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WATER CHEMISTRY MANAGEMENT IN COOLING SYSTEM OF RESEARCH REACTOR IN JAERI

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Water Chemistry Management in Cooling System of Research Reactor in JAERI

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The department of research reactor presently operates three research reactors(JRR-2, JRR-3M and JRR-4). For controlling and management of water and gas in each research reactor are performed by the staffs of the research reactor technology development division. Water chemistry management of each research reactor is one of the important subject. The main objects are to prevent the corrosion of water cooling system and fuel elements, to suppress the plant radiation build-up and to minimize the radioactive waste.

In this report descrive a outline of each research reactor facilities, radiochemical analytical methods and chemical analytical methods for water chemistry management.

Keywords: Research Reactor, Heavy Water, Primary System, Secondary System, Water Chemistry, Radiochemical Analysis, Chemical Analysis.

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*Office of Atomic Energy for Peace in THAILAND

原研研究炉の冷却系統の水化学管理

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原研研究炉部では，現在3基（JRR－2，JRR－3M，JRR－4）の研究炉が運転されている。各研究炉の水・ガス管理は，研究炉を運転管理していく上で重要な技術的課題である。このうち水化学管理は，重要な項目で，主たる目的は，燃料要素や冷却系統の腐食防止並びに放射線レベルの抑制による放射性廃棄物の低減化である。

本報告書では，各研究炉の施設の概要と水化学管理で必要とする放射化学分析方法及び化学分析方法について記述した。

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1. Introduction

In 1956,Japan Atomic Energy Research Institute(JAERI) was founded as a national center of research and development for the nuclear energy in Japan. A series of research reactors JRR-1,JRR-2,JRR-3 and JRR-4 were successively constructed in Tokai Research Establishment,in Ibaraki prefecture. At present, JRR-1 is preserved as the Monumental Hall. JRR-3 was upgraded in 1990 as JRR-3M. JRR-2 and JRR-4 are still opreating now. A lot of experimental and irradiation facilities are equipped and utilized in each research reactor,such as neutron radiography, neutron beam experiments, boron neutron capture therapy(BNCT) on brain tumor, and so on.

These research reactors are being administered by the Department of Research Reactor,which is separated the organization into 6 divisions, namely research reactor administration division, research reactor utilization division, JRR-2 opertation division, JRR-3M opertation division, JRR-4 opertation division and research reator technology deveropment division(RRTDD). Operation, maintenance, technical management of fresh fuel, spent fuel, water and gas system in the reactor and R & D works relevant to research reactors are being performed in this department. Moreover, the researchers are designing and developing to get a new high performance research reactor in the future.

For controlling and management of water and gas in each research reactor is performed by the staffs of the research reactor technology development division. Water chemistry management of each research reactor is one of the important subject. The main objects are to prevent the corrosion of water cooling system and fuel elements, to suppress the plant radiation build-up and to minimize the radioactive waste.

Uitilization of these reactors are classified into material irradiation, neutron beam experiments using thermal and cold neutron and so on. The experiments are mainly for neutron scattering studies, neutron radiography, radioisotope production, neutron activation analysis, silicon irradiation for semiconductor and medical irradiation for tumor therapy research.

2. A brief description of the JRR-2,JRR-3M and JRR-4

2.1 JRR-2(Japan Research Reactor No.2) facilities

2.1.1 JRR-2

JRR-2 is a tank type reactor using heavy water as moderator, coolant and refector. It has a maximum thermal power output of 10 MW and has served with the maximum thermal neutron flux density of 2×10^{14} n/cm^2•sec. The cylindrical BM(UAl x -Al) dispersion type fuel elements with 45% enriched uranium are arranged in the reactor core and placed in a heavy water tank. The core consists of 24 fuel elements and 6 cladded-cadminum with stainless steel control rods. Fuel meat has uranium content 45% wt and is cladded with aluminium alloy. The heavy water tank is installed inside a light water tank for thermal shielding, while the light water tank is enclosed by barytes concrete for biological shielding.

JRR-2 is scheduled for 12 operating cycles per year. Every cycle provides for three weeks. The first week is spent for refueling handling including checking and a few maintenance. The last two weeks is scheduled for continuously reactor operation. During the year, it spends for two weeks for chemical cleaning of heat exchanger in heavy water system and a few repairing. For annual inspection of 11 weeks are spent on overhaul and maintenance work. From FY.1994, the schedule has been changed to 50 hours continuous operation a week as a cycle. It is operated 31 cycles/year.

2.1.2 JRR-2 cooling facilities and purification system

JRR-2 cooling system consists of four systems, namely; a) primary heavy water cooling system b) thermal shield water cooling system c) secondary cooling and d) helium gas system. The heavy water system and the thermal shield cooling system release the heat from the reactor core and from the thermal shield respectively. The secondary cooling system removes total accumulation heat from the heavy water and thermal shield water system and then dissipate the heat to atmosphere by cooling tower. The schematic diagram of JRR-2 cooling system is shown in Figure 1.

2.1.2 A. Primary heavy water cooling system of JRR-2

The main circulating pumps(DP-1,2) supply the heavy water into the main heat exchanger units(DE-1,2). The cooled heavy water leaves the exchangers through parallel pipes which combine to from a single inlet pipe to the core tank plenum chamber, then flows down from two outlet pipes of the heavy water tank to repeat the flow cycle. The temperature at the core inlet and outlet are kept below 50 ℃ and 56 ℃ respectively.

An emergency cooling system was attached in this system. In case that the emergency comes from the leakage of the coolant in the core tank, emergency heavy water storage tank(ET-1) is supplied into the core by the emergency heavy water pump(EP-2 or EP-2A). If the more additional coolant is required, the heavy water which is collected in the sum pit, will be back to the core by recirculating pump for emergency (EP-1,1A).

To maintain a heavy water purity, purification system is installed. A portion of the core tank overflow to the storage tank(DT-1) is constantly pumped through heat exchanger(DE-3) before passing to the purification system. This system consists of two sets(1-set operating,1-set spare). Each set includes two filters, one is the input deminerizer(DF-1A or DF-1B) and the other is at the output(DF-2). Two mixed-bed ion exchanger cartrige(DD-1,2) are installed in parallel. This de-ionnzation system consists of cation exchanger and anion exchanger in the volume resin of 1:2. The total volume of resin is about 75 ℓ and the flow rate of coolant is 1,320 m^3/hr. The dissolved impurities and radioactive materials in the heavy water are removed by adsorbing on the resin. When the deminerizer loses its efficiency, the resin cartridge covered with lead shielding is cut out and is handled after the decay period. after purification, the heavy water is connected to accommodate heavy water analyzer.

2.1.2 B. Helium gas system of JRR-2

A helium system is installed in the heavy water system to act as an inert atmosphere above the heavy water surfaces. It is used for sweeping the dissociated heavy water from the core tank to the recombiner where radiolysis gas of deuterium and oxygen are recombined catalytically. The recombiner(DT-5) contains a catalyst of alumina pellets(4.5 mm ϕ) with 0.5% wt palladium. A helium heater is placed in front of the recombiner, heats the helium gas at the temperature of 60 ℃ to prevent the causing of catalyst in-effective by moisture film. The evaporated heavy water is condensed and return to the heavy water system. Air and moisture are prevented from the system by purging the helium gas from the supply bottles before reactor operation. The helium gas, deuterium, oxygen and nitrogen gas analyzer are provided to connect in this system.

2.1.2 C. Thermal shield water system of JRR-2

This system removes heat generated in the reactor shields and transfer this heat to the secondary cooling system. To require coolant purity and to reduce corrosion the purification system of two filters(PF-1,2), one deminerizer(PD-1), and one heat exchanger(PE-2) are connected in this system. The mixed-bed ion exchanger is treated in a similar manner to that of the heavy water system. The thermal shield water system consists of one light water circulating pump(PP-1), one heat exchanger(PE-1) and the light water storage tank(PT-1). After purification, the water is feed back to the storage tank.

2.1.2 D. Secondary water cooling system of JRR-2

This system consists of two main circulation pumps(HP-1,2), two booster pumps(HP-4,5) and the cooling tower. The circulating pumps supply cool water from the tower basin to the reactor pump room, then to the heat exchangers. Warm water is returned to the sub basin, and is pumped to the spray nozzles of the cooling tower. The cooled water is corrected in the basin for recycling.

Because of the evaporation of water in cooling tower, water is continuously supplied for controlling the water level during operation. By blowing-down of this secondary water, it can reduce the concentration of dissolved salts to prevent a scaling or corrosion problem. And a combination of chemical addition(polyphosphate based:Towercrin S-306) in this cooling water, can prevents a scale formation and is seved for corrosion inhibitor and algae accumulation in the heat exchanger tubes.

2.2 JRR-3M Facilities(Japan Research Reactor No.3 Modification)

2.2.1 JRR-3M

JRR-3M is a light water cooled and moderated pool type research reactor, with a thermal power of 20 MW. The maximum thermal neutron flux is 2×10^{14} n/cm^2•sec. The 26 standard fuel elements,(UAl x -Al) dispersion type with 20% enriched uranium, 6 follower type fuel elements with hafnium control rods and berylium reflectors, were arranged in the reactor core. Fuel meat plates are cladded with aluminium alloy. Cylindrical reactor core is surrounded by a heavy water tank using as reflector and a moderator.

This reactor is operated continuously 4 weeks/cycle and is done for a short maintenance for one week. For summer period maintenance, it will be done not only 4 weeks for checking the process instrument, testing of utilization system equipments and calibration of radiation, gas and dust monitor, but also a long period of 10 weeks maintenance for annual inspection.

2.2.2 JRR-3M cooling facilities and purification system

Figure 2 shows the flow diagram of cooling system of JRR-3M. This cooling system is composed of a primary water cooling circuit, a secondary circuit and a heavy water circuit covered with helium gas. The primary water cooling flows downward through the core and pass into a ^{16}N decay tank installed below the reactor pool, toreduce the heat and radiation dose. Syphon break valves are installed on the core outlet to prevent the core from being unflooded of primary cooling water. The heat from the primary cooling water and the heavy water system are transfered to a secondary cooling system with a heat exchanger, and finally is emitted to the atmosphere through the cooling tower.

