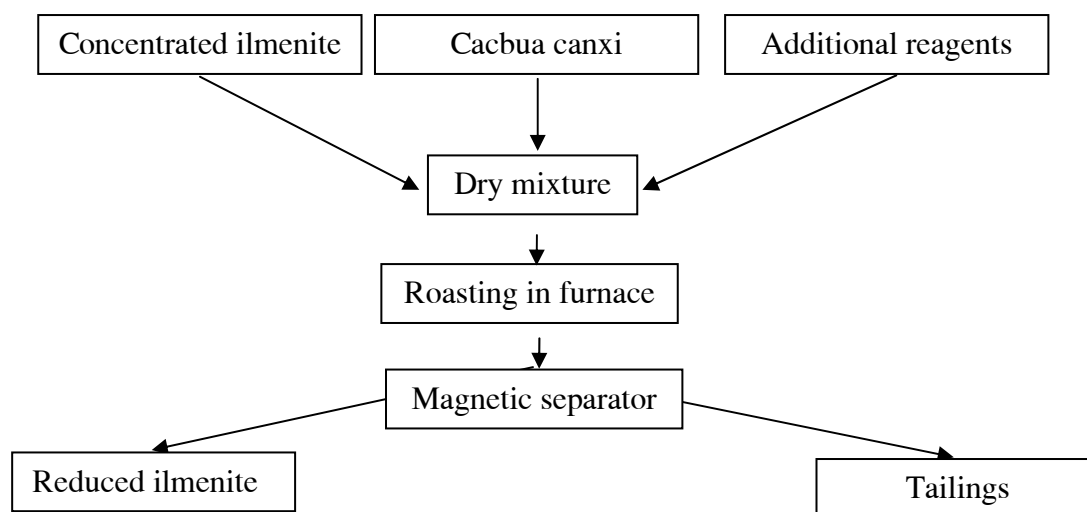
**Tab 1.** Mineralogical analysis of ore samples

Size	Chemical compositions, %										
	TiO <sub>2</sub>	FeO	Fe <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	P	S	C	Wt.
<200 μm	53,97	26,39	15,92	0,02	3,0	0,25	0,04	0,025	0,037	0,29	0,06

### Equipment for study:

Electric furnace (made in Germany), the maximum temperature of furnace is 1200°C. The volume of furnace: 4,0liters, Magnetic separator

The main technological process of reduced ilmenite production can be presented in figure 1.

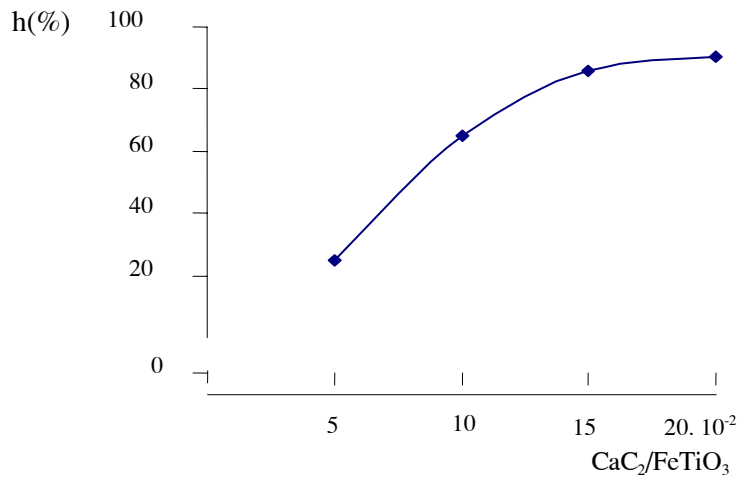


**Fig. 1.** Technological flowsheet for reduced ilmenite production

Based on this technological process, we have studied some factors (such as temperature of roasting process, roasted ore /  $\text{CaC}_2$  ratio, time of roasting process) effecting on ilmenite recovery yield.

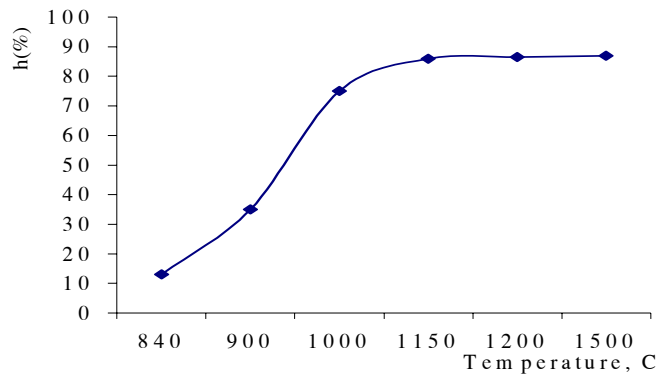
a) Effect of  $\text{CaC}_2/\text{FeTiO}_3$  ratio on recovery efficiency under conditions: roasting temperature 1150°C and roasting time: 4h, are represented in the figure 2.

By increasing  $\text{CaC}_2/\text{FeTiO}_3$  ratio, the recovery efficiency increased and reached maximum at  $\text{CaC}_2/\text{FeTiO}_3 = 0,15$ .



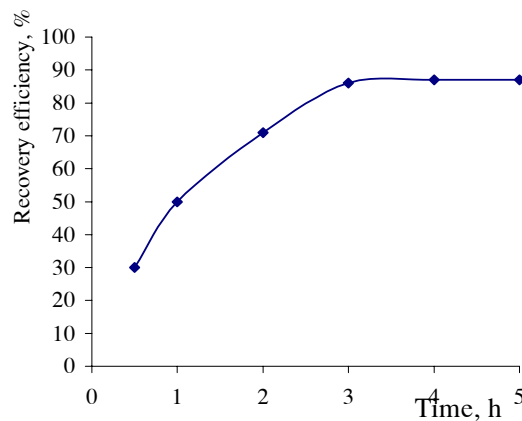
**Fig. 2.** Effect of CaC<sub>2</sub>/FeTiO<sub>3</sub> ratio on recovery efficiency

b) Effect of temperature on recovery efficiency under conditions roasting time: 4h, CaC<sub>2</sub>/FeTiO<sub>3</sub> = 0,15 are presented in figure 3.



**Fig. 3.** Effect of temperature on recovery efficiency

c) Effect of roasting time on recovery efficiency under condition: temperature 1150°C and roasting time: 4h, are represented in the figure 4.



**Fig. 4.** Effect of roasting time on recovery efficiency

Table 2 showed the recovery efficiency, quality and technological characteristic of reduced ilmenite product getting after roasting process with parameters: temperature 1150°C, t = 3h, CaC<sub>2</sub>/FeTiO<sub>3</sub> = 0,15.

**Tab 2.** Technical parameters and Quality of reduced ilmenite product

Technical parameters			Quality of reduced ilmenite product									
CaC <sub>2</sub> / FeTiO <sub>3</sub>	T, °C	Roasting time, h	Efficiency, %	Density g/c m <sup>3</sup>	TiO <sub>2</sub> , %	Fe, %	FeO, %	Fe <sub>2</sub> O <sub>3</sub> , %	CaO, %	C, %	P, %	S, %
0,15	1150	3,0	>86,0	1,45	>50,0	>24,0	<6,5	–	0,75	0,2	0,01	0,02

The table 3 showed the quality of reduced products produced in different countries. It shows that quality of our reduced ilmenite product is as good as one of other countries.

**Tab 3.** The quality of reduced product produced in different countries

Composition	The quality of reduced product produced in different countries		
	ITREE	Europe	China
TiO <sub>2</sub> , %	> 50,0	> 40,0	> 48,0
Fe, %	> 24,0	> 35,0	> 20,0
FeO, %	< 6,5		< 7,0
Fe <sub>2</sub> O <sub>3</sub> , %	–		–
CaO, %	0,75	–	–
C, %	0,20	0,2	0,2
P, %	0,01	0,02 - 0,025	0,03
S, %	0,02	0,02 - 0,025	0,03
Bulk density, g/cm <sup>3</sup>	1,45	–	1,7

The reduced ilmenite product was used for making the welding substances and welding electrodes. The experimental results show that these welding substances and welding electrodes have good quality and meet all practical requirements.

### Conclusion and proposal

- The treatment of Ha Tinh ilmenite ore in high temperature furnace using  $\text{CaC}_2$  in order to get reduced ilmenite products have been carried out. The flowsheet for treatment has been established.
- The optimum parameters for treatment have been determined. The ilmenite recovery yield can reach more than 85% when concentrate is roasted at temperature  $1150^\circ\text{C}$ ,  $t = 3\text{h}$ ,  $\text{CaC}_2/\text{FeTiO}_3 = 0,15$ . The impurities such as P, S, C in reduced ilmenite product are so few and product meets requirements for welding substance production.
- Experimental results showed that reduced ilmenite product can meet all requirements for welding substance and welding electrodes production.
- The successful completion of this project opens a new way in expanding production of reduced ilmenite in the pilot scale. That is why the head of the project proposes ITRRE, VEAC and concerned bodies of MOST to permit to develop the project into P project in coming years, to apply tested results into larger scale production in order to meet the demand of Vietnam welding substance and welding electrodes production.

