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Utilization and Facility of Neutron Activation Analysis in HANARO Research Reactor

Y. S. Chung, Y. J. Chung, J. H. Moon
Korea Atomic Energy Research Institute
P.O.Box 105 Yusong, 305-600, Taejon, Korea

Abstract

The facilities of neutron activation analysis within a muti-purpose research reactor (HANARO) are described and the main applications of NAA in Korea are reviewed. The sample irradiation tube, automatic and manual pneumatic transfer system, are installed at three irradiation holes. One irradiation hole is lined with a cadmium tube for epithermal NAA. The performance of the NAA facility was examined to identify the characteristics of tube transfer system, irradiation sites and polyethylene irradiation capsule. The available thermal neutron flux with each irradiation site are in the range of 3.9×10^{13} - 1.6×10^{14} $n/cm^2 \cdot s$ and cadmium ratios are 15-250. Neutron activation analysis has been applied in the trace component analysis of nuclear, geological, biological, environmental and high purity materials and various polymers for research and development. Analytical services and the latest analytical results are summarized.

I. Facilities for Neutron Activation Analysis.

1. Irradiation Facilities.

There are several types of irradiation facilities such as IP, PTS, HTS, OR, IR and beam tubes in HANARO research reactor. The pneumatic transfer system(PTS) had been mainly used for neutron activation analysis and a neutron beam will be applied for prompt gamma neutron activation analysis in the near future. Figure 1 shows the locations of these irradiation thimbles. PTS is installed at three NAA holes including one Cd lined, and used for neutron activation analysis with low heat generation (no more than 75 W) and lighter rabbit (no more than 50g) irradiated in a short time period (1-30 minutes). Clean dry air and pressure (no more than 1 bar) is used to transfer the irradiation capsule. The available neutron flux with each irradiation site and general characteristics of pneumatic transfer system are presented in Table 1. PTS consists of manual(PTS #1) and automatic(PTS #2) types and has been operated since the end of 1996. A 42 cc irradiation capsule is available for manual PTS. Up to one hundred 27 cc irradiation capsules can be loaded for automatic PTS at a time. The photograph of PTS laboratory is presented in Figure 2 and the process flow diagram of automatic PTS is presented in Figure 3. PTS#1 is designed for the production of short, medium and long-lived isotopes as well as neutron activation analysis. It is a simple shuttle system which delivers a capsule to the reactor core for a preset irradiation time under 1 bar of air pressure. At the time-out, the capsule is returned to the shielded loader/receiver for retrieval by the operator manually and automatically. PTS#2 is designed only for neutron activation analysis of short and medium-lived isotopes. It is a somewhat complicated shuttle system which delivers a capsule according to given paths by a computer control program ; start from sample loader via automatic sample loader, deverter, two reactor core, radiation detector, delay stacker, two counters with and without window, finish to discharged receiver under 0.6 bar of air pressure. The control program is written in Microsoft's Visual Basic for Windows which is an extension of Quick Basic that employs many of the structured features of C and other high level languages. Visual Basic allows superior implementation of the graphical user interface which is one of the key features of this capsule transfer program. The graphical user interface allows the operator to easily determine the exact status of the system at any time by glancing at the computer screen. The operation of the program starts from main menu of Windows screen disply.

2. **Examination of Irradiation.**

A new NAA facility is examined to identify the characterization of tube transfer system, irradiation sites and polyethylene irradiation capsule. The constituent of gamma-ray counting system for the measurement of radioactivity is presented in Table 2. The temperature of three irradiation sites were measured with irradiating time using Thermo-Label. In the case of PTS#1, the internal temperature of PE capsule was no more than 60 ℃ within 1 hour and the dose rate was about 3500 rads/sec. in 15MW. The variation of neutron flux in short and long irradiation intervals were measured in 17MW continuously and were plotted in Figure 4. Average neutron flux during the period of irradiation was $1.50 \pm 0.02 \times 10^{13}$ n/cm$^2 \cdot$ s. and the deviation was < 1.5%. The neutron flux was stable relatively. Thermal, epithermal and fast neutron flux of NAA irradiation holes and cadimium ratios were measured in 22MW and presented in Table 3. To make a suitable polyethylene irradiation capsule, heat resistance test and physical properties test such as melting index(20.7), density(0.95), melting point(131. 6℃), and a measurement of impurities(< 1-100 pm) were carried out and the best materials were chosen. The analytical results of trace elements in polyethylene rabbit and various polyethylene materials by INAA and ICP were presented in Table 4.