2.2.2 A. Primary water cooling system of JRR-3M

The diagram is shown in Figure 3. This system serves to remove reactor core generated heat to the secondary cooling water with heat exchanger. The coolant passes into the lower plenum at the bottom of the core. The core outlet and inlet temperature are about 36.5 ℃ and 29.5 ℃ respectively. This difference temperature is kept under 7.7 ℃. The tritium activity in the primary system is held about 600 Bq/cm^3. Then this coolant passes into ^{16}N decay tank, which causing by (n,p) reaction of ^{16}O. The delay time for this coolant in this tank is about 5 half-lives ^{16}N, that is 40 second.

For normal operation, two main pumps are supplied for coolant flow rate of 2,400 m^3/hr. Even though normal power supply is lost, two auxiliary pumps are required to run in order to remove heat from the reactor core. The outlet of coolant passes into the two heat exchangers and trasfer its heat to the secondary water cooling, then passes through a strainer for trapping the impurity before return into the reactor pool. A diffuser which is installed along the pool wall, blows up the primary water cooling into the pool.

To remove the radioactive impurities in the primary coolant, such as ^{54}Mn, ^{59}Fe, ^{51}Cr, ^{65}Zn, ^{60}Co, etc, the purification system is installed in the same manner of primary heavy water cooling system in JRR-2. But the larger volume of resin had been supplied. Each deminerizer required 400 ℓ of cation resin and 800 ℓ of anion resin. When an ion-exchanger loses an exchange capacity, a new resin will be replaced.

2.2.2 B. Heavy water cooling system of JRR-3M

This system works as both a reflector and moderator. Figure 4 shows the diagram of this system. It is closed circuit type. The surface of heavy water is covered with helium gas. This system consists of a heavy water overflow tank, a circulating pump, a heat exchanger and two sets of deminerizer with filter. Heavy water in the heavy water tank overflows to the overflow tank in order to maintain the water level uniformly. A circulating pump supplies a heavy water with flow rate of 70 m^3/hr, passing through a heat exchanger and return to the heavy water tank in the reactor pool. Purification circuit bracches at the outlet of heat exchanger. Two mixed-bed ion-exchanger cartridge are installed in parallel. Each cartridge required 12 ℓ of storongly acidic cation exchanger and 24 ℓ of strongly basic anion exchanger.

2.2.2 C. Helium system of JRR-3M

The helium system in JRR-3M acts as the helium system in JRR-2 reactor, and the diagram is shown in Figure 5. For recombination of D_2 and O_2 in the recombiner(diameter:126 mm, long:550 mm, volume:7 ℓ), helium is passed continuously at a rate of about 170 ℓ /min and the pressure is maintained at 150 mmHg. If the system is pressurized up to a pressure of 200 mmHg, two relief valves will open automatically.

2.2.2 D. Secondary water cooling system of JRR-3M

This system is shown in Figure 6. It removes generated heat in four parts, namely a) in the reactor core, b) in the heavy water system, c) in the spent fuel pool and d) from control rod driving mechanism(CRDM). The heat is transfered to a secondary coolant in the heat exchangers and finally is dissipated to outside atomsphere through a cooling tower. The cooled water is collected in the basin of cooling tower for recycling. The flow rate of this system is about 3,200 m^3/hr.

2.3 JRR-4 Facilities(Japan Research Reactor No.4)

2.3.1 JRR-4

JRR-4 is a swimming pool type reactor using light water for its moderator and coolant. This reactor has a maximum thermal power output of 3.5 MW with the maximum thermal neutron flux density of $7x10^{13}$ n/cm^2.sec. The reactor core consists of 20 fuel elements and 7 control plates surrounded by reflectors. The MTR-type of fuel elements,i.e.uranium-aluminium alloy (U-Al) with aluminium claddings,is currently used in this reactor. The degree of enrichment in this reactor is 93 % U-235. Stainless steel dispersion of boron is used in the control elements,and the graphite are used as the neutron reflector in this reactor. The reactor core is located in the bottom of a reactor tank which is a corrosion resisting with aluminum alloy cylinder. The reactor tank can be settled in both pool,no.1 and no.2 pool.

The continuous operation time of full power is 6 hrs/cycle, and it is operated 43 weeks/year. The maintenance schedule of this reactor is daily,monthly check and periodical inspection of twice per year.The periodical inspection is carried out,due to confirmation of the reactor performance,such as shut down equipments,back up rod device, reactor body,storage facility of nuclear fuel materials,cooling system, waste system,radiation control system and so on.

2.3.2 JRR-4 cooling facilities and purification system

A schematic diagram of JRR-4 cooling system and liquid waste system is shown in Figure 7. This cooling facilities are classified into primary cooling water system and secondary cooling system. The purification system in reactor consists of two systems of primary coolant and pool water.The orther facilities that concern with this reactor,are a pure water supply system and liquid waste system.This pure water supply is supplied to JRR-2,JRR-3M and JRR-4 as deminerized light water in cooling system.

2.3.2 A. Primary water cooling system of JRR-4

The primary cooling system,which removes heat from the reactor core,is composed of three main circulating pumps,one auxilliary pump and two heat exchanger with double straight tupes type. During reactor operation,three main pumps are operated and is kept the primary coolant flow rate at about 7 m^3/min. This coolant passes through the core inlet pipe,then flows downward through the reactor core. From the core outlet,the primary coolant transfers the heat to the secondary cooling system with two sets of heat exchanger,then turns back to the core tank.

Both water pools of no.1 and no.2 which are separated with a canel, have outlet and inlet pipes of coolant in each pool.Each pipe is equipped with syphon breaker to prevent the pool water flowing out in case of the failure of piping.

2.3.2 B. Secondary cooling system of JRR-4

This system consists of two main pumps,two heat exchangers and cooling tower. The secondary circuit works as open system where absorbed heat is vented to the atmosphere through the cooling tower. Chemical processing for preventing the scale or corrosion formation has not added in this system.With checking the heat exchangers twice per year and by blowing down or circulation of secondary cooling water can reduce the concentration of dissolved solid that preventing the scale formation problem.

2.3.2 C. Purification system of JRR-4

Two sets of purification system are installed for reduction of impurities in primary coolant and the pool water. Each purification circuit contains two units of mixed-bed ion-exchanger (1 set operation,1 set spare). During reactor operation is setting the flow rate of primary coolant of 10 m^3/hr. From the main pump outlet,the primary coolant passes through the purification system ,and then flows back to the main pump inlet. It is expected to give a water conductivity of 1 μS/cm.

The purification system of pool water is installed for purifying the water in both water pools (no.1 and no.2 pool). This circuit can be changed the position line to no.1 or no.2 pool. It is operated only once per month and checking the conductivity ,total activity of pool water with monitor.

2.3.3 Liquid waste system of JRR-4

The overflowed water from the pool and the core tank drains into the pit,then removes to a disposal tank by two drain pumps (1-set operating,1-set spare).If this liquid waste is contaminated with high radioactivity, it will be passed through the purification system of pool water.

2.3.4 Pure water production system

This system has been supplied to the reactor pool of JRR-2,JRR-3M and JRR-4. It is shown in figure 8. This production system is operated into two parts,that are purification of water and regeneration of resin. The ion-exchange resin tank consists of cation exchanger and anion exchanger in the volume of 600 l:1,400 l. The air system consists of air compressor,cooler,oil separater and air receiver, is equipped to mix the resin. The water line from filtration plant is passed through this resin with flow rate of 10^3/hr. The pure water is stored in pure water storage tank and is supplied to the reactor with water supply pump, or is supplied directly without storing the water in the tank. Some water is drained to the common drain line.It is operating automatically with a control panel. If the conductivity of pure water is more than 1 μS/cm, it will alarm on the control panel.

For the regeneration of resin, the steam line is used for increasing the efficiency of the regeneration. This system is operated three times per year. Sodium hydroxide and hydrochloric acid are kept in separated in storage tank,and is passed

through the used-resin with the volume of 760 l and 155 l respectively from the measuring tank. This system is controled automatically with the control panel of five hours regeneration time.

3. Water chemistry specification and management

Water chemistry specification of each reactor concerns about pH value, temperature,conductivity, concentration of heavy water,helium gas,deuterium gas, oxygen gas,tritium, radionuclides (e.g Mn-54,Fe-59,Cr-51,Zn-65,Tc-99m,Co-60), non-radioactive impurities (Al, Fe, Ca, Mg, SO_4^{-2}, PO_4^{-3}, CO_3^{-2}, SiO_2) and gaseous fission products (Ar-41,Kr-85).

Since changes the pH may occur as a result of precipitation of salts or the release of dissolved gases. The temperature of coolant system may be as a guide in detecting the presence of abnormalities. The conductivity of coolant is a measurement of the total concentration of ionized substances and is affected by temperature, ion mobility and concentration of ions in solution. The conductivity value is used to approximate the dissolved solids concentration in coolant.Non-radioactive impurities in secondary cooling water may affect to cause scale formation or corrosion. Heavy water system which is pressurized with helium gas,the primary water cooling system have to purify during reactor operation.The pure light and heavy water must be detected the conductivity in the range of 1-5 μS/cm.The purposes of the purification system are to remove of dissolved and suspended solid impurities from reactor coolant, to maintain the reactor coolant at its normal pH value (pH 5 to 8) and to remove radioactive waste. .

For the wet storage of spent fuel in water pool,are attached the monitor of water level,temperature and conductivity, and are installed purification system in the pool. This pool water has been analyzed to get data of radioactivities and impurities.The another method of management of spent fuel is a dry storage method for avoiding a corrosion of aluminium-cladded fuel problem.Spent fuel is packed into stainless steel can,and helium gas is supplies in the can to prevent a corrosion of aluminium cladding and a leakage of Kr-85.The air is continuously monitored to measure Kr-85.After more than 90 days cooling of the spent fuel in the spent fuel pool,the spent fuel are sent abroard for reprocessing.