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# RESEARCH METHODOLOGY OF SCALING-UP HEAP LEACHING PROCESS FOR URANIUM ORE OF NONG SON BASIN OF VIETNAM

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**Abstract:** *The project carried out researches of the heap leaching process of uranium ore in a systematic way with equipment of 9 liter in volume; hence developed a model that is capable to apply for a larger scale equipment. A heap leaching equipment with volume of 800 liter had been constructed and run to test the prediction about its performance from the model.*

**Key words:** *Uranium, heap leaching, modeling.*

## Contents

### 1. Preliminary tests

Preliminary tests were carried out with 15 kg of ore in a column of 9L volume and the bed height  $H = 1$  m. The lixiviant is 50 g/l sulphuric acid. Data about acid consumption in the first few days revealed that after about 5 hours of reaction it is possible to consider that the reaction moves into the inner part and the internal diffusion is the factor determining the rate of the whole process. Hence, the suitable procedure of leaching was developed where acid is not sprayed continuously onto the head of column but intermittently by a predetermined procedure. This procedure helps reduce acid consumption while increase uranium content in the leach solution and the overall uranium yield. The final leaching procedure was developed based on the principle of “reverse capillarity”.

The most important result of the research is to reveal the rule governing the kinetic factors of heap leach. Experimental relationship between overall uranium yield, duration of leaching and concentration of sulphuric acid used for leach was established, thus facilitating prediction of leach performance in larger scales.

### 2. Results obtained from experiments

Leaching experiments had been carried out for non-weathered ore with different acid concentrations: 30, 40, and 50 g  $H_2SO_4/l$ . When using acid concentration of 50 g  $H_2SO_4/l$ : total leaching time is 47 hours, acid consumption is around 27.5 kg/t of ore. The recovery of uranium is 78.4%, and the acidity of the leach liquor is 21.6 g/l with the uranium concentration of 1.09 gU/l.

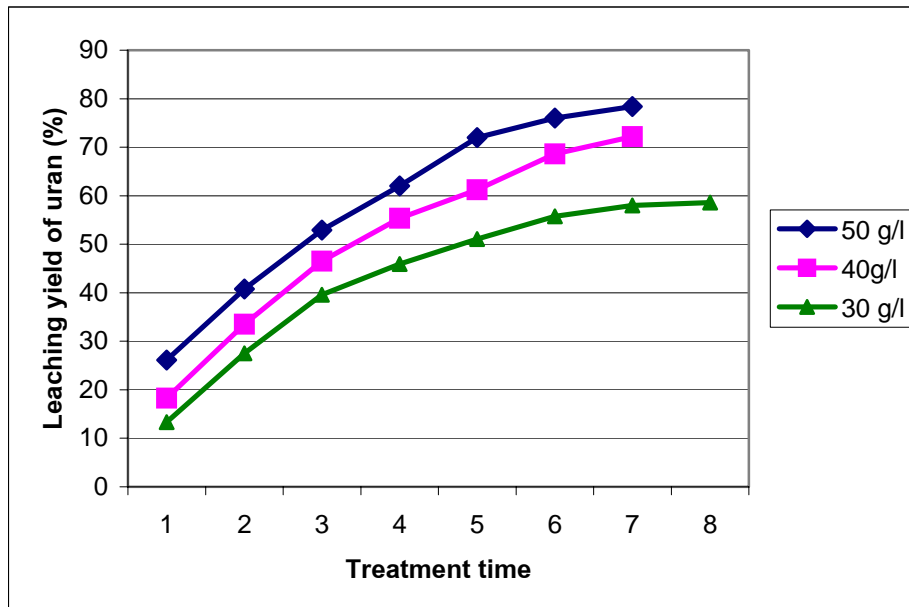
Other results for the cases of using acid concentrations of 30 and 40 g/l were obtained similarly.

### 3. Development of leaching model from experimental results

#### 3.1 General principles:

Based on principles of reverse capillarity, a static leaching model was set up using a new concept of “**treatment time**”. One treatment time is thought to include one time of acid

spraying through the ore bed until the reaction rate between acid and the ore become negligibly small, and the subsequent draining of all solution from the ore bed. Arranging experimental results as leaching yields versus treatment times, we can obtain the results as in the chart 1 below:



**Chart 1:** Leaching yields versus treatment times

It is clearly seen from the above chart that the concept of “treatment time” is extremely suitable to represent the factor of “leaching time” for the case of static leaching. Development of leaching model is to find relationship between leaching yield and number of treatment times.

### 3.2 Development of the mathematical model:

A suitable form of mathematical equation that can describe the above relationship was determined as:

$$R = \frac{k_1 t^n}{1 + k_2 t^n} \quad (1)$$

Where: R: leaching yield (at the treatment time t)

t: treatment time

k1, k2, n: rate parameters, determined by experiments

By using the new concept of “treatment time” instead of real time, a new mathematical relationship between leaching yield and number of treatment times has been established. Values of rate parameters k1, k2, n are determined by least square method where the sum of squared errors . . . is minimized with the help of Solver tools in Microsoft Excel. The typical values of those rate parameters are shown in the Chart 2 below:

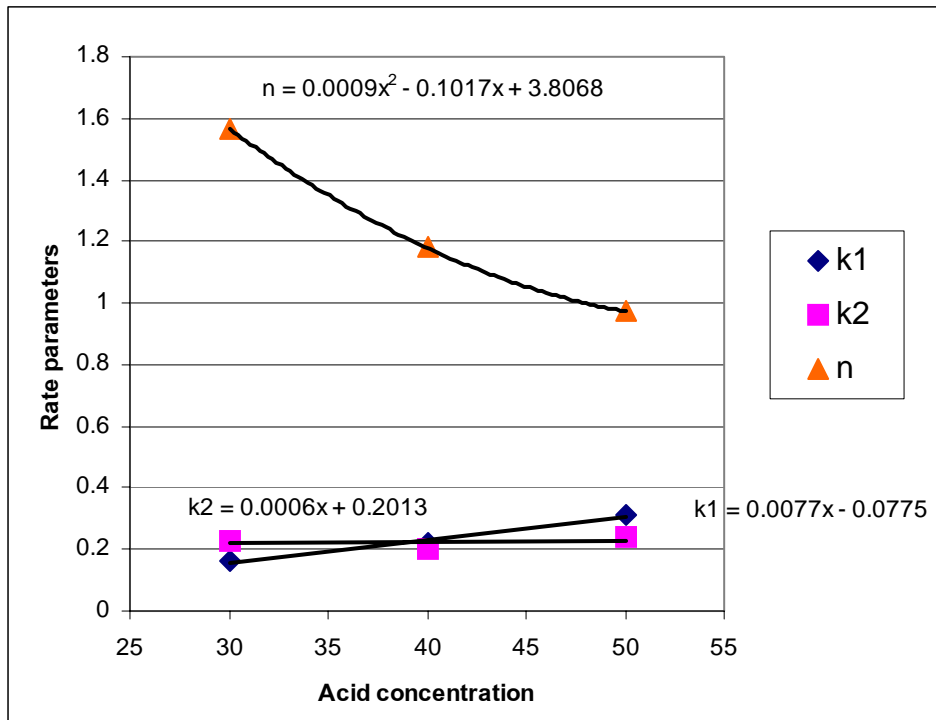


Chart 2: Effect of acide concentration on  $k_1$ ,  $k_2$ ,  $n$

The summarized results of rate parameters in relation with sulphuric acid concentration used for leaching is given below:

$$\begin{aligned}
 k_1 &= 0,0077 X - 0,0775 \\
 k_2 &= 0,2013 \\
 n &= 0,0009 X^2 - 0,1017 X + 3,8068
 \end{aligned}
 \tag{2}$$

Where X is the initial concentration of sulphuric acid used for leaching, g/l.

The empirical model for recovery of uranium depending on acid concentration in heap leaching is determined as follows:

$$R = \frac{(0,0077 X - 0,0775).t^{0,0009 X^2 - 0,1017 X + 3,8068}}{1 + 0,2013.t^{0,0009 X^2 - 0,1017 X + 3,8068}}
 \tag{3}$$

With the equation (3) above we can calculate the uranium leaching yield R after each treatment times knowing the initial concentration of sulphuric acid.

### 3.3 Application for actual cases:

In general, there are two most important factors affecting the accuracy of the model. They are: 1/ the type of ore to be processed should be the same in physico-chemical nature, and 2/ the ore are to be precessed mechanically in the same way so that the size distribution between the experimental and the actual cases are similar. Hence, the results of calculation and that of actual experiments are most likely in good agreement.

#### 4. Test on a 800 liter leaching vat

To check the application ability of the model for scaling-up purpose, the calculation results were checked in an actual big experimental equipment of 800 liter in capacity.

##### 4.1 Calculation of ore leaching yield:

From experimental results from laboratory, when using acid concentration of 50g/l, it is possible to recover about 80% of uranium from ore after 7 treatment times. Specifically calculation result by the model is as follow:

From the equation (3), replacing  $X = 50$  and  $t = 7$ , we have

$$R = \frac{(0,0077.50 - 0,0775).7^{0,0009.50^2 - 0,1017.50 + 3,8068}}{1 + 0,2313.7^{0,0009.50^2 - 0,1017.50 + 3,8068}} = 80,45\%$$

Experiment has been carried out and the results after 7 treatment times were compared.