II. Application of Neutron Activation Analysis in Korea.

Since 1960s, neutron activation analysis (NAA) has been widely used in industry, agriculture, geology, environmental pollution, biology, archaeology, forensic science and many other fields in Korea. There are two NAA groups ; Korea Atomic Energy Research Institute (KAERI) and Korea Institute of Geology, Mining and Materials (KIGAM) and many users of universities and other organizations in Korea. In the future, an applied field of NAA will be extended and users will be increased. The examples of applications of NAA from 1970s are as follows :

- *Nuclear Science* : Trace impurities in nuclear fuel and materials such as uranium oxide, graphite, reactor coolant and alloy metals were determined using radiochemical NAA mainly. For the analysis of boron, prompt gamma counting technique was also studied in 1980s. To improve analytical accuracy, spectral and isotope interference occuring from uranium fission product were studied and interference calibration program was developed and anticoincidence counting method was studied.
- *Environmental Science* : For a long-term study of the environmental pollution monitoring, trace and toxic elements in enviromental samples such as air dust, coal and fly-ash, soil, sediment, plants and sea and river water, rain- and snow fall samples were analyzed. Recently, KAERI is participating in international cooperative research which is organized by IAEA (sub-project on air pollution, UNDP/RCA/IAEA Project). NAA was applied for the analysis of environmental samples and the migration of trace elements were studied using tracer method.
- *Biological and Medical Science* : Analysis of a number of animal and plant tissues, serum and blood, fishery, etc. are carried out. Analysis of trace elements in cancer tissues was performed together with the Korea Cancer Center Hospital.
- *Industrial Science* : Analysis of the composition of high purity materials, noble metals, rare earth elements and inorganic compounds are carried out. Analytical quality service for QA/QC in industries are supported. Trace element analysis of high purity metals and a study on improvement of accuracy were performed ; an analytical method of high purity silicon semiconductor was developed by INAA and analytical methods of high purity Mo, Ni, Ta and W were also developed by RNAA.
- *Geological Science* : To improve the analytical sensitivity, a nuclear and a spectral interferences related to spectrum analysis and irradiation methods were studied. The composition of trace elements in soils, rocks, minerals, etc. were determined using thermal and epithermal neutron activation analysis. Analysis of rare earth elements in cosmic materials such as meteorites were carried out as the Apollo project. The isotopes from the reactions of fast neutron were studied and the interference was also corrected and 40 elements in geological samples were determined.
- *Life Science* : For clinical, nutritional and contamination research, the concentration level of essential, toxic elements and heavy metal in biological samples such as foodstuff, rice, human milk, human hair, tabacco and smoke, Korean Ginseng, etc. were analyzed by INAA and RNAA. Iodine analysis of the colostrum and mature milk of Korean lactating mothers related to diseases and metabolism of infants were performed.

- *Archaeology, Forensic Science* : The origin and classification of Korean antiques was investigated using chemometrics and multivariate analysis of multi-elements composition in the pottery and coinages in the laboratory of a university. To study individual identification for a criminal investigation, several kinds of human hair samples were analyzed by INAA.
- *Certification of Reference Materials* : Using NAA technique, cross-checking and identification of standards has been performed and obtained a good scores in international and domestic intercomparison and certification of reference materials. Our laboratory is also carrying out the IAEA's data intercomparison study.

III. Summary of Applied Research using Neutron Activation Analysis.

1. Study on Air Pollution Monitoring in Korea using High and Low Volume Air Sampler by Instrumental Neutron Activation Analysis[1-6] : The aim of this research is to enhance the use of nuclear analytical techniques for air pollution studies and to study the feasibility of the use of instrumental neutron activation analysis as a routine monitoring tool to find out environmental pollution sources. Trace elements in samples collected at two suburban residential sites, Taejon and Wonju city in the Republic of Korea, were analyzed by INAA. For the verification of the analytical method, NIST SRM-1648 and NIES CRM No. 8 were chosen to be analyzed among the environmental standard reference materials. The accuracy and precision of the analysis of 43 and 22 trace elements in the samples were compared with the certified and reported values respectively. The analytical method was found to be reliable enough when the NIES sample analytical data were compared with the data from different countries. In the analytical result of SRM, relative standard deviation was within the 15% except the few elements and the relative error was within the 10%. First, 33 trace elements in airborne particulate matter collected, with the high volume air sampler(PM 10), and silica filters were analyzed. Enrichment factors were calculated using Taylor's crustal concentration data to investigate the source apportionment. Second, the Gent stacked filter unit low volume sampler and Nucleopore membrane filters were employed. Variations of the elemental concentrations were measured monthly and the enrichment factors were calculated for the fine (PM 2.5) and coarse size (PM 2.5-10) fractions, respectively. Total suspended particulate matter and elemental concentrations in samples collected in the urban area are measured. The analytical data were treated statistically to estimate the relationship between two variables, the concentrations of elements and total suspended particulate matter. The results were used to describe the emission source and their correlation and also confirmed the possibility to use this method as a routine monitoring tool to find out environmental pollution sources.