Water chemistry specification of cooling system in JRR-2,JRR-3M,JRR-4 and analytical methods are shown in Table 1,2,3 respectively

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Water chemistry specification of cooling system in JRR-2,JRR-3M,JRR-4 and analytical methods are shown in Table 1,2,3 respectively

Table 1 Water chemistry specification of cooling system in JRR－2 and analytical methods

cooling system	items	specification	analytical methods	frequency of routine work
primary heavy water coolant	conc. of D_2O	high purity (>90%)	IR-spectrophotometry	continuously
	pH	5-8	pH meter	3 times/cycle
	conductivity	< 1 μS/cm	conductivity monitor	continuously
	impurities*	< 0.5 ppm	AAS	upon request
	radionuclides**		γ-ray spectroscopy	1 time/cycle
	conc.of ^3H		liq. scintillation counter	upon request
helium system	conc. of He	>90 vol. %	gas-chromatography	continuously
	conc.of D_2	< 0.5 vol. %		
	conc. of O_2,N_2			
	gaseous nuclides***		γ-ray spectroscopy	1 time/cycle
thermal shield water	pH	5-8	pH meter	3 times/cycle
	conductivity	< 1μS/cm	conductivity monitor	continuously
	conc.of ^3H	≒ 520 Bq/ml	liq. scintillation counter	3 times/cycle
secondary water coolant	conductivity	< 450 μS/cm	conductivity monitor	continuously
	pH	6-9	pH monitor	continuously
	conc. of ^3H	< 0.19 Bq/ml	liq. scintillation counter	3 times/cycle

* impurities = Al, Fe,etc.

** radionuclides = Mn-54,Mn-56, Fe-59, Co-60,Tc-99m,Ar-41, Na-24,etc.

*** gaseous nuclides = Xe-135, Ar-41

Table 2 Water chemistry specification of cooling system in JRR-3M and analytical methods

cooling system	Items	specifications	analytical methods	frequency of routine work
primary water coolant	pH	5-8	pH monitor	continuously
	conductivity	< 5 μS/cm	conductivity monitor	continuously
	impurities*	< 0.5 ppm	AAS	upon request
	radionuclide**		γ-ray spectroscopy	2 times/week
	conc.of ^3H	≅820 Bq/ml	liq. scintillation counter	upon request
helium system	conc. of He	>90 vol. %	gas chromatography	continuously
	conc.of D_2	< 2 vol. %		
	conc. of O_2,N_2			
	gaseous nuclides***		γ-ray spectroscopy	1 time/cycle
heavy water system	pH	5-8	pH meter	3 times/cycle
	conductivity	< 2 μS/cm	conductivity monitor	continuously
	conc. of D_2O	> 99.0 %	IR spectrophotometer	continuously
	impurities*	< 0.5 ppm	AAS	upon request
	radionuclides**		γ-ray spectroscopy	2 times/week
	conc.of ^3H		liq. scintillation counter	upon request
secondary water coolant	conductivity	< 450 μS/cm	conductivity monitor	continuously
	pH	6-9	pH meter	continuously
	conc. of ^3H	< 0.19 Bq/ml	liq. scintillation counter	upon request
	scale impurities****		ion-chromatography & AAS	upon request

* impurities = Al, Fe,etc.

** radionuclides = Mn-54, Mn-56, Fe-59, Cr-51, Co-60,Tc-99m,Ar-41, Na-24,etc.

*** gaseous nuclides = Xe-135, Ar-41

**** scale impurities = Al ,Fe, Ca, Mg, SO_4^{-2}, PO_4^{-3}, CO_3^{-2}, SiO2

Table 3 Water chemistry specification of cooling system in JRR－4 and analytical methods

cooling system	Items	specifications	analytical methods	frequency of routine work
primary water coolant	pH	5-8	pH monitor	continuously
	conductivity	< 1 μS/cm	conductivity monitor	continuously
	conc.of ^{3}H	≅2-3 Bq/ml	liq. scintillation counter	upon request
secondary water coolant	conductivity	< 450 μS/cm	conductivity monitor	continuously
	pH	6-9	pH meter	continuously
	conc. of ^{3}H	< 0.19 Bq/ml	liq. scintillation counter	upon request
	scale impurities****		ion-chromatography & AAS	upon request

**** scale impurities = Al ,Fe, Ca, Mg, SO_4^{-2}, PO_4^{-3}, CO_3^{-2}, SiO2

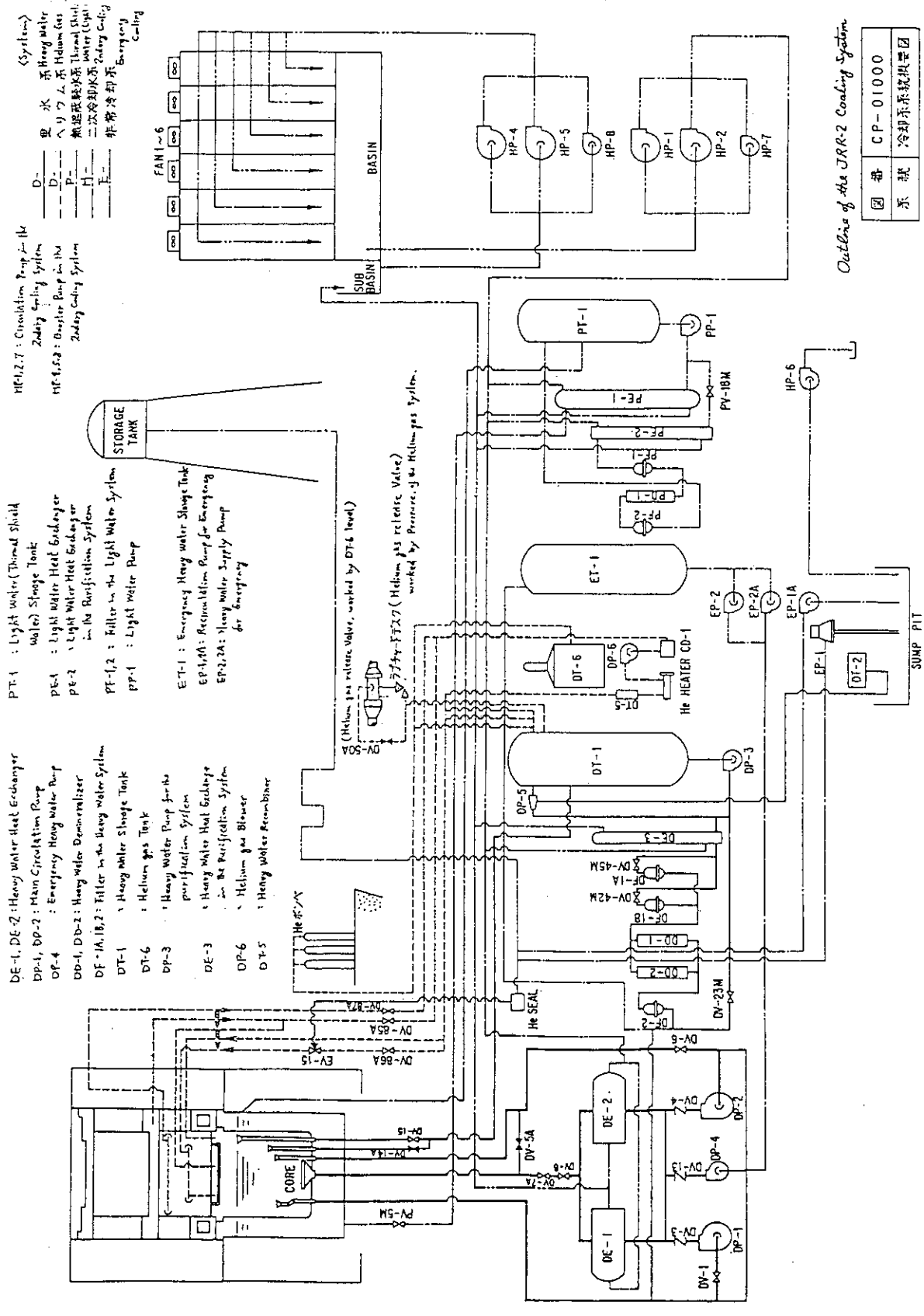


Fig.1 Schematic diagram of JRR-2 heavy water cooling, helium gas system, thermal shield water system, secondary cooling system