##### 4.2 Experimental results:

**Tab 1.** Uranium recovery by treatment times

Lần xử lý	Số gam uran thu được/lần	Hiệu suất thu hồi uran
1	485.7	25.70%
2	306.2	41.90%
3	241.9	54.70%
4	179.6	64.20%
5	151.2	72.20%
6	83.16	76.60%
7	48.19	79.15%

The obtained results from the big equipment showed clearly the agreement between calculation experiments, hence creating the possibility to apply the model for actual applications. The relative discrepancy of the “big experiment” can be estimated simply by the formula

$$\text{discrepancy} = \frac{80,45 - 79,15}{80,45} = \frac{1,30}{80,45} = 1,62\%$$

#### 5. Conclusion

The research project had fulfilled its objectives: to find out method to scale-up, from laboratory to commercial scale, the heap leaching process for uranium ore. The obtained result from researchs in the project is a new tool – a mathematical model obtained from experimental results – for determining in advance leaching results depending on leaching conditions. With this tool. It is possible to design an ore leaching

system that can meet prior requirements of productivity and recovery, which facilitates the design of a uranium pilot plant in future.

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# 1.10 - Computation and Other Related Topics

## **MCNP4C2: MONTE-CARLO N- PARTICLE TRANSPORT CODE SYSTEM**

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***Abstract:** MCNP4C2 is a powerful computing tool for solving complicated three-dimensional continuous energy time-dependent radiation transport problems. In this report the basic features of MCNP4C2 and the results of MCNP shielding calculations for the isotropic monoenergetic gamma source and isotropic gamma one with 18 group energy spectrum from uran with the various shields are presented.*

In the recent years the use of radiation transport modeling codes has become more and more widespread. On one hand, this is connected with the pressing requirement of solving of many practically important problems ranging from reactor design to radiation shielding and medical physics. On the other hand, increasing experimental costs and decreasing computational costs are also making numerical transport simulation more attractive, especially when experiments might, otherwise, have to be carried on in hazardous environments. Furthermore, improved computational techniques in these codes as well as faster and better computers make reliance upon numerical modeling more feasible.

MCNP is a general-purpose radiation transport code that have been developed in the Los-Alamos national laboratory, U.S.A. It is a large code, a very powerful computing tool.

MCNP treats an arbitrary three-dimensional configuration of materials in geometric cells bounded by first- and second-degree surfaces and some special fourth-degree surfaces. Pointwise continuous-energy cross-section data are used, although multigroup data may also be used. Fixed-source adjoint calculations may be made with the multigroup data option. For neutrons, all reactions in a particular cross-section evaluation are accounted for. Both free gas and S (alpha, beta) thermal treatments are used. Criticality sources as well as fixed and surface sources are available. For photons, the code takes account of incoherent and coherent scattering with and without electron binding effects, the possibility of fluorescent emission following photoelectric absorption, and absorption in pair production with local emission of annihilation radiation. A very general source and tally structure is available. The tallies have extensive statistical analysis of convergence. Rapid convergence is enabled by a wide variety of variance reduction techniques.

In MCNP, the N-particle stands for neutron, photon, electron. The neutrons' energy ranges from  $10^{-11}$  MeV to 20 MeV. For photons and electrons, the energy regime is from 1 KeV to 1000 MeV.

MCNP4C2 is the internationally distributed version of MCNP, released in 2001. In order to calculate any problem with using MCNP it is needed to create the input file that is subsequently read by MCNP. This file contains informations related to the calculated problem: geometry specification, the description of materials and cross-section libraries (XSDIR file), location and characteristics of particle (photon, electron, neutron) source, type of tallies (detectors) and variance reduction technique.

MCNP is operable on Cray computers under UNICOS, workstations or PCs running Unix or Linux, Window-based PCs, and VAS computers under VMS.

MCNP has revolutionized science not only in the way it is done, but also by becoming the repository for physics knowledge. At present, there are about 250 active users at Los-Alamos. Worldwide there are about 3000 active users at about 200 installations. The knowledge and expertise that contain in MCNP are formidable. Learning to use correctly the MCNP code system requires considerable time and effort.

With the purpose to study on the use of MCNP in application for nuclear radiation shielding calculation we have installed MCNP4C2 on Window-based PC with DVF 6.0 and microsoft C++ 6.0 and carried on the shielding calculations of the 1 MeV isotropic point gamma source and the isotropic point gamma source from uran (with 18-group energy spectrum) with the various shield. The results of these calculations are displayed in tables 2,4,5,6.

For comparison, shielding calculations of the 1 MeV isotropic point gamma source were also performed by us based on the semi-empirical method with using the point kernel technique. The results obtained from semi-empirical calculations are shown in tables 1, 3. We note that in general, MCNP calculation results are greater than semi-empirical calculation ones. This is caused by the fact that the calculation method in MCNP is different from semi-empirical calculation method. The total fluences calculated with using MCNP consider lower energies, but the total fluences calculated by semi-empirical method consider one energy only.

**Tab 1.** Fluences created at the point on distance of 100cm from a 1 MeV isotropic point gamma source in the void medium with the various shield, obtained from semi-empirical calculations

Thickness (cm)	Semi-empirical fluence			
	Shield	Concret	Iron (Fe)	Lead (Pb)
10		$5,9 \cdot 10^{-6}$	$7,11 \cdot 10^{-7}$	$1,06 \cdot 10^{-8}$
20		$2,38 \cdot 10^{-6}$	$1,98 \cdot 10^{-8}$	$6,8 \cdot 10^{-12}$
30		$8,05 \cdot 10^{-7}$	$4,41 \cdot 10^{-10}$	$3,66 \cdot 10^{-15}$

**Tab 2.** Fluences created at the point on distance of 100cm from a 1 MeV isotropic point gamma source in the void medium with the various shield, obtained from MCNP calculations

Thickness (cm)	MCNP fluence			
	Shield	Concret	Iron (Fe)	Lead (Pb)
10		$(6,9347 \pm 0,0935) \cdot 10^{-6}$	$(8,700 \pm 0,4263) \cdot 10^{-7}$	$(1,3063 \pm 0,3402) \cdot 10^{-8}$
20		$(2,9118 \pm 0,0070) \cdot 10^{-6}$	$(2,5210 \pm 0,0620) \cdot 10^{-8}$	$(9,1159 \pm 0,2206) \cdot 10^{-12}$
30		$(1,0892 \pm 0,0020) \cdot 10^{-6}$	$(6,1431 \pm 0,7550) \cdot 10^{-10}$	$(5,1764 \pm 2,1234) \cdot 10^{-15}$



**Tab 3.** Doses created at the point on distance of 100cm from a 1MeV isotropic point gamma source in the void medium with the various shield, obtained from semi-empirical calculations

Thickness (cm)	Semi-empirical dose (Sv)		
<i>Shield</i>	Concret	Iron (Fe)	Lead (Pb)
10	$2,71.10^{-17}$	$3,27.10^{-18}$	$4,07.10^{-20}$
20	$1,10.10^{-17}$	$9,11.10^{-20}$	$3,13.10^{-23}$
30	$3,70.10^{-18}$	$2,03.10^{-21}$	$1,69.10^{-26}$

**Tab 4.** Doses created at the point on distance of 100cm from a 1 MeV isotropic point gamma source in the void medium with the various shield, obtained from MCNP calculations

Thickness (cm)	MCNP dose (Sv)		
<i>Shield</i>	Concret	Iron (Fe)	Lead (Pb)
10	$(2,0495 \pm 0,0220).10^{-17}$	$(2,5613 \pm 0,1000).10^{-18}$	$(5,4149 \pm 1,4068).10^{-20}$
20	$(7,7527 \pm 0,0163).10^{-18}$	$(7,1137 \pm 0,1630).10^{-20}$	$(3,6744 \pm 0,0860).10^{-23}$
30	$(2,6718 \pm 0,0045).10^{-18}$	$(1,6487 \pm 0,1817).10^{-21}$	$(2,3036 \pm 0,9424).10^{-26}$

**Tab 5.** Fluences created at the point on distance of 100cm from a isotropic point gamma source from uran with 18-group energy spectrum in the void medium with the various shield, obtained from MCNP calculations

Thickness (cm)	MCNP fluence		
<i>Shield</i>	Concret	Iron (Fe)	Lead (Pb)
10	$(7,1984 \pm 0,0360).10^{-7}$	$(3,9573 \pm 0,0847).10^{-8}$	$(1,1584 \pm 0,1118).10^{-9}$
20	$(1,9537 \pm 0,0135).10^{-7}$	$(1,5221 \pm 0,1227).10^{-9}$	$(1,7751 \pm 0,0932).10^{-11}$
30	$(5,7585 \pm 0,0754).10^{-8}$	$(1,0428 \pm 0,2227).10^{-10}$	$(2,3721 \pm 0,4502).10^{-13}$

**Tab 6.** Doses created at the point on distance of 100cm from a isotropic oint gamma source from uran with 18-group energy spectrum in the void medium with the various shield, obtained from MCNP calculations

Thickness (cm)	MCNP dose (Sv)		
<i>Shield</i>	Concret	Iron (Fe)	Lead (Pb)
10	$(1,4490 \pm 0,0073).10^{-18}$	$(1,2866 \pm 0,0255).10^{-19}$	$(7,8674 \pm 0,7262).10^{-21}$
20	$(4,4429 \pm 0,0302).10^{-19}$	$(6,7092 \pm 0,4482).10^{-21}$	$(1,2169 \pm 0,0630).10^{-22}$
30	$(1,4416 \pm 0,0187).10^{-19}$	$(6,3579 \pm 1,4132).10^{-22}$	$(1,6481 \pm 0,3181).10^{-24}$

In conclusion, we would like to thank the reactor physics computation group of the Nuclear Research Institute, Dalat, for having kindly handed the MCNP4C2 code system over to us.