2. Intercomparison and Determination of Trace Elements in Sediments by Instrumental Neutron Activation Analysis[7] : For the application of study on pollution and conservation of environment, determination of elemental concentrations in different sediment samples (river, estuarine and marine sediment) were carried out using INAA. For verification and evaluation of the analytical method, three standard reference materials (two NIST SRM and one NRCC CRM) were chosen and the accuracy and precision of the analytical procedure were estimated by comparison to the certified values. In addition, two IAEA's sediment samples which were performed as the IAEA's AQCS Programme were analyzed according to the pre-established analytical method, the analytical results of elements such as Ag, Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, Sn and Zn were intercompared with those of other laboratories.

3. **Determination of Toxic and Trace Elements in Algae by Instrumental Neutron Activation Analysis :** Instrumental neutron activation analysis has been applied in the determination of toxic and other trace elements in a set of three algae materials provided by the International Atomic Energy Agency, with the aim of environmental preservation through enhanced applications of nuclear analytical techniques. The quality of the analysis method has been evaluated by analyzing a number of biological standard reference materials. By adding mineral nutrients, the cultivation of algae for metals is enhanced, in particular, selected toxic heavy metals such as As, Cd, Cr, Hg, Ni and Pb. It is believed that the level of elemental concentration in algae samples are dependent on environmental conditions due to its biochemical properties. Algae materials may be useful as an indicator or controller of environmental water pollution.

4. **Determination of Trace Elements in High Purity Copper by INAA, GFAAS and ICP/AES[8] :** Trace elements in high purity copper metal were analyzed by INAA and analytical results are compared with those of other analytical methods. To identify the accuracy and precison of analytical procedure, analyses of the standard reference materials (NIST SRM 398) were carried out. The homogeneity of samples were assessed by means of the elements such as Ag, As, Co, Sb, Se and Zn. The uncertainties and the concentration of consitituent elements were determined and also showed the possibility of use for analytical quality control.

IV. Future Plans for Research and Development

We will carry out the analysis of airborne particulate matter as well as other environmental and biological samples for air and marine environmental pollution studies. This workscope is also involved as a part of our long term project related to a intensive study on application of NAA. Particularly, we are interested in analytical quality assurance of NAA. In addition, to improve the analytical accuracy and detection limit, to increase the number of available elements, we are making plans for the development of various irradiation facilities and equipment and the research of analytical techniques using chmical analysis. However, to make the above project a success application of international standards are essential, i.e., standardization and harmonization of analytical techniques in sampling and sample preparation, analytical procedures and data evaluation, including K_o method as well as chemometrics. Collaboration with RCA member states, IAEA and other nations will be promoted.

V. References

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Table 1. Characteristics and Available Maximum Neutron Flux(30MW) with Irradiation Sites of Pneumatic Transfer System for Neutron Activation Analysis.

Irradiation Hole	Neutron Flux, Φ = n/cm^2.s		Utilization	Specification
	Fast (>0.82 MeV)	Thermal (<0.625 eV)		
System # 1 (NAA 1)	2.4 x 10^{10}	3.9 x 10^{13}	· For Production of RI and NAA	· Manual System: Auto/Hand Control, Loader and 2 Receivers, Air Cushion · PE Capsule: 42cc, O.D28mm, L80mm · Air Pressure: 1.0 bar · Simple shutter: Shielded loader and Receiver
System # 2 (NAA 2)	2.5 x 10^{11}	9.4 x 10^{13}	· For NAA only (ENAA, DNAA)	· Automatic System: Auto PC & Emergency Control, Air Cushion, 100 Sample Loader, 11 Diverters and Delay Stacker · PE Capsule : 27cc, O.D25mm, L62mm · Air Pressure : 0.6 bar · Preset T_i, T_d, T_c · Two Count End
(NAA 3)	1.3 x 10^{12}	1.6 x 10^{14}		

Table 2. Gamma-Ray Counting System of NAA Laboratory.