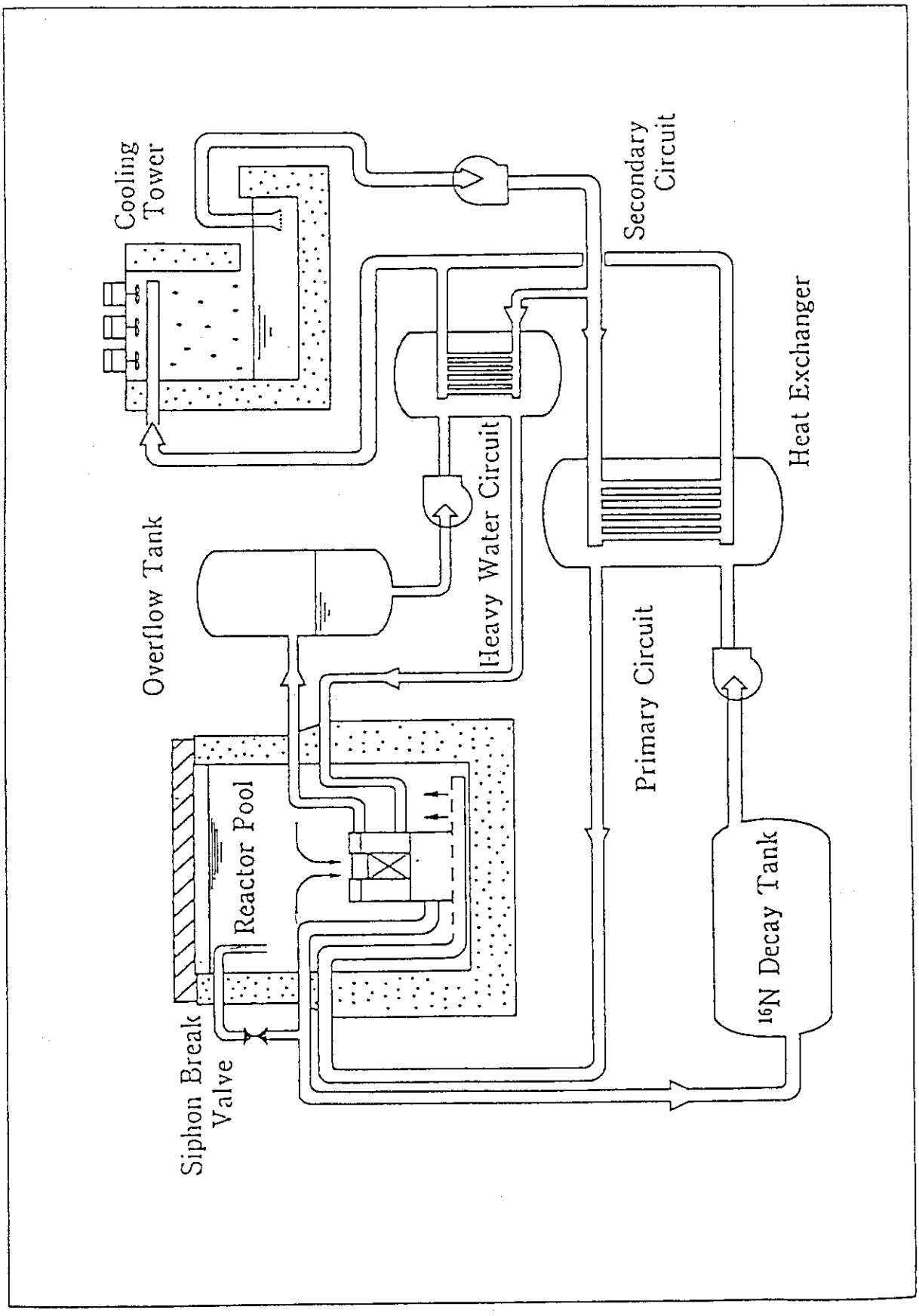


Fig.2 Schaematic Diagram of JRR-3M Cooling System

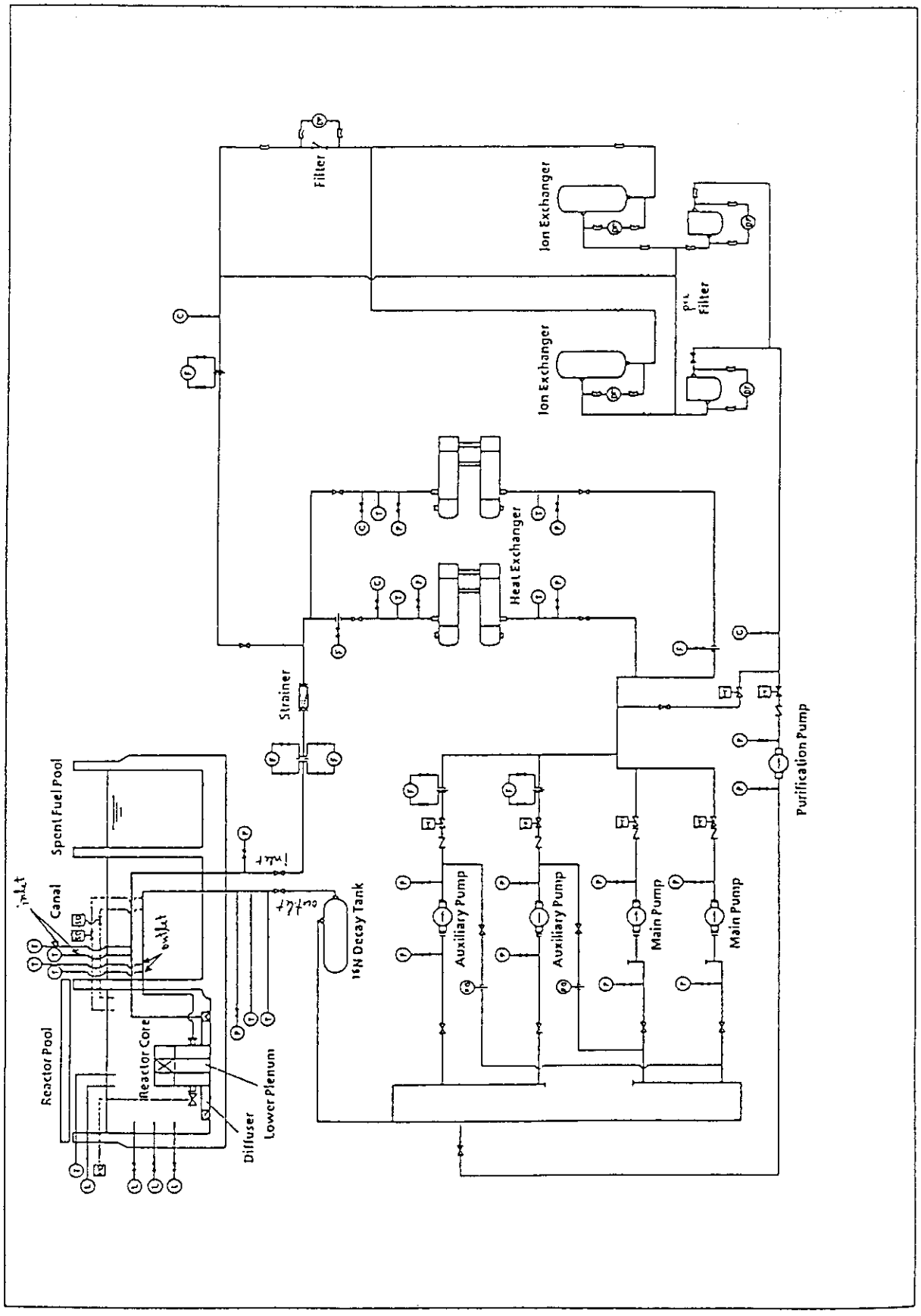


Fig.3 Schematic Diagram of Primary Cooling System of JRR-3M

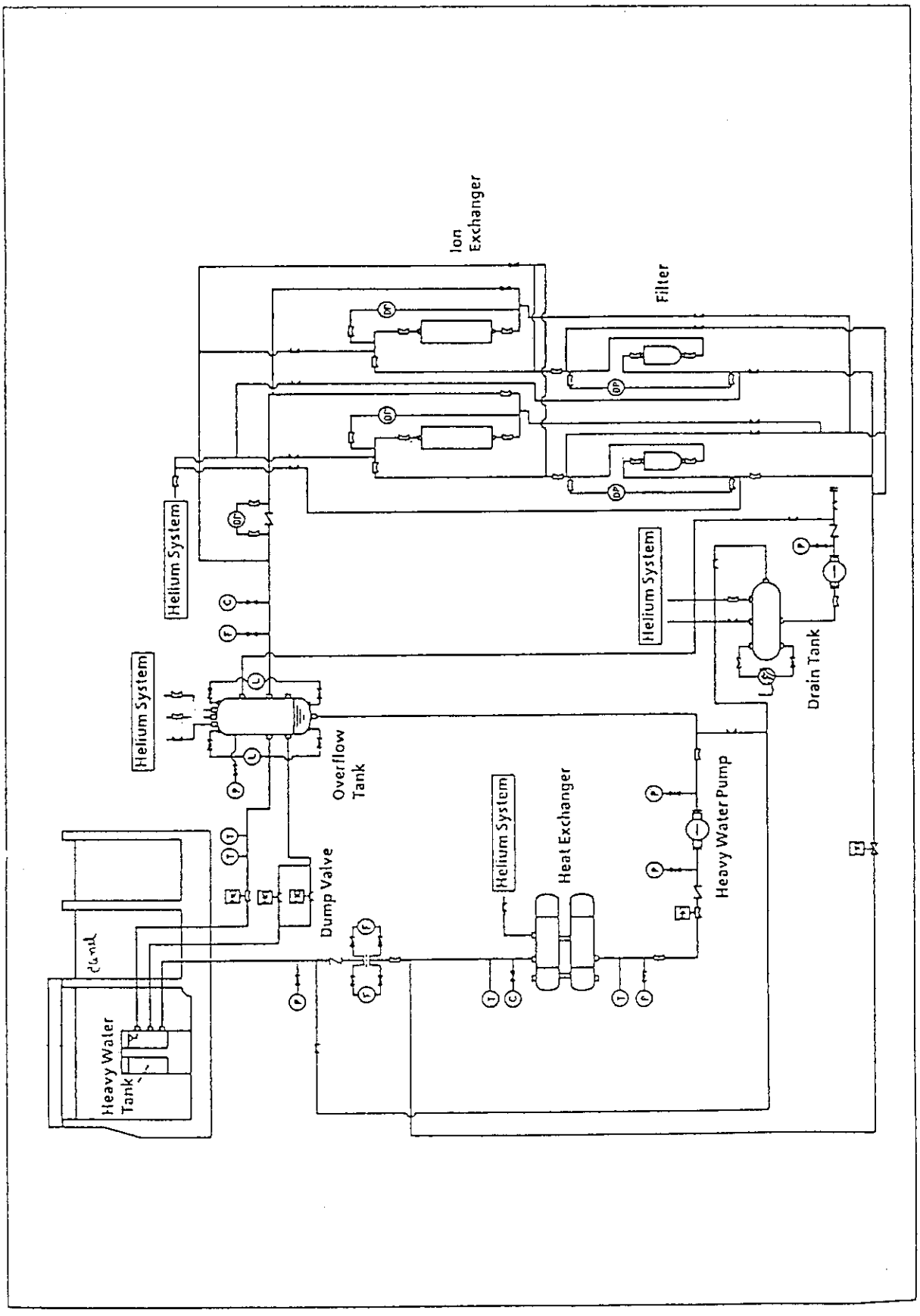


Fig.4 Schematic Diagram of Heavy Water System of JRR-3M

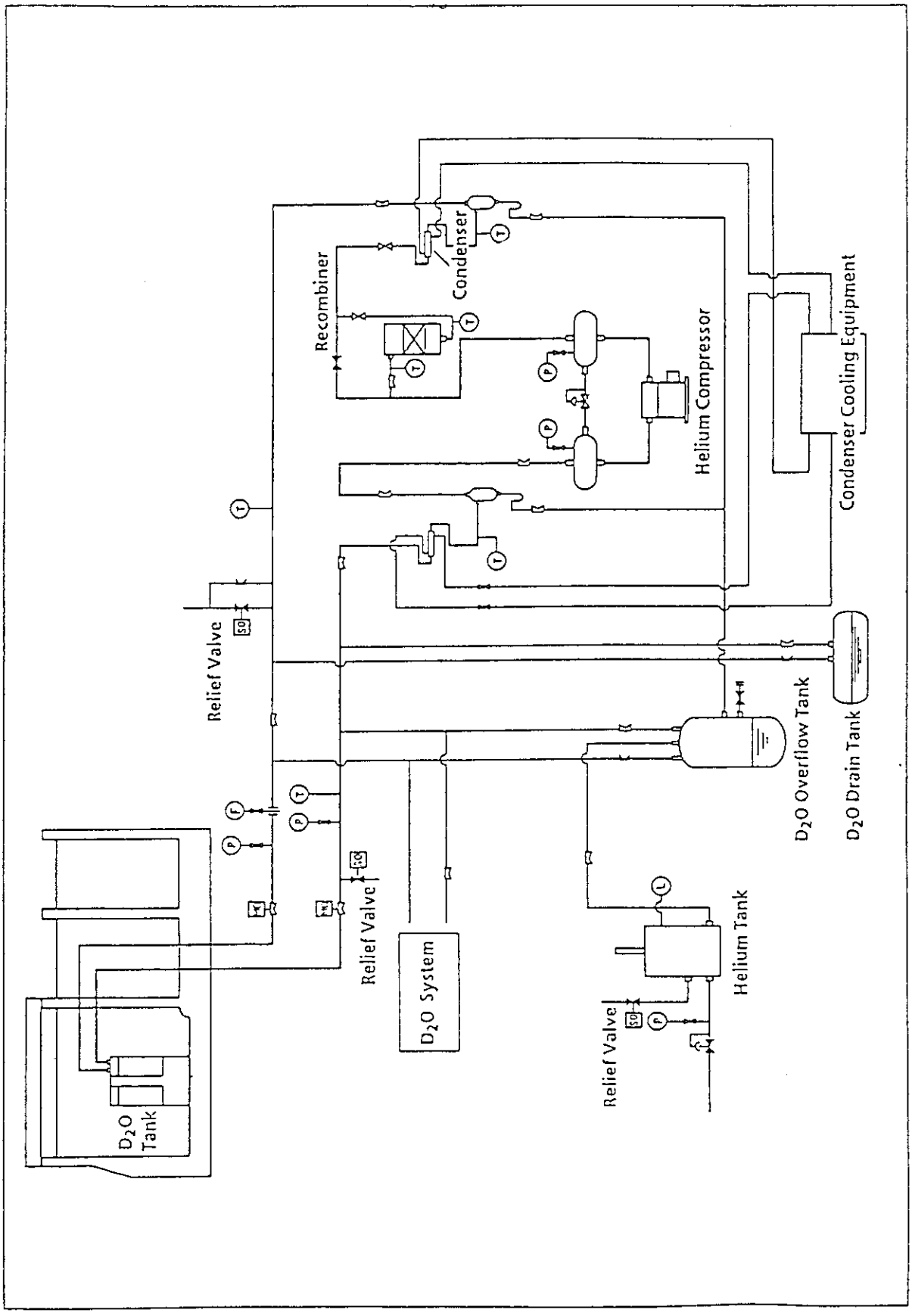


Fig.5 Schematic Diagram of Helium System of JRR-3M

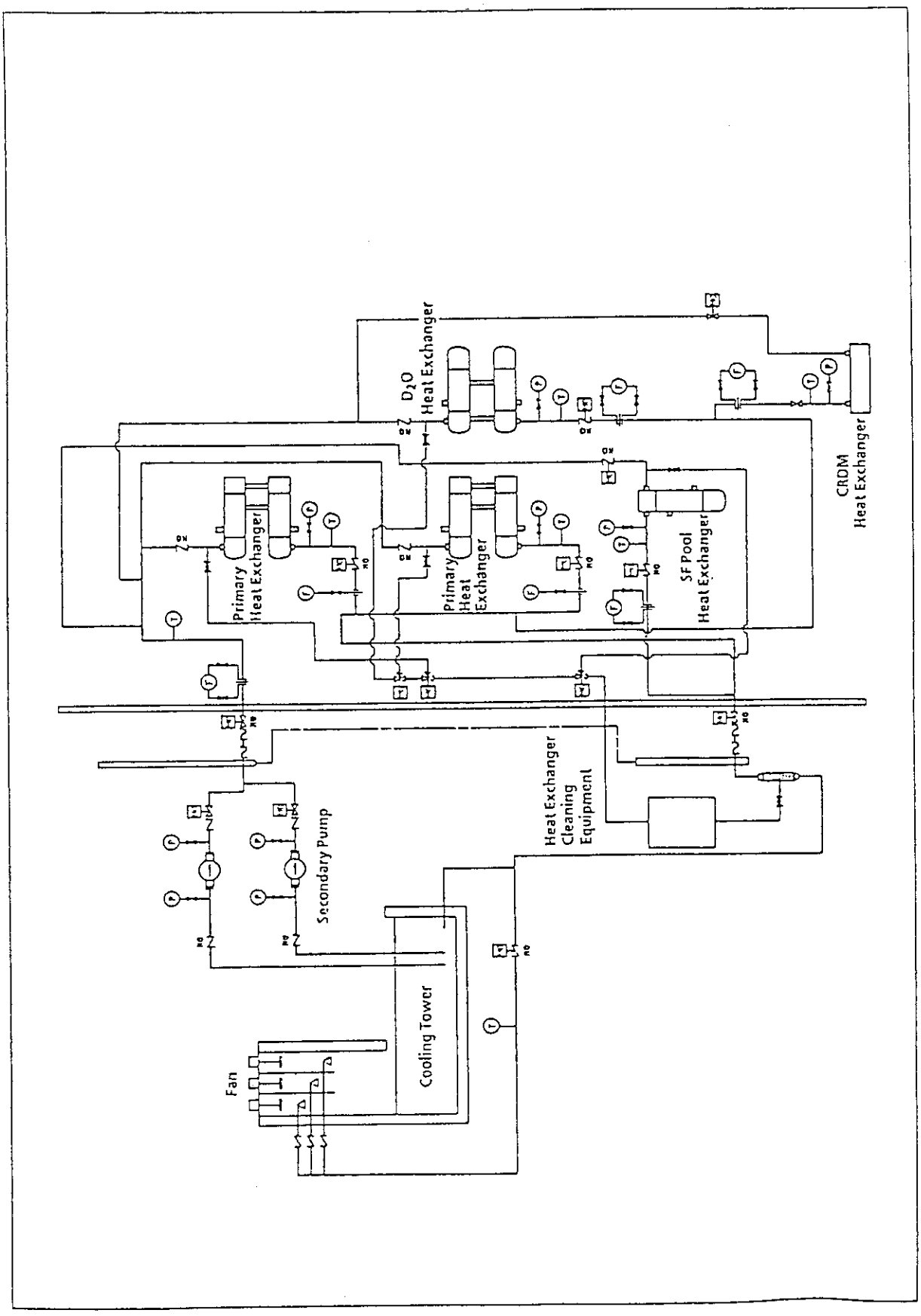


Fig.6 Schematic Diagram of Secondary Cooling System of JRR-3M

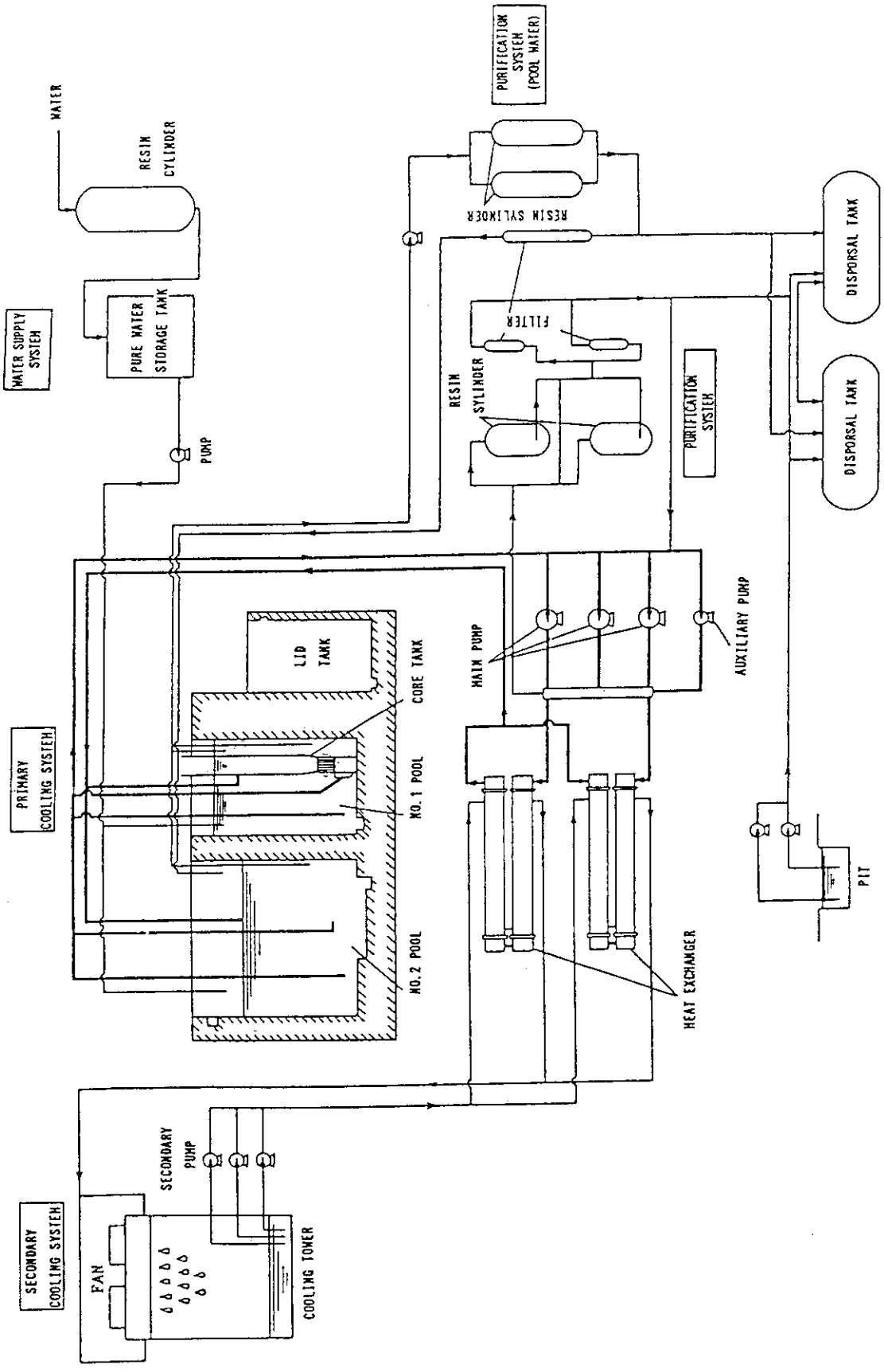


Fig.7 JRR-4 COOLING SYSTEM

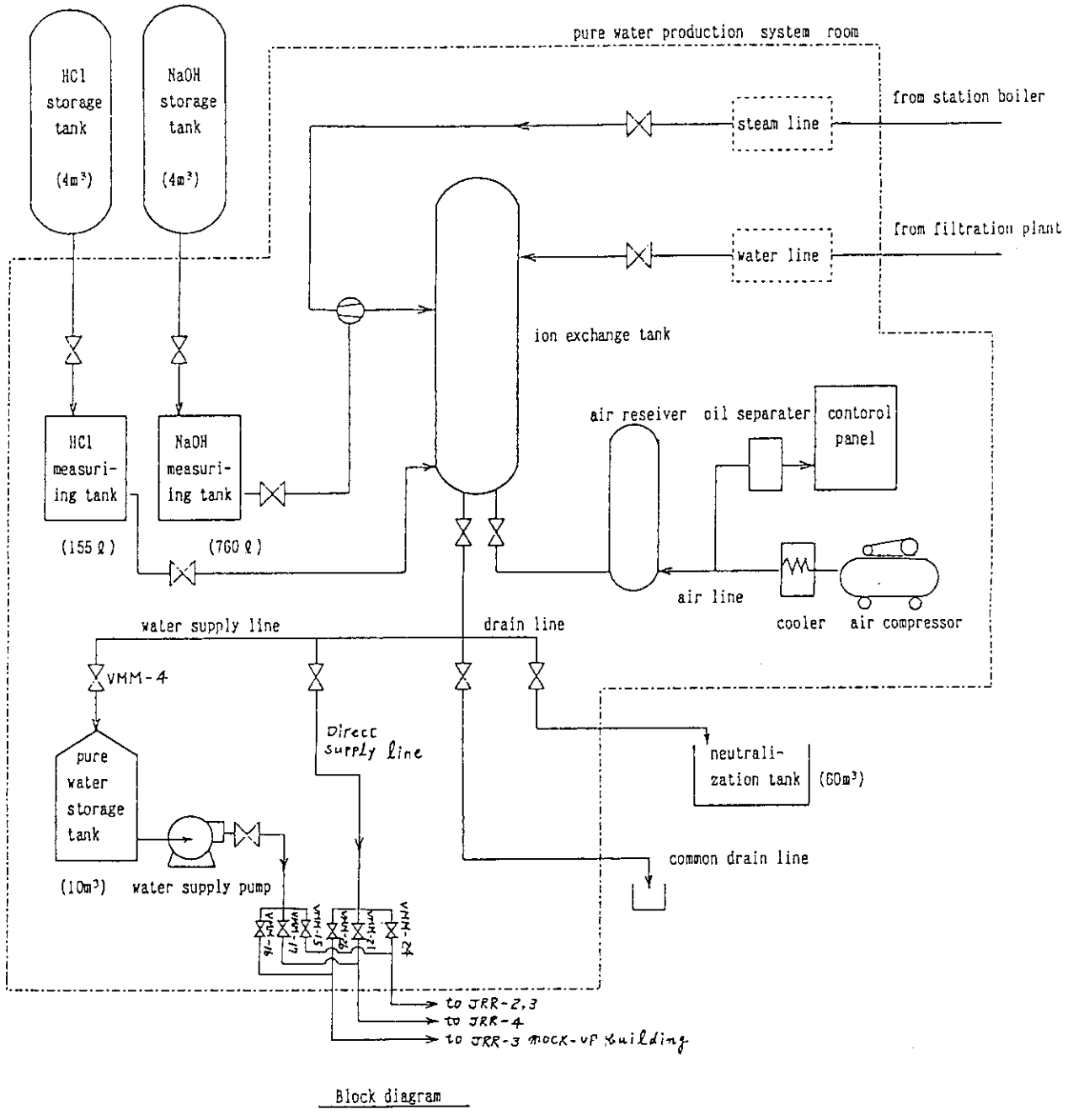


Fig.8 Schematic diagram of pure water production system

4. Routine work of water and gas management

4.1 Helium gas analysis by Gas Chromatography

4.1.1 Principle of gas chromatography [1]

Chromatography is a separating procedure, but can also be used to isolate or confirm components present in complex mixtures. The mixture under investigation is injected into a stream of carrier gas at the head of a column of separating medium. The sample mixture is swept by carrier gas on to the column, where the