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## INVESTIGATION INTO PROCESSING AND SYSTEMATISATION OF ENVIRONMENTAL RADIOACTIVE DATA IN THE PROJECT OF RADIOACTIVE POLLUTION

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**Abstract:** This Project was established for processing the experimental data of the National Project 1997-1999 "Investigation into artificial radioactive pollution in Vietnam by nuclear activities and nuclear accidents in the world". The maps of specific activities of <sup>238</sup>U, <sup>232</sup>Th and <sup>40</sup>K nuclides in the entire Vietnam were established. The average activities of 464 soil samples were (43,6 ± 19,0) Bqkg<sup>-1</sup> for <sup>238</sup>U; (59,7 ± 19,8) Bqkg<sup>-1</sup> for <sup>232</sup>Th and (403,7 ± 244,1) Bqkg<sup>-1</sup> for <sup>40</sup>K. The dependence of specific activities of these nuclides on the three main soil types in Vietnam, which are gray soils (Acrisols), alluvial soils (Fluvisols) and red soils (Ferallsols), was investigated. The absorbed dose rates in air at 1 m above the ground level for 464 sampling positions were calculated on the basis of activities of terrestrial <sup>238</sup>U, <sup>232</sup>Th and <sup>40</sup>K radionuclides. The map of absorbed dose rates for the entire territory and the curve of distribution of population versus absorbed dose rate were established. The population-weighted absorbed dose rate of Vietnam was (71.67 ± 30.34) nGyh<sup>-1</sup>, which lies in the range of (32 - 93) nGyh<sup>-1</sup> of the world but is higher than the world mean value of 59 nGyh<sup>-1</sup>. It is calculated in the basis of the obtained absorbed dose rates that, the population-weighted effective dose rate was (50.17 ± 21.24) nSvh<sup>-1</sup> and the population-weighted outdoor effective dose rate was (7.02 ± 2.97) nSvh<sup>-1</sup>.

### 1. Introduction

The investigation in the world on natural radioactive background is related to the cosmic rays and terrestrial radiation [1]. In Vietnam, in some past years there were the publications on radionuclide activities in surface soils of Ho Chi Minh City and the Southern Vietnam [2, 3]. In 1997-1999 years the Institute of Nuclear Science and Technique Hanoi in cooperation with the Institute of Nuclear Research Dalat and the Center for Nuclear Techniques Ho Chi Minh city carried out the National Project "Investigation into artificial radioactive pollution in Vietnam by nuclear activities and nuclear accidents in the world". The main objective of the Project was to investigate the distribution of <sup>137</sup>Cs specific activity of surface soils in the entire territory of Vietnam. In the Project, 464 soil samples were collected and analyzed in HPGe gamma spectrometers. The result of the Project was reported by Huynh Thuong Hiep and co-authors [4] and was published in the Journal of Environmental Radioactivity [5]. Besides <sup>137</sup>Cs concentration, the specific activities of <sup>238</sup>U, <sup>232</sup>Th and <sup>40</sup>K nuclides were obtained as a by-product accompanied on the <sup>137</sup>Cs analysis. But in the Project [4], this data was

not processed and the valuable information about natural radioactivity from this experiment was not obtained. So the aim of the existing Project is to process and evaluate the above-mentioned experimental data.

## 2. Control Measurements of Gamma Spectrometers

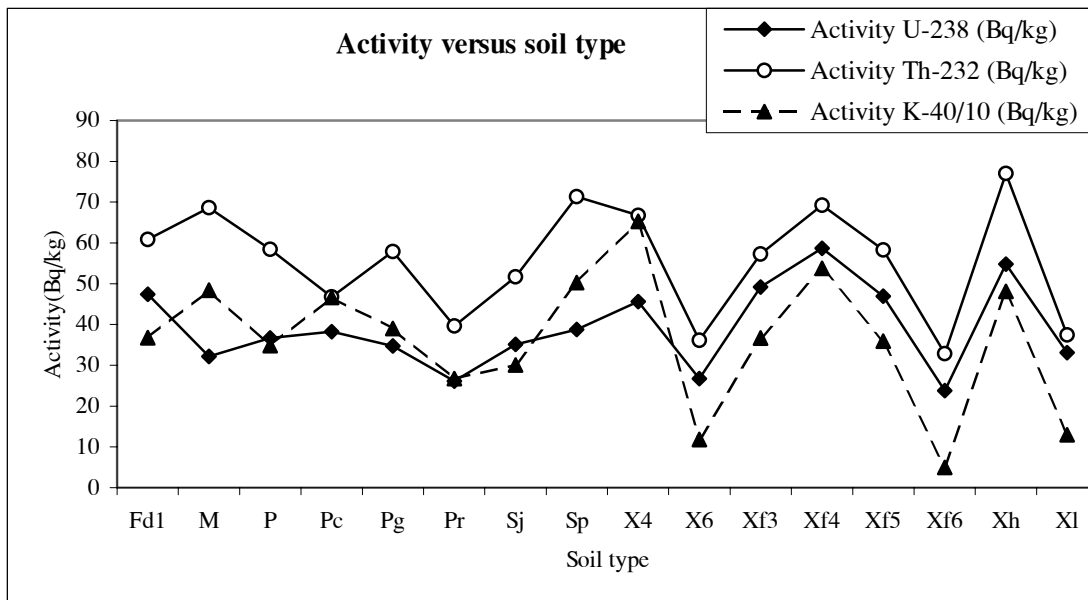
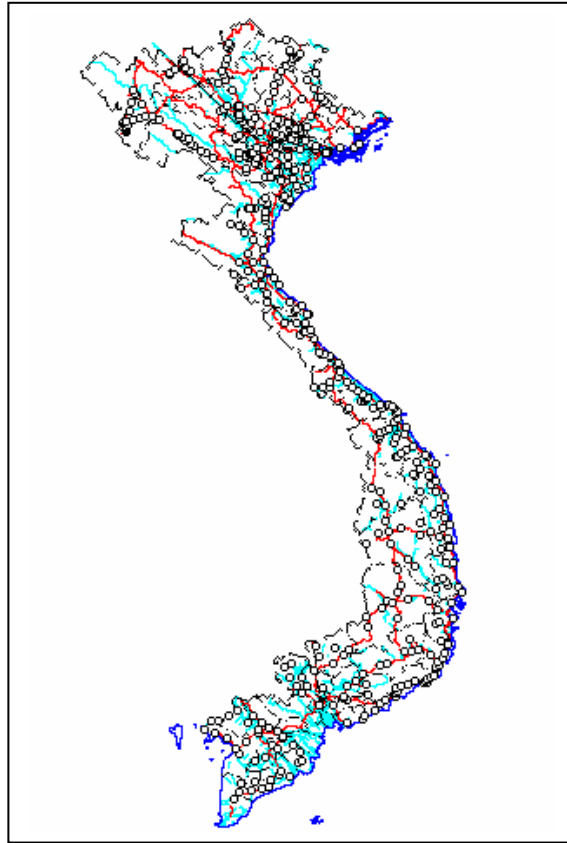
In the Project [4] three laboratories of the Institute of Nuclear Science and Technique Hanoi, the Institute of Nuclear Research Dalat and the Center for Nuclear Techniques Ho Chi Minh city participated in sample collection and measurement. Therefore then a control measurement was carried out for a  $^{137}\text{Cs}$  reference IAEA sample and three soil samples. The results of  $^{137}\text{Cs}$  analysis from the three laboratories were in good agreement. However the agreement between the laboratories for  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  radionuclides was not obtained. Therefore in order to enhance the reliability of comparison, in this Project the control measurements were carried out for 10 soil samples with four laboratories and four analytical methods: gamma spectrometry, alpha spectrometry, neutron activation and ICP-MS. The analytical results for  $^{238}\text{U}$ ,  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  nuclides were in good agreement between laboratories. In the Project [4] the activity of  $^{238}\text{U}$  nuclide was determined through  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$  nuclides, which are daughters of  $^{226}\text{Ra}$  nuclide, therefore it must be corrected due to geochemical disequilibrium between  $^{238}\text{U}$  and  $^{226}\text{Ra}$  isotopes [6]. Furthermore the activity of  $^{238}\text{U}$  nuclide in the Project [4] has an uncertainty of about 20% because it was obtained by the gamma spectrometry analysis without sample containment [19]. The direct measurement of  $^{238}\text{U}$  activity in soils was developed in the works [7, 8].