- HP Ge Semiconductor Detector, EG&G ORTEC.
  GMX Series (3 keV-10 MeV) and GEM Series (50 keV-10 MeV) 25 % Relative Efficiency, 1.9 keV Resolution at 1332 KeV of ^{60}Co, Peak to Compton Ratio ; 45:1
- HP Ge Semiconductor Detector, Oxford/TENNELEC.
  CP Series (40 keV-10 MeV) 25 % Relative Efficiency, 1.85 keV Resolution at 1332 KeV of ^{60}Co, Peak to Compton Ratio ; 57:1
- LEPS Si(Li) Detector, EG&G ORTEC.; SLP Series (1 keV-60 keV)
- Low Background Pb Shield for Ge Detector, EG&G ORTEC.
  4π-10 cm thick Low Background Virgin Lead, Graded Cu & Cd Liner 28 x 41 cm Cavity Pb Shielding Box (35 x 40 cm, 40 x 45 cm Cavity, Cu & Cd Lined)
- Multichannel Analyser, EG&G ORTEC.
  918A MCB; 8K Channel ADC(10μs), 8K C Data Memory, Counting Loss Correction
  919A MCB; 16K Channel ADC(7μs), 64K C Data Memory, Digital Stabilizer, MASTRO-II Emulation Software(ADCAM 100)
- Multichannel Analyser, Oxford
  Assayer S/W and OxfordWIN-MCA S/W including Auto Sample Changer Program.
- Application Software Program for NAA : Gamma-Ray Spectrum Analysis Software : KNAA/UNICAL(KAERI), GANAAS(IAEA), GELIGAM/OMNIGAM(EG&G ORTEC)

Table 3. Measured Thermal, Epithermal and Fast Neutron Flux of NAA Irradiation Holes and Cadimium Ratios at 22MW Thermal Power.

Irradiation Hole	Neutron flux, $n/cm^2sec.$			Cadimium Ratio(Au)
	Thermal, Φ_t	Epithermal, Φ_e	Fast, Φ_f	
NAA 1	$1.75 \pm 0.02 \times 10^{13}$	$3.62 \pm 2.13 \times 10^{10}$	$3.25 \pm 0.14 \times 10^{10}$	250
NAA 2 (Cd lined)	$5.78 \pm 0.56 \times 10^{11}$	$3.40 \pm 0.41 \times 10^{10}$	$3.85 \pm 0.31 \times 10^{9}$	35
NAA 3	$7.60 \pm 0.06 \times 10^{13}$	$4.35 \pm 1.85 \times 10^{11}$	$6.80 \pm 0.70 \times 10^{11}$	13

Table 4. Analytical Results of Trace Elements in Polyethylene Rabbit and Various Polyethylene Samples by INAA and ICP. Concentration in ppb.