various components are separated from each other. Some components may be swept through the column without being retarded, some may be completely absorbed by it,whilst other components will undergo partition between the solid or liquid adsorbent and the carrier gas, and be separated from other compounds present during passage through the column. The presence of these sample components in the stream of carrier gas is indicated by the detector.A responseis obtained a thermal conductivity This response is usually converted to an electrical signal for ease of recording. The chromatogram is the plot of detector response against either time or the volume of carrier gas.The peak area is calculated by equation: $A = H \times L$ (A is peak area, H is peak height, L is the peak width at half peak height).

The operation of calibration is undertaken in order to relate the magnitude of the detector response to the concentration of sample components, that usage in the field of qualitative and quantitative analysis. The schematic diagram of gas chromatography is shown in Figure A.

4.1.2 Experiment of helium gas analysis

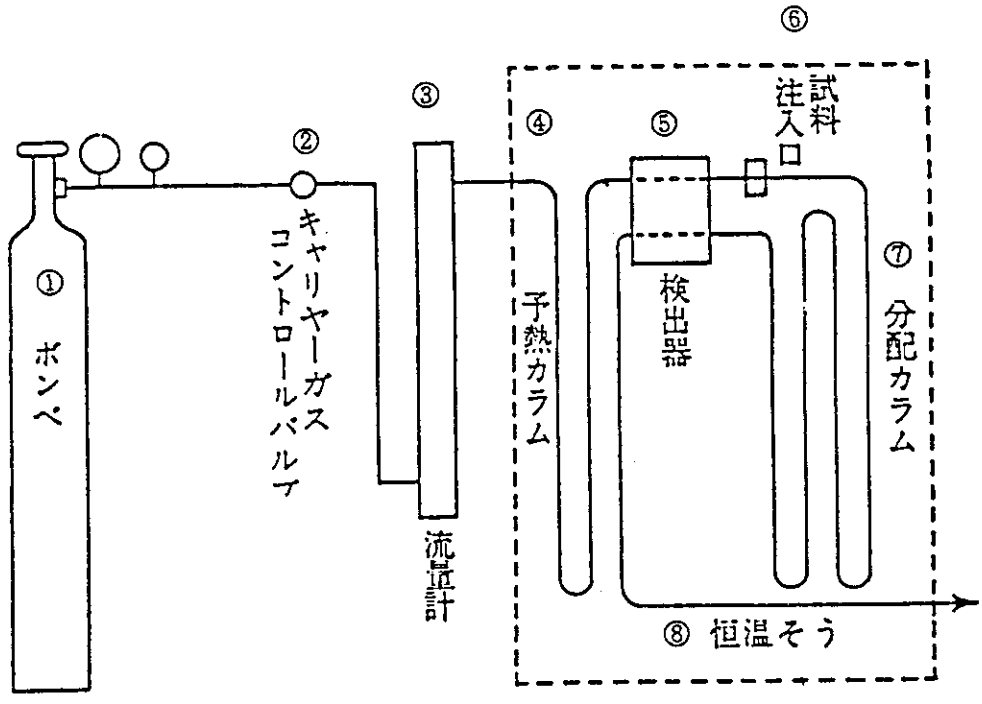
conditions:

Instrument: YANACO Gas Chromatography , model G80
column : 1 m long, diameter: 0.3 cm
column packing : molecular sieve 5 A (calcium aluminium silicate), 30–40 mesh
carrier gas flow rate : He gas 15 ml/min
detector current : 100 mA

procedure:

The calibration curve of standard gas is constructed with standard gas of D_2 ,O_2, N_2 and He balance. The concentration of D_2 ,O_2, and N_2 gas are 1.04,3.94 and 3.94 vol.% respectively. The attenuator is suitable setting for each gas. The standard gas is injected into the column ,then the chromatogram is ploted and shows in Figure B. The retention time of D_2 ,O_2, and N_2 gas are obtained at 1.08, 1.50 and 3.00 minutes respectively.The peak area of each gas is calculated and the calibration curve of standard is ploted and shows in Figure C. The concentration of helium gas in the sample is balanced with D_2 ,O_2, and N_2 concentration in the sample.

This routine work is concerned with helium system in JRR–2 and JRR–3M continuously. The permissible concentration of helium gas must be more than 90 vol.%.