## 3. The Dependence of Activities of $^{238}\text{U}$ , $^{232}\text{Th}$ and $^{40}\text{K}$ Radionuclides on the Soil Types and the Provinces/cities

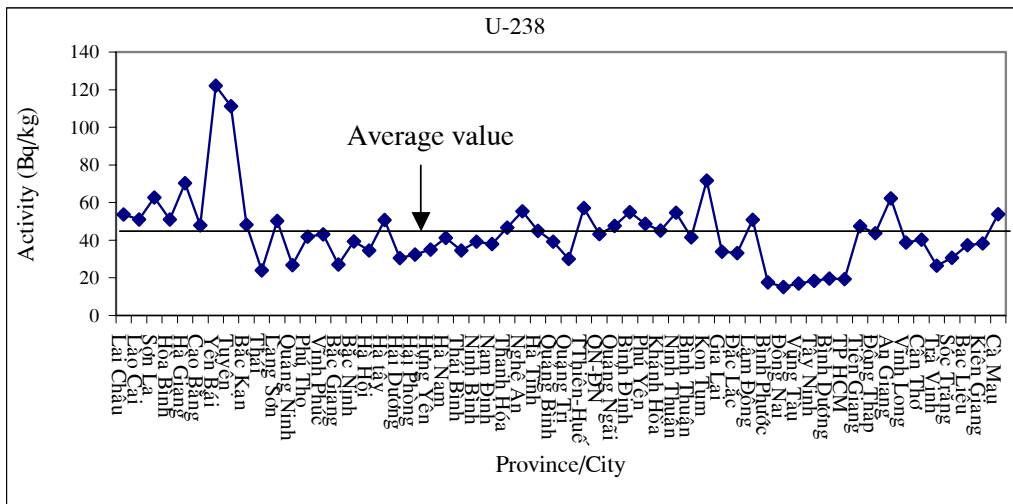
**3.1. The sample distribution versus 58 provinces/cities:** Figure 1 illustrates the map of Vietnam with 464 sampling locations. It is noted that the numbers of samples were unequally distributed, namely Thua Thien - Hue province has the maximum number of samples (22 samples), while two provinces (Long An and Ben Tre) have not any sample collected. The average number of collected samples was  $7.73 \pm 5.36$  samples/province. The second note is that the almost samples were collected along the roads, that is maybe because of convenience for the travel.

**3.2. The sample distribution against soil types:** According to the soil classification of Vietnam based on the method of FAO-UNESSCO classification, Vietnam has 14 groups of soils with 31 soil units and 6 soil sources [9, 10, 11]. Among 14 groups there are three main soil groups, which encompass 93.3% soil area of Vietnam. They are gray soils (Acrisols) with 63.8%, alluvial soils (Fluvisols), including saline soils and acid sulphate soils, with 19.9% and red soils (Ferallsols) with 9.6%. Among the collected samples number of samples of these three soil groups encompass 93.1%, in which the gray soils - 64.7%, alluvial soils - 22.3% and red soils - 6.1%. So the distribution of the collected samples against soil types well reflects the soil components of Vietnam.

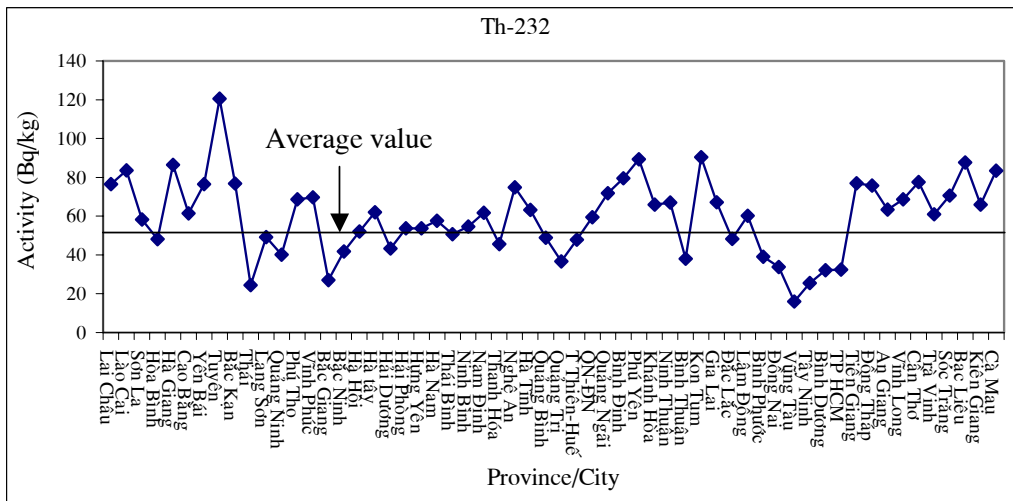
**Fig. 1.** Map of Vietnam with 464 sampling locations.



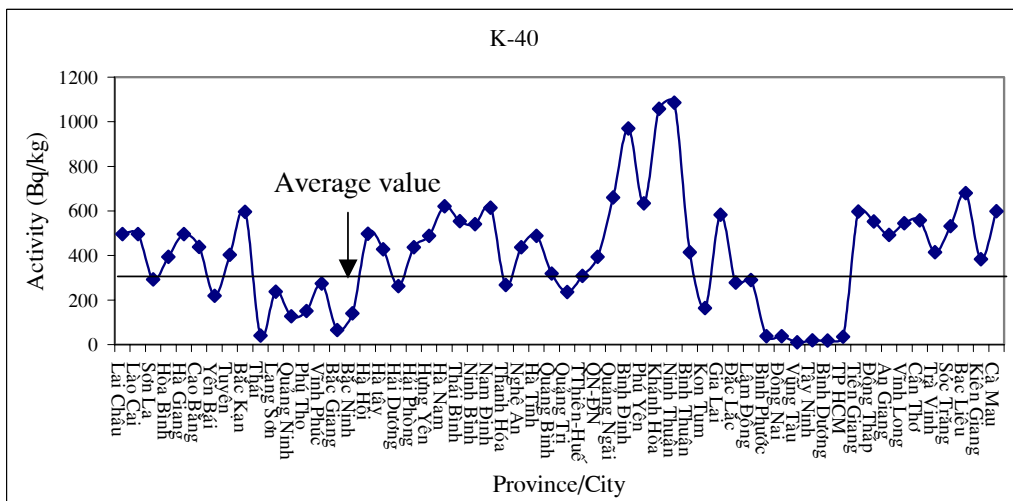
**Fig. 2.** Distribution of average activities of  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  in respect to soil types.



a



b



c

Fig. 3. Distribution of activities of <sup>238</sup>U (Fig. a), <sup>232</sup>Th (Fig. b) and <sup>40</sup>K (Fig. c) in respect to 58 provinces/cities.

**3.3. The dependence of specific activities of  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  nuclides on soil types:** The collected samples composed of 10 soil groups, among them three main soil groups encompass 93.1%, therefore our consideration will be concentrated into these three soil groups (Fig. 2). From Fig. 2 it is noted that the nuclide activities insignificantly vary with alluvial soils and red soils but strongly depend on the units and sources of gray soils. The maximum values of nuclide activities are obtained for Xf4 and X4 soil units and the minimum values for Xf6, X6 and Xl soil units.

**3.4. The distribution of specific activities of  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  nuclides against provinces/cities:** The average activities of  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  nuclides for 464 samples and the distribution of specific activities of  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  nuclides against 58 provinces/cities were obtained (Figure 3). Some comments are as follows:

- The average activities for 464 samples are  $43,6 \pm 19,0 \text{ Bqkg}^{-1}$  (15 - 111  $\text{Bqkg}^{-1}$ ) for  $^{238}\text{U}$ ;  $59,7 \pm 19,8 \text{ Bqkg}^{-1}$  (16 - 120  $\text{Bqkg}^{-1}$ ) for  $^{232}\text{Th}$  and  $403,7 \pm 244,1 \text{ Bqkg}^{-1}$  (10 - 1085  $\text{Bqkg}^{-1}$ ) for  $^{40}\text{K}$ .

- In the South-East Region of Southern Vietnam all activities of the three  $^{238}\text{U}$ ,  $^{232}\text{Th}$  và  $^{40}\text{K}$  nuclides are very lower than the corresponding average values. This is maybe due to soil sources of this region, which are almost old alluvial soils X6.

- In Yen Bai, Tuyen Quang and Bac Kan provinces, the activities of  $^{238}\text{U}$  and  $^{232}\text{Th}$  are extremely high. This could be because that the soils of this region consist of gray soils Xf4 and Xf3.

- The  $^{40}\text{K}$  activity decreases in the East Region of Northern Vietnam and increases in the South Region of Central Vietnam.

#### **4. The Relationship Between the Specific Activities of $^{238}\text{U}$ , $^{232}\text{Th}$ và $^{40}\text{K}$ Nuclides and the Soil Parameters**

**4.1. The soil parameters:** The soil parameters of 464 soil samples measured in 1997-1999 years were pH(KCl), organic material, humic, fulvic,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ , total alkali,  $\text{K}^+$ ,  $\text{Na}^+$ , distribution against particle sizes of 2-0.02 mm, 0.02-0.002 mm and < 0.002 mm. Their average values for 58 provinces/cities and for the entire Vietnam were obtained.

**4.2. The correlation between specific activities:** There were the moderate correlations between the activities of  $^{238}\text{U}$  and  $^{232}\text{Th}$  ( $R = 0.69$ ) and between  $^{40}\text{K}$  and  $^{232}\text{Th}$  ( $R = 0.59$ ). It is noted that the activities of the three nuclides  $^{238}\text{U}$ ,  $^{232}\text{Th}$  và  $^{40}\text{K}$  decrease in the South-East Region of Southern Vietnam and the activities of the two nuclides  $^{238}\text{U}$  and  $^{232}\text{Th}$  increase in Yen Bai and Tuyen Quang provinces.

**4.3. The correlation between soil parameters:** There were the significant correlations for the following parameters: between the organic material and humic ( $R = 0.83$ ); between the organic material and fulvic ( $R = 0.81$ ); between the total alkali and  $\text{Ca}^{++}$  ( $R = 0.89$ ); between the total alkali and  $\text{Mg}^{++}$  ( $R = 0.85$ ).