Element	Rabbit	HN1	HN2	TR1	TR2	TR3	LG1	LG2
Ca(ppm)	-	150	160	270	<3.7	<23	230	300
Mg(ppm)	140	110	110	3.6	150	0.28	23	26
Al(ppm)	74	76	52	8.7	57	0.20	13	23
Cl(ppm)	38	100	79	19	53	0.19	140	140
Ti(ppm)	6.1	4.1	5.2	1.4	4.1	0.17	9.4	13
Cu	-	<280	<240	<130	680	54	<170	<240
V	20	<4	<3	<2	440	1.5	<2	<2
Mn	170	<6	<6	6.78	<19	4.4	8.8	10
Na(ppm)	1.3	0.26	0.43	<0.02	0.20	1.0	0.65	0.92
Fe(ppm)	2.3	1.5	<0.75	<0.84	<0.46	<0.55	0.52	0.81
Mo	280	-	-	-	<1100	<1600	<260	<260
As	0.51	<0.71	0.66	<.1.3	1.2	<1.2	<0.35	<0.43
Br	90	<2.4	3.0	5.0	4.6	5.4	8.00	51
Sb	3.1	<1.1	2.9	2.3	<1.8	<2.4	4.4	55
La	10	<0.16	<0.14	<0.18	1.1	9.9	1.3	0.72
Au	0.44	0.028	<0.015	<0.015	0.059	0.067	<0.009	<0.019
Cd	30	<24	<28	<12	<32	<51	<6.7	<15
Cr	310	21	20	37	<7.5	18000	5.2	12
Ga	2.9	<38	<42	<26	<25	<6.2	<1.3	<1.5
Hf	0.66	<0.72	<0.69	<0.71	<0.64	2.5	<0.4	<0.75
Hg	1.7	<2.9	<2.8	<2.1	<2.2	<3.0	<1.1	<1.6
Co	4.3	9.2	8.6	3.8	5.5	6.3	2.8	3.4
Zn	60	<74	110	<70	160	74	<30	55
Cs	1.3	<3.1	7.1	<2.5	<1.2	<1.4	<0.71	<2.6
Eu	-	<2.0	1.7	1.1	<1.1	<1.3	<0.86	<0.34
Ba	0.18	0.11	840	<860	<270	<310	<190	<210
Sc	-	<0.06	0.23	0.20	<0.044	<0.061	0.076	0.057
K	250	<2600	<5500	<1060	<3300	<530	<820	<240
Zr	-	<660	800	<760	<210	<260	<280	<300
Ce	50	9.5	<5.9	17	<4.5	<9.5	<2.8	<2.8
Sm	0.07	0.23	<0.11	<0.13	0.10	0.27	0.13	0.060
Rb	-	<24	<47	57	<21	100	<17	<20
Th	1.4	<1.2	<1.1	<0.84	<0.59	<0.90	<0.31	<0.48
W	1.1	<4.3	<4.0	<3.4	<2.9	<5.0	<0.85	<1.4