① Carrier gas bomb

② Control valve

③ Flow meter

④ Pre-column

⑤ T.C Detector

⑥ Sample inlet

⑦ Separation column

⑧ Temperature bath

Fig.A Schematic diagram of Gas Chromatography

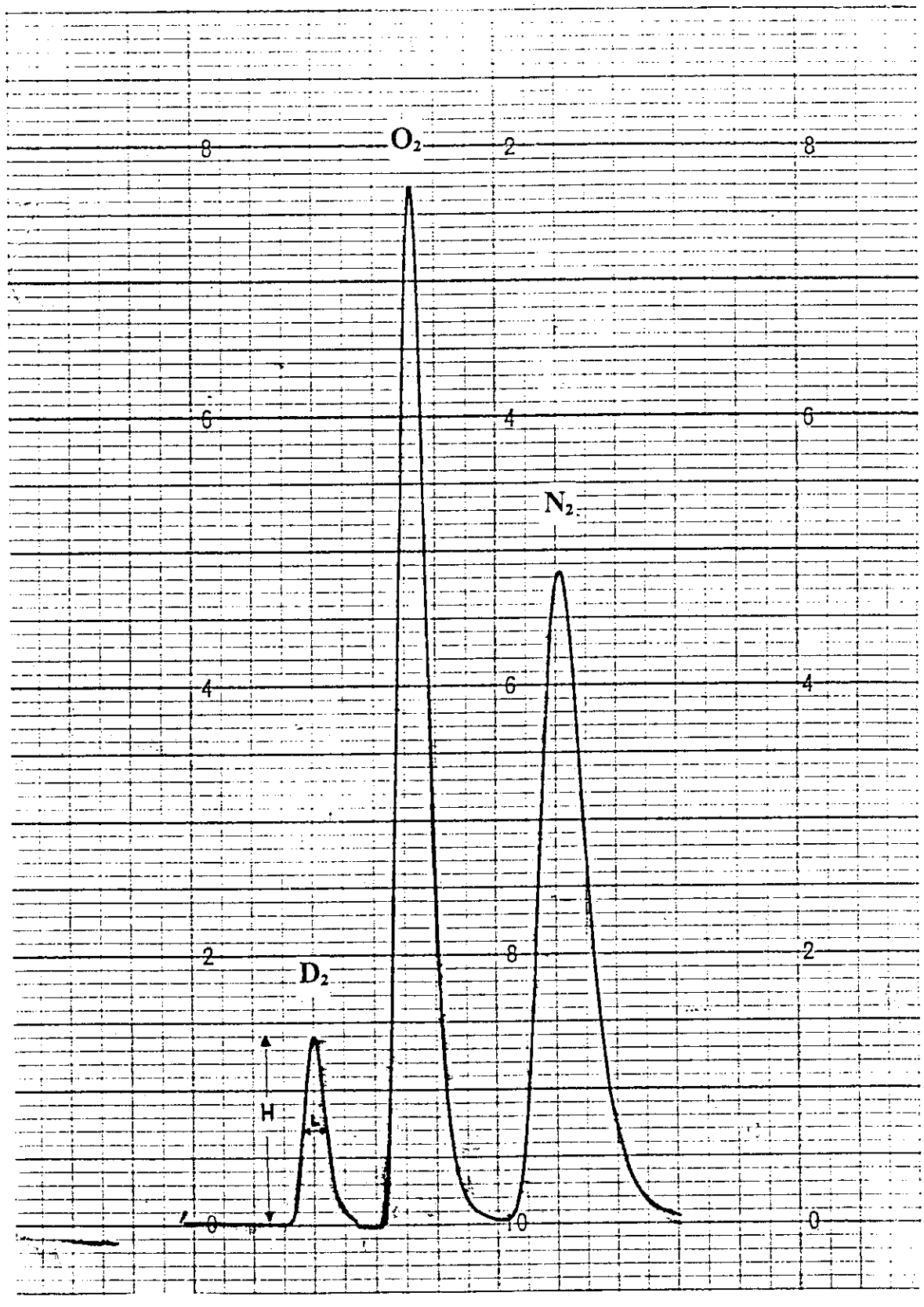


Fig.B The Chromatogram of D_2, O_2, and N_2 gas

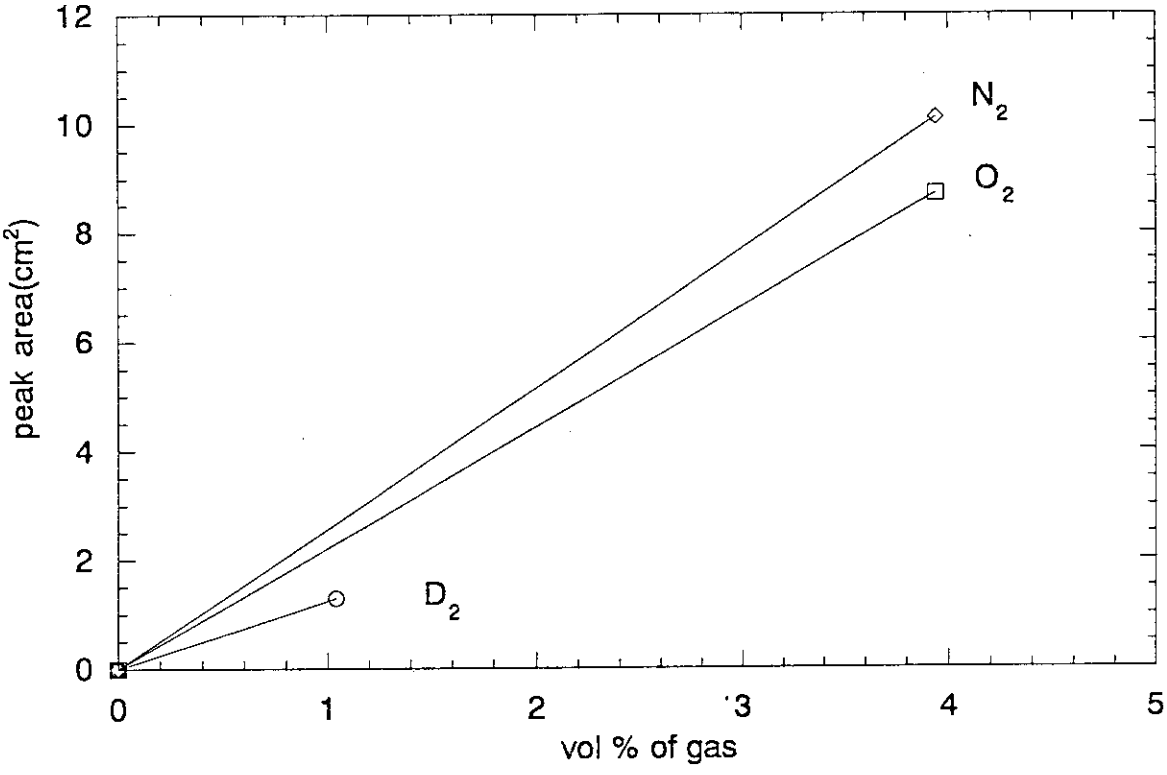


Fig.C Standard curve of D_2, O_2, N_2

4.2 Tritium analysis by Liquid Scintillation Counter

4.2.1 Principle of Liquid Scintillation Counter (LSC) [2]

This method is used for the detection and quantity of radioactivity. This measurement technique is applicable to all forms of nuclear decay emission (alpha–, beta–,particle, electron capture, and gamma ray). All scintillation counting techniques involve converting nuclear energy into emitted photon by the incorporation with a liquid chemical medium.

A simple diagram of the liquid scintillation process is shown in Figure D. In this method, the sample is dissolved in a liquid scintillation cocktail to obtain a homogeneous solution. The process is initiated when the beta particle (electron) transfer its energy to an organic solvent.It results in an excited solvent molecule,then transfers its energy to a dissolved organic scintillator molecule. When the organic scintillator returns to its natural ground state, energy is lost in the form of light and/or heat. The intensity of light produced is directly proportional to the energy of the beta particle and the light is subsequently quantitated by a liquid scintillation counter. Chemical and color Quench are two kinds of interferences that are associated with the liquid scintillation process, due to absorbing energy and photons respectively.

A simple block diagram of LSC is shown in Figure E. This instrument is composed of a counting chamber, two PMT, a coincidence circuit, a summation circuit, a sorting circuit and a computer. The resultant pulse height versus energy spectrum of the sample can be displayed and analyzed. The count rate of the sample can then be determined and reported.

Consider the case of tritium,this is a radioactive isotope of hydrogen with an excess of neutrons in its nucleus. The decay results in the emission of two particles,an electron (beta particle) and a neutrino, that means , tritium is a pure beta emitter which has a half life of 12.35 years. The region of interest for tritium is from 0.0 to 18.6 keV (^{3}H E_{max} = 18.6 keV)

4.2.2 Experiment of tritium analysis by LSC

Instrumentation : Packard Tri–carb Liquid Scintillation Analyzer,
model 1600 TR

The scintillator solution standards : Packard Instrument Company

- Background standard
- .Unquenched Std. Carbon–14 Toluene
- Unquenched Std. Tritiated Toluene
- Quenched Series Tritiated Toluene

These standards contain 4 grams of PPO and 0.25 grams of Dimethyl–POPOP per liter of toluene and the large vials are used for experiments.

A. Self–Normalization and Calibration [3]

The counting efficiency of the solvent and solute system may be reduced because of quenching effect. As a result, the energy spectrum detected from the

radionuclide appears to shift toward lower energies. It is therefore essential to monitor the counting efficiency in each sample by comparison with standards. The two parameters provide for accurate radionuclide efficiency to correct for quenching are namely: the Spectral Index of the sample (SIS) and the Transformed Spectral Index of the External Standard Spectrum (tSIE)

It is performed self-normalization and calibration by inserting a special protocol plug (CNC) and an unquenched carbon-14 standard into the first sample position of a cassette and counting that sample for 10 minutes. After finishing this calibration,the result will show . system normalized .

A series of Quenched Tritium Standard is used to establish a correlation between the counting efficiency in a region of interest and a quench indicating parameter (QIP). The QIP can be SIS which include the tSIE. Efficiency correlation curves determined with these standards will apply to a wide varity of scintillation solutions. This accomplised by comparing the correlation curves of the standards and the scintillator solution containing a known amount of the same radionuclide. A single label ^{3}H Quench Correlation Curve is shown in Figure F.

B. Daily Performance Verification Procedures [3]

Unquenched standard are used for verification of instrument performance. These datas should be kept in a log for the instrument that provides convenient comparisons of data over an extended period of time. The Unquenched Tritium Standard, Unqenched Carbon-14 Standard are used to verify the counting region of interest for efficiency and reproducibility, while the Background Standard is used to verify the instrument backgroud, which could be affected by radioactivity contamination, changes in environmental radiation, and electrical noise entering the counting channels.

(b/1) QIP/^{14}C Efficiency check :

It is performed by selecting and inserting correct protocol plug into a cassette, loading an unquenched ^{14}C Standard and counting for 10 minutes. The range of energy has been set at 0.0-156 keV in region A and 4.0-156 keV in region B. The three repeat counts had repeated, and the result of the efficiency is calculated by equation:

$$\% \text{ Eff.} = \frac{\text{CPM of Region A}}{\text{DPM of } ^{14}C \text{ Standard}} \times 100$$

The minimum acceptable efficiency for carbon-14 is 95 % for large vials and 94 % for small vials. The result of checking is within the defined value, that is 97 %.

(b/2) ^{3}H Efficiency check

The ^{3}H Efficiency check can be treated in a similar manner to that of ^{14}C efficiency check, but different energy region has been set.The range of energy are 0.0-18.6 keV in region A and 2.0-18.6 keV in region B. An unquenched ^{3}H standard was counted. The minimum acceptable efficiency for ^{3}H is 60 % for large vials and 58 % for small vials. This result check is acceptable value,that is 67 %.