**4.4. The correlation between specific activities and soil parameters:** The correlation between these two parameter systems are weak with  $|R| < 0.42$ . So we can say that the activities of  $^{238}\text{U}$ ,  $^{232}\text{Th}$  và  $^{40}\text{K}$  nuclides insignificantly correlate with soil parameters. It can lead to the conclusion that the values of activities are determined mainly by soil sources.

## 5. The Absorbed Dose Rate and the Effective Dose Rate Calculated From the Activities of Terrestrial $^{238}\text{U}$ , $^{232}\text{Th}$ and $^{40}\text{K}$ Radionuclides

**5.1. Conversion coefficients  $CC_{^{238}\text{U}}$ ,  $CC_{^{232}\text{Th}}$  and  $CC_{^{40}\text{K}}$ :** They are conversion coefficients from activities of  $^{238}\text{U}$ ,  $^{232}\text{Th}$  và  $^{40}\text{K}$  nuclides in surface soils to absorbed dose rates in air at 1 m above the ground level. These conversion coefficients are mean values of experimental and theoretical ones published elsewhere [12-18]. The average values used in this work are:

$$CC_{^{238}\text{U}} = 0.4368 \text{ nGyh}^{-1}/\text{Bqkg}^{-1}; CC_{^{232}\text{Th}} = 0.5993 \text{ nGyh}^{-1}/\text{Bqkg}^{-1} \text{ and } CC_{^{40}\text{K}} = 0.0417 \text{ nGyh}^{-1}/\text{Bqkg}^{-1}.$$

**5.2. Absorbed dose rates in air at 1 m above the ground level:** Formula to calculate absorbed dose rates ADR in air depending on specific activities of  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  nuclides is as follows:

$$\text{ADR (nGyh}^{-1}) = \text{SA}_{^{238}\text{U}} \times CC_{^{238}\text{U}} + \text{SA}_{^{232}\text{Th}} \times CC_{^{232}\text{Th}} + \text{SA}_{^{40}\text{K}} \times CC_{^{40}\text{K}}$$

where  $\text{SA}_{^{238}\text{U}}$ ,  $\text{SA}_{^{232}\text{Th}}$  and  $\text{SA}_{^{40}\text{K}}$  are specific activities ( $\text{Bqkg}^{-1}$ ) of  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  nuclides correspondingly.

The values of ADR for 464 soil samples were ranged from 17.45  $\text{nGyh}^{-1}$  to 137.63  $\text{nGyh}^{-1}$  with the mean value for the entire country of  $\text{ADR} = (71.67 \pm 30.34) \text{ nGyh}^{-1}$ . The distribution of absorbed dose rates in respect to 58 provinces/cities were obtained and illustrated in Fig. 4. It is noted that absorbed dose rates of the East Region of Northern Vietnam (Yen Bai, Tuyen Quang and Bac Kan provinces) and the South Region of Central Vietnam (Quang Ngai, Binh Dinh, Phu Yen, Khanh Hoa, Ninh Thuan provinces) are higher than average value. Whilst in the South-East Region of Southern Vietnam (Binh Phuoc, Dong Nai, Ba Ria - Vung Tau, Tay Ninh, Binh Duong provinces and Ho Chi Minh City) the absorbed dose rates are too less than average value.

**5.3. Effective dose rates and outdoor effective dose rates for the provinces/cities without taking into account the population distribution:** Effective dose rates EDR and Outdoor effective dose rates OEDR are calculated as follows:

$$\text{EDR (nSvh}^{-1}) = 0.7 \times \text{ADR (nGyh}^{-1})$$

$$\text{OEDR (nSvh}^{-1}) = 0.2 \times 0.7 \times \text{ADR (nGyh}^{-1}) = 0.14 \times \text{ADR (nGyh}^{-1})$$

The calculated values of EDR ranged from 12.21  $\text{nSvh}^{-1}$  to 96.34  $\text{nSvh}^{-1}$  with the average value for the entire Vietnam of  $(50.17 \pm 21.24) \text{ nSvh}^{-1}$ . The corresponding values for OEDR were  $(1.71 - 13.49) \text{ nSvh}^{-1}$  and  $(7.02 \pm 2.97) \text{ nSvh}^{-1}$ .

**5.4. Effective dose rates and outdoor effective dose rates for the provinces/cities with taking into account the population distribution:** The populations of provinces/cities at the time of experiment and the average absorbed dose rates were used for calculating population-weighted average absorbed dose rates PW-ADR, population-weighted average effective dose rates PW-EDR and population-weighted average outdoor effective dose rates PW-OEDR. They are  $\text{PW-ADR} = 71.67 \text{ nGyh}^{-1}$ ;  $\text{PW-EDR} = 50.17 \text{ nSvh}^{-1}$ ;  $\text{PW-OEDR} = 7.02 \text{ nSvh}^{-1}$ .



**5.5. Population distribution versus absorbed dose rate:** The distribution of population of Vietnam versus absorbed dose rate is presented in Fig. 5, which has two maximums at about  $30 \text{ nGyh}^{-1}$  and  $80 \text{ nGyh}^{-1}$  with the mean value of PW-ADR =  $71.67 \text{ nGyh}^{-1}$ . The first maximum corresponds to the South-East Region of Southern Vietnam, including Ho Chi Minh City, with a large population and a low absorbed dose rate. The second maximum is located near to the average value of the entire Vietnam. It is seen from Fig. 5 that the population distribution versus absorbed dose rate of Vietnam lies in the right hand in comparison with that from other 25 countries. In consequence the average value PW-ADR =  $71.67 \text{ nGyh}^{-1}$  of Vietnam is 1.2 times higher than the value of  $59 \text{ nGyh}^{-1}$  of the world. However the value of  $71.67 \text{ nGyh}^{-1}$  of Vietnam is acceptable because it lies within the range of (32 - 93)  $\text{nGyh}^{-1}$  for 53 countries in the world [1].

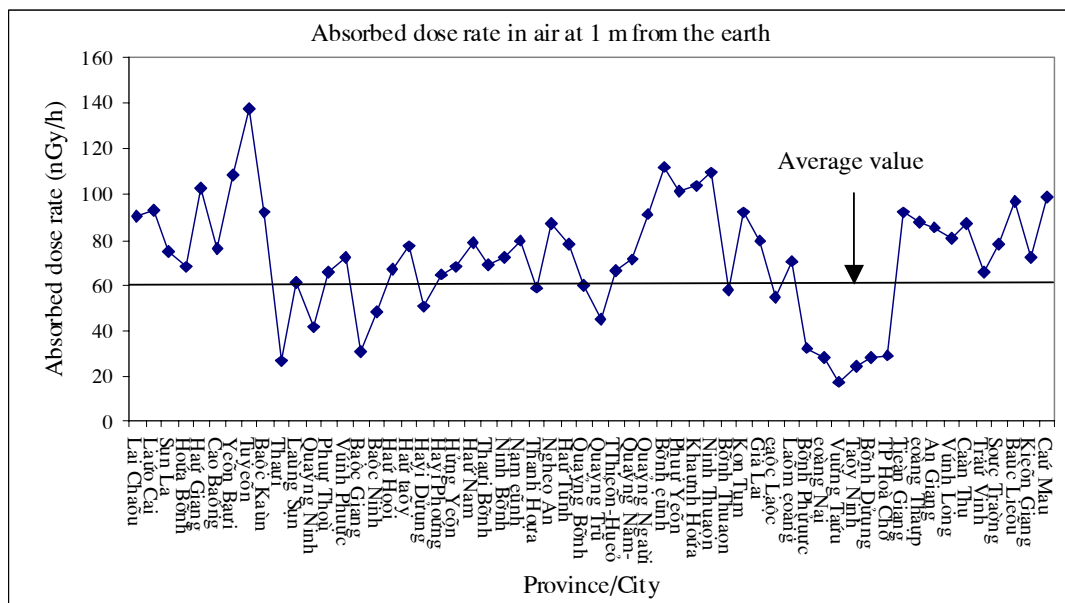


Fig. 4. The distribution of absorbed dose rates in air at 1 m above the ground level versus 58 provinces/cities.

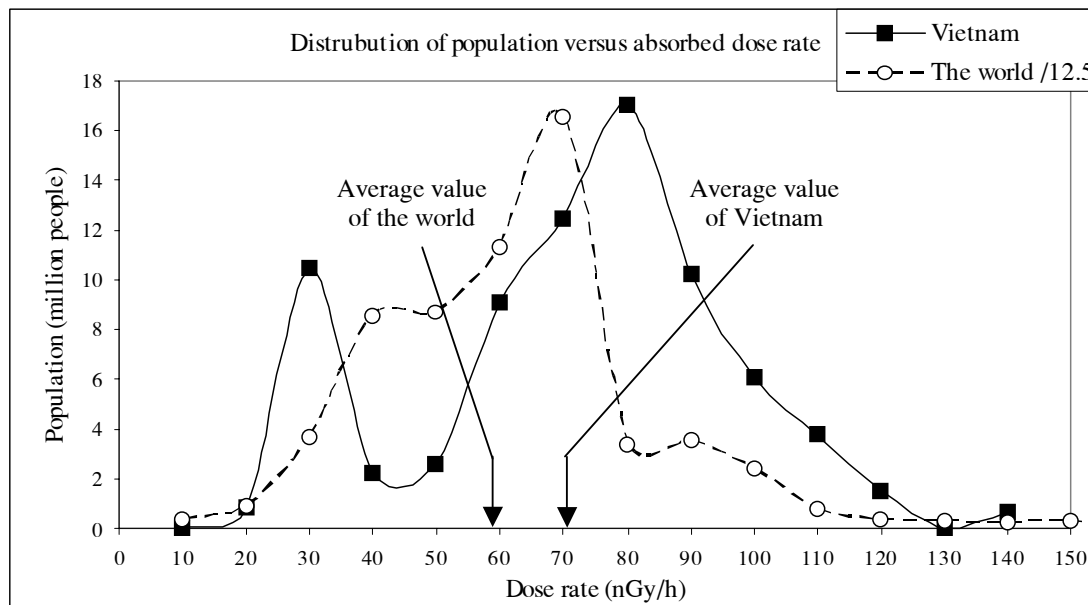


Fig. 5. The distribution of population of Vietnam and 25 countries in the world [1] in respect to absorbed dose rate.