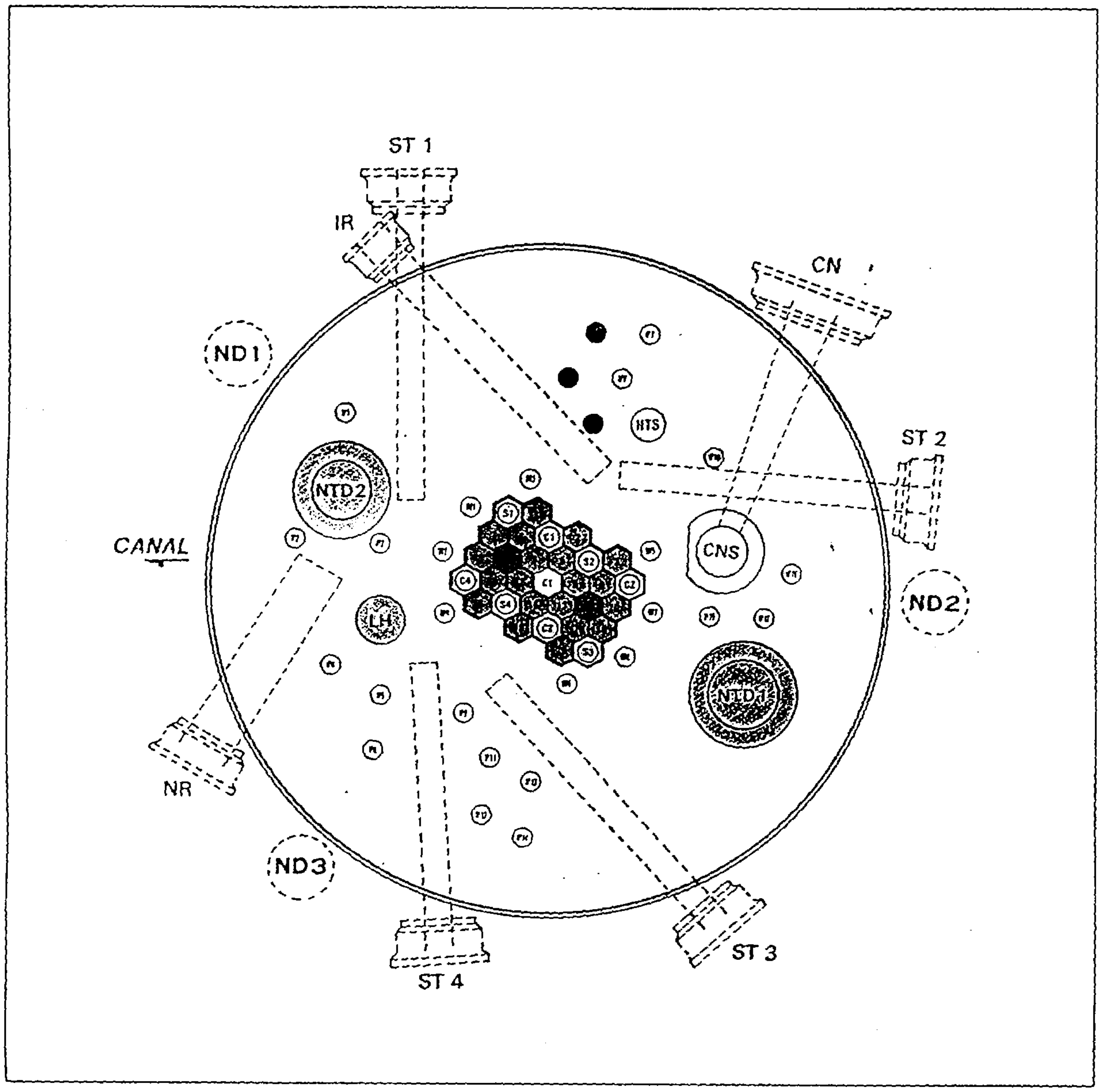

Figure 1. Location of irradiation thimbles.