## 6. Conclusion

Investigation results based on the data of 464 soil samples collected in 1997-1999 years are valuable from the view point of scientific research and also database collection. This is the first time we have a database of activities of  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  radionuclides in surface soils of the entire Vietnam. From this data we obtained the absorbed dose rates in air at 1 m above the ground level and the outdoor effective dose rates. However the collection of soil samples has some disadvantages because the experimental design only meets the inventory of artificial radionuclides in surface soils. Therefore it is recommended to establish a new project for complete research of environmental radioactive background of Vietnam.

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19. Phan Son Hai and Pham Ngoc Son. “*Analysis of radioactive isotopes of low activity in environmental samples by gamma spectrometry*”. Proceedings of 3th National Conference “Nuclear Physics and Technique”, Science and Technique Publisher, pp. 417-419 (2000), in Vietnamese.

## 2. TC Projects and Resaerch Contracts

## 2.1- IAEA TC Projects

Project Code	Project Title		Institute	Star ting	Fund
VIE0008	Human Resource Development and Nuclear Technology Support	Phát triển nhân lực và trợ giúp công nghệ hạt nhân	VAEC	1995	118689 7
VIE0010	Technical Support for Training in Nuclear Engineering at the Hanoi University of Technology	Hỗ trợ kỹ thuật để đào tạo kỹ sư về công nghệ hạt nhân	HUT	2003	203340
VIE0011	Human Resource Development and Nuclear Technology Support	Phát triển nhân lực và trợ giúp công nghệ hạt nhân	VAEC	2003	896960
VIE2005	Automation and QA-QC in Neutron Activation Analysis	NC tự động hoá và bảo đảm chất lượng trong phân tích kích hoạt nơtron	NRI	1999	189240
VIE4014	Modification of the Dalat Reactor Control System	Đổi mới hệ điều khiển lò PƯ Đà Lạt	NRI	2003	243220
VIE2007	QA/QC of Mineral and Environmental Sample Measurements Using Nuclear Analytical Techniques	Kiểm tra bảo đảm chất lượng mẫu quặng và mẫu môi trường bằng kỹ thuật phân tích hạt nhân	ITRRE	2001	157330
VIE5014	Rice Mutant Varieties for Saline Land	Tạo giống lúa cho vùng nước mặn	AGRI.	1999	731725
VIE6021	Application of Accelerator Technique for Medical Treatment	Ứng dụng kỹ thuật LINAC trong điều trị bệnh	INST	2001	351660
VIE6022	Upgrading Nuclear Medicine Services	Nâng cấp dịch vụ Y học hạt nhân	HEALTH	2001	173483

VIE8012	Ground Water and Nutrient Management	NC quản lý nguồn nước ngầm và dinh dưỡng cây trồng bằng kỹ thuật hạt nhân	CNT	1999	225860
VIE8013	Advanced NDT Methods for the Construction Industry	Kỹ thuật kiểm tra không huỷ thể trong công nghiệp	CNT	1999	149760
VIE8014	Upgrading the Irradiation Facility at Hanoi Irradiation Centre	Nâng cấp Trung tâm Chiếu xạ Hà Nội	INST	2001	34300
VIE8016	Isotope and Nuclear Techniques for Better Management of Groundwater	Ứng dụng kỹ thuật hạt nhân và đồng vị trong quản lý nước ngầm	INST, NRI	2001	139940
VIE9008	Establishment of a National Radiation Safety Training Centre	Xây dựng Trung tâm quốc gia đào tạo về An toàn bức xạ	MOSTE + NRI	2001	131666

## 2.2 - INTERNATIONAL RESEARCH CONTRACTS

Code	Year		Budget	Chief Investigator	Institutions	RC title
11488/R3	2004	15/6/2004	5000	Bui Si Doanh	Plant Protection Department	Strengthening of quality control of pesticide products.
11829/R1	2004	15/2/04-14/2/05	5000	Nguyen Phuc	INST	Development of distance learning (DL) module on troubleshooting of nuclear instrument in Vietnam.
12331/R0 /RB	2004		8000	Phan Son Hai	NRI	Estimation of soil erosion and redistribution on the coffee and tea crop land using <sup>137</sup> Cs, <sup>210</sup> Pb and <sup>7</sup> Be tracer.
12708	2004		4000	Truong Thi Hanh	NRI	Combined treatment using chemical oxidation and radiation for enhancement degradation of chitosan.
12568	2004		5000	Nguyen Kien Chinh	CNT	Isotope compositions of Mekong river flow water in the south of Vietnam.
7	2004	15/9/2004	4000	Nguyen Huu Quang	NRI	Tracers in high temperature and fractured basement rock reservoir.
12951/R0 /RB	2004	1/11/2004	2500	Bui Hoc	Hanoi University of Mining and Geology	Interaction between water from Red River and groundwater in catchment of the river.

	2004		3000	Ha Van Thong	INST	Identification of regional requirements for small reactors with out on-site refuelling and Neutronics calculations of FBNR.
12965	2004		5000	Nguyen Cong Duc	Cho Ray Hospital	Development of QC in houseprepared radiopharmaceutical.
13013	2004		12000	Le Thi Thuy	National Inst. of Animal Husbandry	Determination of genetic diversity in Vietnamese indigenous goat breed based on molecular marker.
12957	2004		5000	Phan Thi Cong	IAS	Agronomic validation of a phosphate rock formation system.
13003	2004		10000	Nguyen T Thanh	Inst of Biology	Validation and pyramiding of drought resistant/genes.
13027	2004		5000	Le Duc Khanh	MARD	Development of rearing techniques for <i>Bactrocera pyrifoliae</i> in Vietnam.



# 3. Scientific Reports and Conference Papers

## SCIENTIFIC PAPERS PUBLISHED ABROAD

1. **Dao Tien Khoa, Hoang Sy Than, Tran Hoai Nam, Nguyen Van Giai and M. Grasso.** Microscopic calculation of the interaction cross section for stable and unstable nuclei based on the non-relativistic nucleon-nucleon t matrix – *Physical Review* 2004, C69, 044605 (12 pages)
2. **Dao Tien Khoa, and W.von Oertzen.** Di-neutron elastic transfer in the  $^4\text{He}(^6\text{He}, ^6\text{He})^4\text{He}$  reaction - *Physics Letters*, 2004, B595, pp.193-201.
3. **Dao Tien Khoa, Hoang Sy Than.** Isospin Dependence of  $^6\text{He}+p$  optical potential and the symmetry energy – *Physical Review C* (to appear).
4. **Hien P.D., Bac V.T., Thinh N.T.H.** (2004). Source and properties of mineral dust in urban and rural air in northern Vietnam. *Atmospheric Environment* (in press).
5. **N.H.Quang.,N.Q.Long.,D.B.Lieu.,T.T.Mai.,T.Ha.,D.D.Nhan.,P.D.Hien.**  $^{239+240}\text{Pu}$ ,  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  inventories in surface soils of Vietnam. *Journal of Environmental Radioactivity* 75,329-337.
6. **N.takata<sup>a</sup>, N.T. Tran<sup>b</sup>, E. Kim<sup>c</sup>, P. Marsoem<sup>d</sup>, T.Kurosawa<sup>a</sup>, Y. Koyama<sup>a</sup>**(in press). Loss of ion in cavity ionization chambers. *Int. Journal of Applied Radiation and Isotopes*.
7. **Vo Van Thuan, Dang Quang Thieu, Pierre Darriulat, Pham Ngoc Diep, Pham Ngoc Dinh, Nguyen Hai Duong, Pham Thi Tuyet Nhung, Nguyen Thi Thao.** Measurement of the East-West asymmetry of the cosmic muon flux in Hanoi.- *Nuclear Physics B678* (2004)3-15.
8. **Ngo Quang Huy, Tran Van Luyen.** A method to determine  $^{238}\text{U}$  activity in environmental soil samples by using 63.3keV-photopeak-gamma HPGe spectrometer *Applied Radiation and Isotopes* 61 (2004).
9. **Tran Que.** “ Ionizing radiation or chemical mutagen induced chromosome aberration in lymphocytes from epidemiological data at Vietnam”, *International Journal low Radiation*, Vol.1, No.3, 2004.PP.309-317, 2004.
10. **Tran Que.** “ Interference of chromosome aberrations and the manner of deinterference in biodosimetry and radiation epidemiological investigation”; Submitted and Accepted for publishing in *International Journal low Radiation*, 2004.
11. **Hirokazu HASEGAWA, Satoshi AKASAKA, Kazuhiro YAMAUCHI, Le Hai, Nguyen Tan Man, Tran Thu Hong.** “ Synthesis of natural Rubber thermoplastic Elastomers by  $\gamma$ -ray Radiation and Their Structures and Properties”; Submitted and Accepted for publishing in 2004.
12. **Ho Manh Dung, Pedro Carlos Domingo Lemos, Maria Perira Teixeira. Cao Dong Vu, Nguyen Trong Ngo, Truong Y, Duong Hien Luong.** Application of Neutron Activation Analysis based on the ko-Standardization method for APM, Crude Oil, Base Rock, Human Hair and Marine Sediment Sample; Submitted and Accepted for publishing in *J. Radioanal. Nucl. Chem*.
13. **Doan Thi The, Fumio Yoshii, Naotsugu Nagasawa, Tamikazu Kume.** Synthesis of Poly(butilen succinate) Glass Fiber Composite by Irradiation and Its Biodegradability. *Journal of Applied Polymer Science*, Vol.91, pp.2122-2127 (2004).