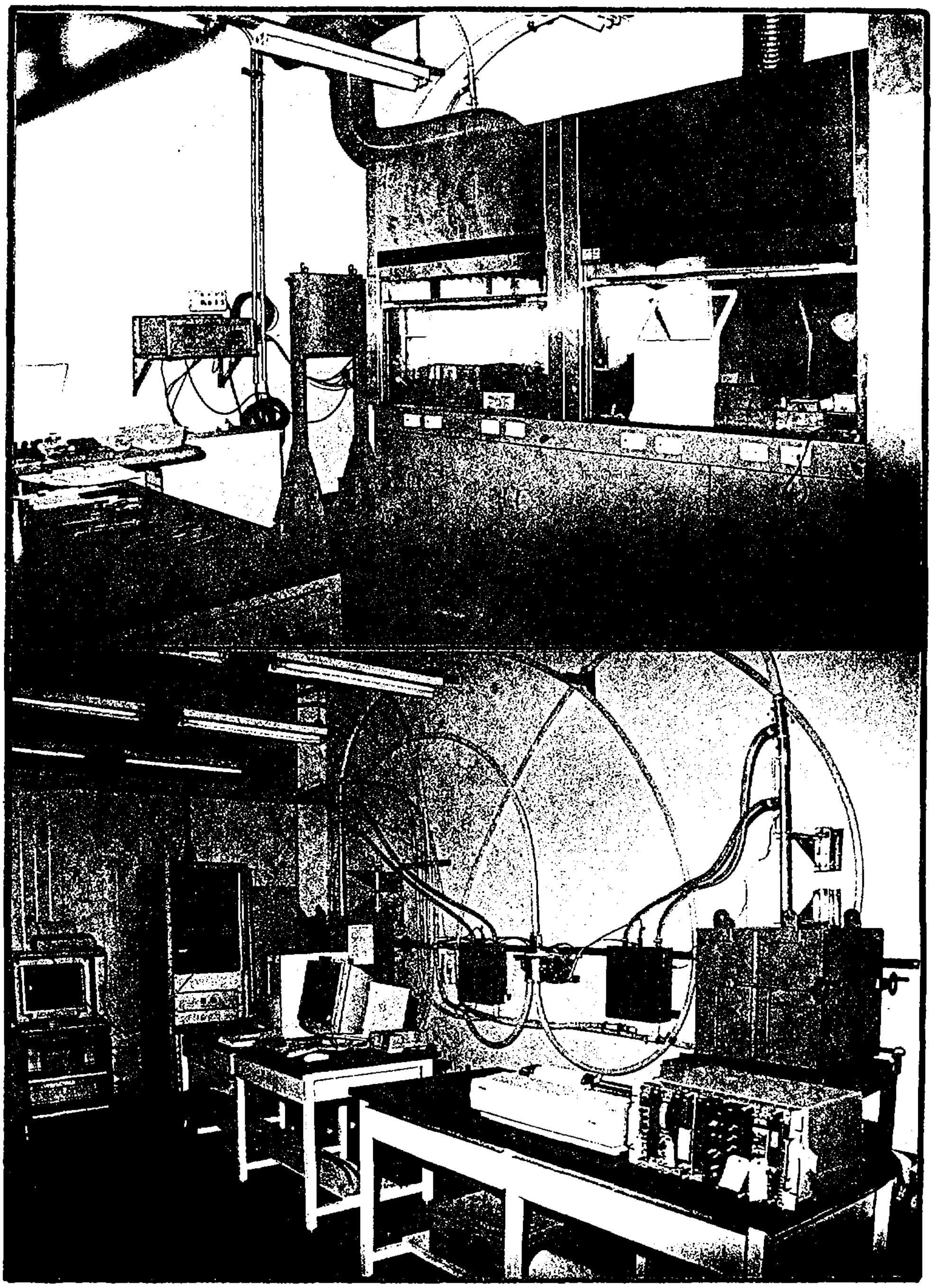

Figure 2. The photograph of PTS laboratory.

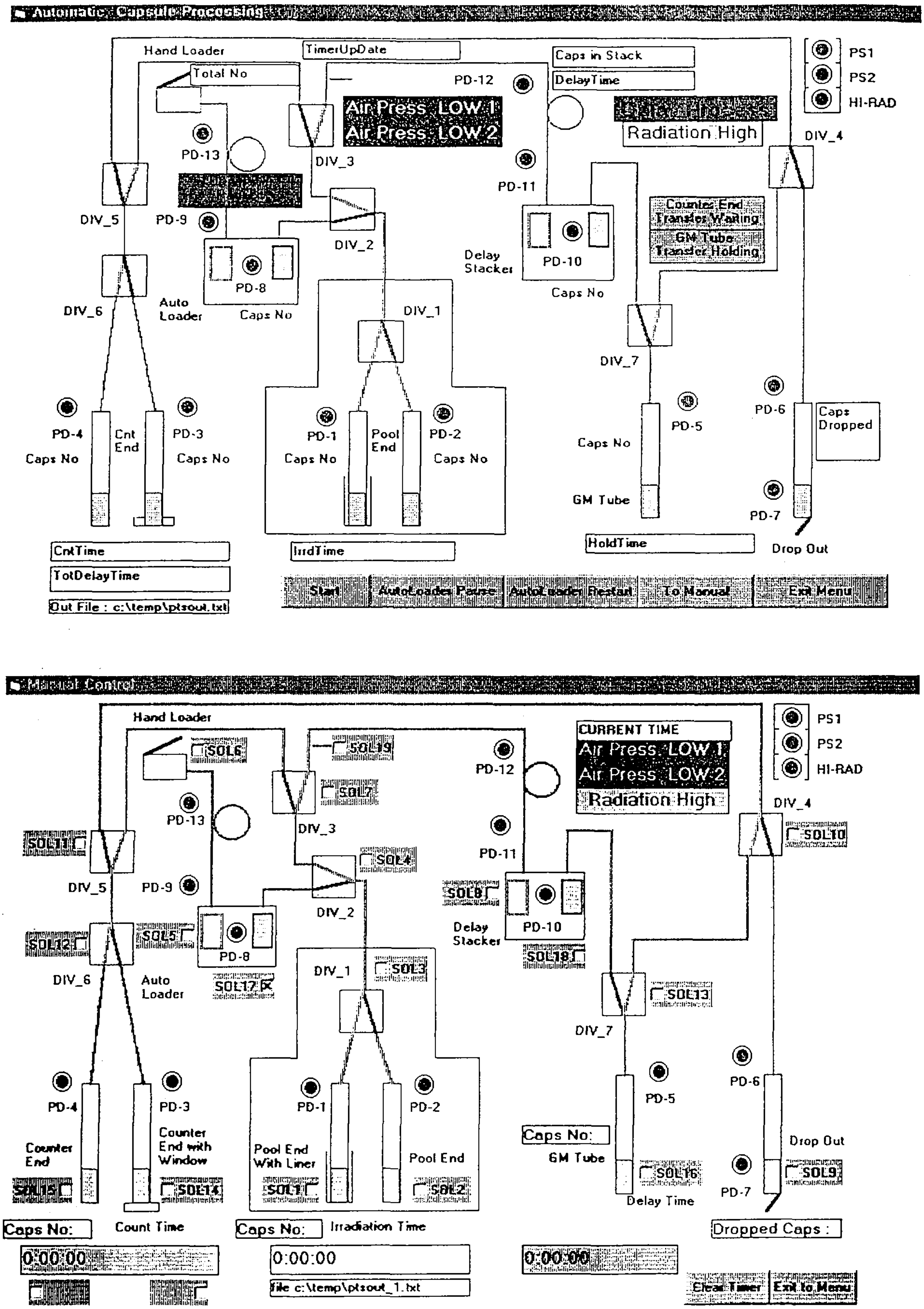

Figure 3. The process flow diagram of automatic pneumatic transfer system.