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2. **Lê Xuân Thám và các cộng sự.** Nghiên cứu nuôi trồng nấm bào ngư *Pleurotus eryngii*. *Tạp chí Khoa học và Công nghệ*.
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4. **Thân Văn Liên.** Nghiên cứu khả năng hoà tách quặng urani bằng phương pháp cacbonat. *Tạp chí Hoá học T 42, số 1/ 2004*.
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8. **Nguyễn Ngọc Tuấn, Lê Tất Mua.** Xác định thủy ngân và metyl thủy ngân trong một số mẫu cá nước ngọt và cá biển bằng phương pháp sắc ký khí và kích hoạt neutron có xử lý mẫu. (Determination of Mercury and Methyl Mercury in some freshwater fish and salt-water fish samples by Gas Chromatographic and Radiochemical Neutron Activation analysis methods). *Tạp chí Phân tích Hóa, Lý và sinh học, Tập 9 số 1-2004, trang 3-9*.
9. **Nguyễn Trọng Ngo, Nguyễn Thanh Bình, Nguyễn Văn Phúc, Trương ý, Lê Như Siêu, Mai Thị Hương, Nguyễn Thị Linh, Phan Sơn Hải, Nguyễn Mộng Sinh.** Xác định các đồng vị Th và U Trong các mẫu trầm tích và sinh vật biển bằng phương pháp phổ alpha ( The determination of thorium and uranium isotopes in marine esediment and biota samples by alpha spectrometric techniques). *Tạp chí Phân tích Hóa, Lý và sinh học, Tập 9 số 2-2004, trang 66 -69*.
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14. **Phan Sơn Hai, et al.** preliminary studies of the use of naturally-occurring radio nuclides for identification of sediment sources, *J. Nuclear Science and Technology, No.3, 2004.*
15. **Vuong Huu Tan, Nguyen Canh Hai, Pham Ngoc Son, Tran Tuan Anh.** Neutron Capture Cross Section Measurement of  $^{109}\text{Ag}$ ,  $^{186}\text{W}$  and  $^{158}\text{Gd}$  on filtered Neutron beam of 55 keV and 144 keV. *Nuclear Science and Technology Vol.3, No 1, 2004.*
16. **Nguyen Hao Quang, Dang Duc Nhan, Pham Van Toan, Vu Thuy Nga.** Use of Tracer Technique to investigate the Dependence of Soil-to-plant Transfer Factor of Sr and Cs on the types of soil. *Nuclear Science and Technology Vol.3, No 1, 2004*
17. **Hoang Van Nguyen, Vuong Huu Tan.** A Photon-beta Personal Dosimeter Type based on a Thermoluminescent  $\text{CaSO}_4:\text{Dy}$  Phosphor. *Nuclear Science and Technology Vol.3, No 1, 2004.*
18. **Le Ba Thuan, et al.** Purification of Yttrium by solvent Extraction Technique Using Aliquat 336 as an Extractant. *Nuclear Science and Technology Vol.3, No 1, 2004.*
19. **Do Ngoc Lien, Nguyen Van Sinh.** Assessment for the Role of Lanthanum Oxide in the Pt- $\text{La}_2\text{O}_3$ - $\text{RuO}_2$ - $\text{LaRuO}_3$  Composite Electrode. *Nuclear Science and Technology Vol.3, No 1, 2004.*
20. **Nguyễn Văn Súc, Ngô Quang Huy, Nguyễn Quốc Hiến, Nguyễn Văn Hùng.** Hấp phụ uran bằng chitin/chitosan có độ deacetyl thấp. *Tạp chí Hoá học, T.42 (1), Tr. 1-4, 2004.*

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2. **Nguyễn Đức Thành và các cộng sự.** Positronium formation associated with macro-porosity medium and study on the porosity determination using positron lifetime spectroscopy. *Proc.9th Asia-Pacific Physics Conference, Hanoi 23-31 Nov. 2004.*
3. **Tran Quoc Dung.** Improvement of the segmented gamma scanning technique for assay of radioactive wastes. *Proc.9th Asia-Pacific Physics Conference, Hanoi 23-31 Nov. 2004.*
4. **Le Xuan Tham et al.** Development of pure mutant lines of aromatic rice in Vietnam. *Conference of World Rice Research, Tsukuba, 5-7 Nov. 2004, Japan.*
5. **Nguyễn Kiên Chính.** Salinisation Mechanism of Ground Water in Ho Chi Minh City, Vietnam. *IAEA conference in India.*
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7. **Nguyen Mong Sinh, Ho Manh Dung, Nguyen Thanh Binh, etc.**“Facility and Application of Nuclear and Supplementary Analytical Techniques in Dalat NRI”, Proceedings of FNCA workshop on utilization of research reactor, Dalat, 12-16 January 2004.
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3. **Duong Van Su.** Preparation of concentrate from Vietnamese Yen Phu rare earths ore. *Hội thảo lần thứ nhất Việt Nam –Hàn Quốc về ứng dụng và chế biến đất hiếm,* Hà Nội 8-9/6/2004.
4. **Pham Quang Trung.** Recovery of rare earths from Yen Phu xenotime by pressure- alkaline attack. *Hội thảo lần thứ nhất Việt Nam –Hàn Quốc về ứng dụng và chế biến đất hiếm,* Hà Nội 8-9/6/2004.
5. **Nguyen Trong Hung.** Recovery of cerium and rare earth element oxides from Dong Pao bastnaesite concentrate. *Hội thảo lần thứ nhất Việt Nam –Hàn Quốc về ứng dụng và chế biến đất hiếm,* Hà Nội 8-9/6/2004.
6. **Le Ba Thuan.** Process development for separation of rare earths by solvent technique-current status in ITRRE. *Hội thảo lần thứ nhất Việt Nam –Hàn Quốc về ứng dụng và chế biến đất hiếm,* Hà Nội 8-9/6/2004.
7. **Hoang Nhuan.** Extraction of Ce(IV) with PC88A/DEHPA in HNO<sub>3</sub> medium and its use for cerium purification. *Hội thảo lần thứ nhất Việt Nam –Hàn Quốc về ứng dụng và chế biến đất hiếm,* Hà Nội 8-9/6/2004.
8. **Nguyen Van Hai.** Purification of yttrium by solvent technique using Aliquat 336. *Hội thảo lần thứ nhất Việt Nam –Hàn Quốc về ứng dụng và chế biến đất hiếm,* Hà Nội 8-9/6/2004.
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11. **Pham Duc Thai.** Preparation of Fe-REE-Mg alloy at ITRRE. *Hội thảo lần thứ nhất Việt Nam –Hàn Quốc về ứng dụng và chế biến đất hiếm,* Hà Nội 8-9/6/2004.
12. **Nguyen Ba Tien.** Study on preparation of some RE products for increasing the

yield of tea plant. *Hội thảo lần thứ nhất Việt Nam –Hàn Quốc về ứng dụng và chế biến đất hiếm, Hà Nội 8-9/6/2004.*

13. **Tran Thi Thu Phuong, Elena Pereloma.** Ảnh hưởng của hiện tượng ageing lên cấu trúc và tính chất của các hợp kim sắt và sắt mangan chứa rất ít carbon. *Hội nghị ứng dụng vật lý vào đời sống và sản xuất, Đại học quốc gia Tp.Hồ Chí Minh, 11-12/12/2004.*

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1. *Ngô Quang Huy.* Bức xạ ion hoá. Nhà xuất bản Khoa học kỹ thuật.
2. *Lê Xuân Thám.* Năm trong công nghệ và Chuyển hoá môi trường. Năm tua. Nhà xuất bản Khoa học kỹ thuật.
3. *Thân Văn Liên.* Thủy luyện urani. Nhà xuất bản Đại học Quốc gia Hà Nội, 2004.

**TUYỂN TẬP**  
**BÁO CÁO CÁC CÔNG TRÌNH KHOA HỌC**  
**NĂM 2004**

**BAN BIÊN TẬP**

PGS.TS Vương Hữu Tấn	<i>Trưởng ban</i>
TS. Lê Văn Hồng	<i>Phó Trưởng ban</i>
TS. Hoàng Anh Tuấn	<i>Ủy viên</i>
KS. Nguyễn Hoàng Anh	<i>Ủy viên thu ký</i>
CN. Trịnh Đăng Hiệu	<i>Ủy viên</i>
KS. Đặng Thị Hồng	<i>Ủy viên</i>
CN. Nguyễn Trọng Trang	<i>Ủy viên</i>

*Trình bày, vẽ bìa: Trịnh Đăng Hiệu*