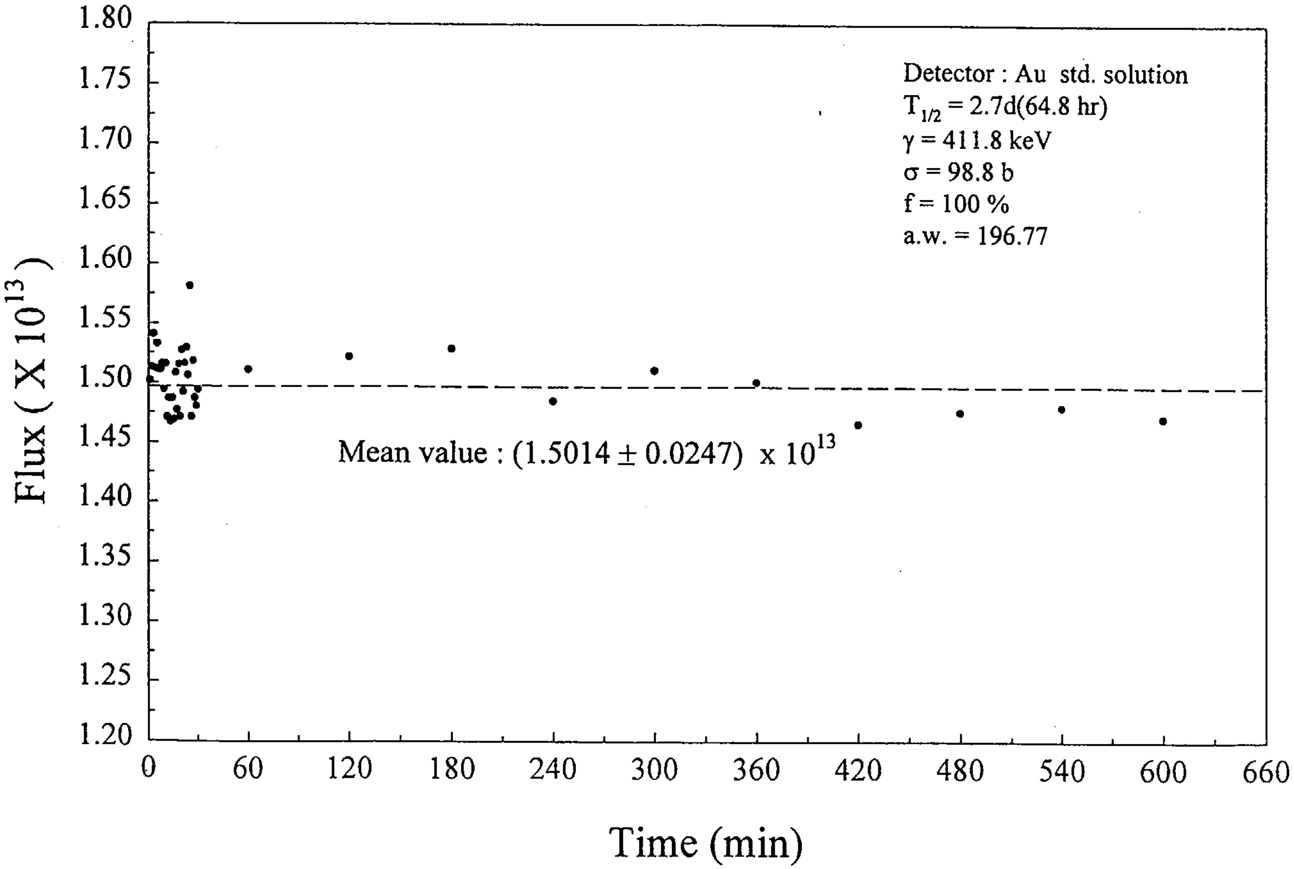

Figure 4. **Typical Fluctuation Test of the Thermal Neutron Flux on PTS Irradiation Hole in 17MW.**