If the efficiency results for carbon-14 and tritium are not within the defined values, then performed a system Self-Normalization and Calibration and it must be repeated these tests.

(b/3) Background Check

Instrument background may vary due to environmental conditions. The count rate of background should not exceed three times of normal background level (20 cpm). Three of energy regions has been set ; 0.0-18.6 keV for region A, 0.0-156 keV for region B and 0.0-2000 keV for region C. An unquenched background standard is counted for 10 minutes. The result is in normal background level,that is 17 cpm.

C. Measurement of Tritium Concentration by LSC

Standard : Series of quenched tritium standard

Sample : Thermal shield water in JRR-2

Liquid scintillation cocktail used : xylene based : AQUASOL-2, DUPONT Company

This cocktail is composed of primary solute (PPO or 2,5- diphenyl oxazole),secondary solute (POPOP or 1,4-di-{2-(5-phenyloxazole)}-benzene) with xylene as solvent.

Procedure:

A 7 ml of liquid scintillation cocktail was pipetted into 20 ml of vial, then added 1 ml of sample or 1 ml of pure water as blank,followed by shaking until solution was clear. The samples were counted by LSC for one minute after laying the samples for one hour. The activity of tritium in Bq/ml (Cn) is calculated by equation :

$$Cn\ (Bq/ml) = \frac{Nn}{60 \times \eta \times V}$$

Nn = net counts of ^3H

η = efficiency

V = volume of sample (ml)

while $$\eta = \frac{(\text{STD source (cpm)} - \text{Background (cpm)}) \times 100}{\beta \text{ ray STD source (dpm)}}$$

The detection limit; Ni(cpm) and Ci(Bq/ml) are calculated by equation :

$$Ni(cpm) = K/2 \{ K/Ts + \sqrt{(K/Ts)^2 + 4Nb(1/Ts + 1/Tb)} \}$$

K = correlation factor = 3

Ts, Tb = counting time of sample and background respectively

Nb = count rate of background or blank

while $$Ci(Bq/ml) = \frac{Ni(cpm)}{60 \times \eta \times V}$$

Results :

The tritium activity in thermal shield water of JRR-2 is shown in the table below.

sample	total count rate (cpm)	net count rate (cpm)	^3H activity (dpm)	% η	^3H activity (Bq/ml)
blank	13.7				
sample-1	15,282	15,268	31,964	47.81	532
sample-2	15,210	15,196	31,800	47.83	529
sample-3	15,266	15,252	31,915	47.83	531
means	15,252	15,239	31,893	47.82	531
% RSD					0.29
detection limit (Bq/ml)					0.1895

This routine work is carried out in pure water cooling and secondary cooling water in JRR-2,JRR-3M and JRR-4 and in heavy water system in JRR-2 and JRR-3M. This tritium radionuclide exists in these systems because of nuclear reaction of beryllium which is used as reflector in reactor core of JRR-3M, and nuclear reaction of deuterium in heavy water system that may affect in primary and secondary cooling system.

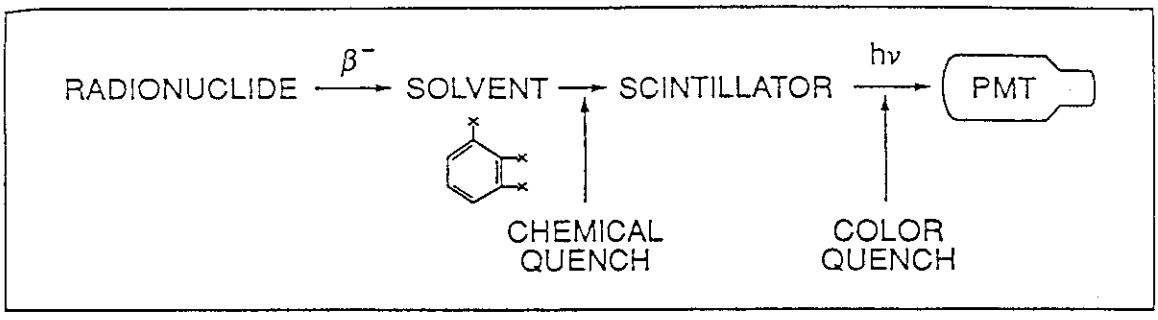


Fig.D Basic Liquid Scintillation Process.

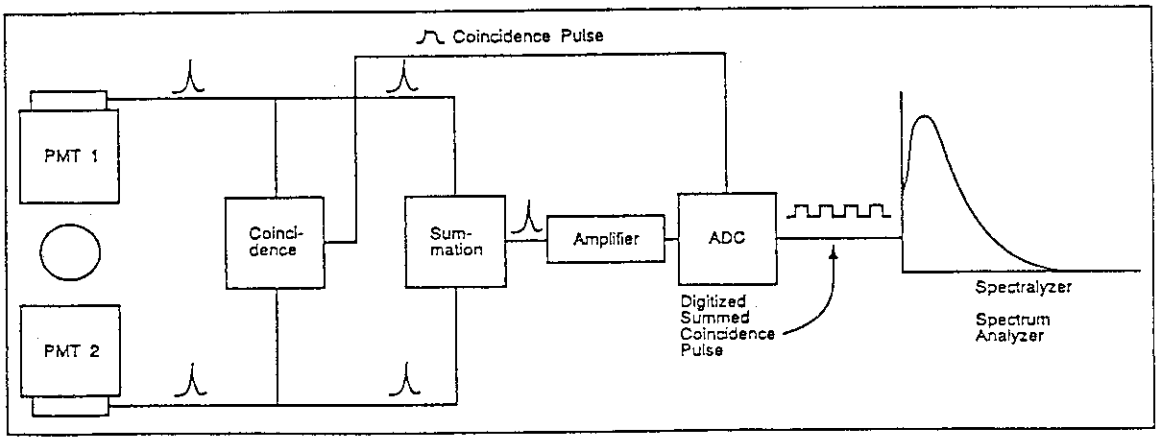
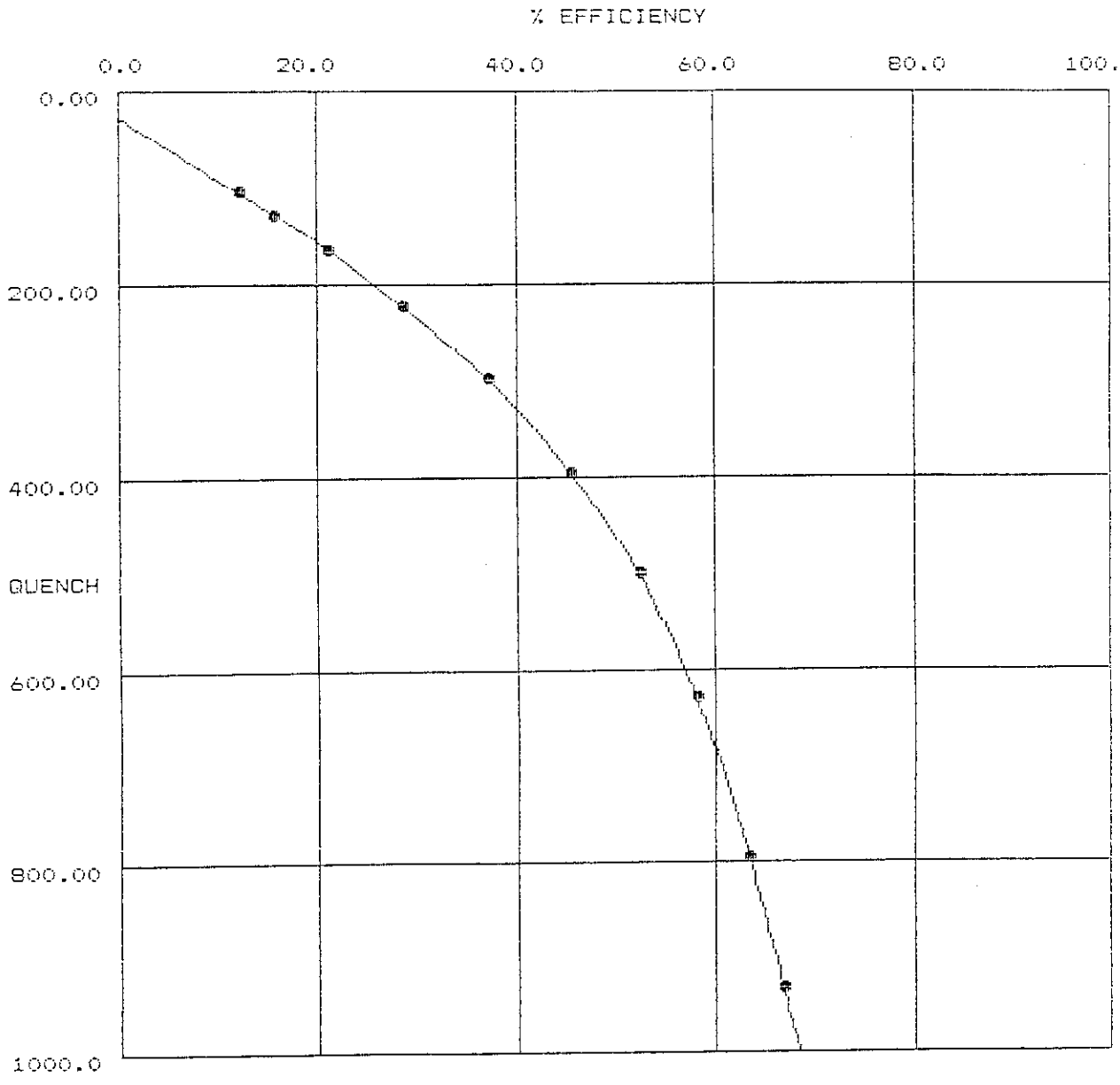


Fig.E Simplified Block Diagram of a Liquid Scintillation Analyzer.



QUENCH	ELA	QUENCH	ELA	QUENCH	ELA
104.97	12.35	128.19	15.98	162.63	21.41
223.78	28.87	297.19	37.42	395.25	45.59
500.96	52.63	627.93	58.27	795.35	63.73
932.40	67.07				

Fig.F A single label ^{3}H Quench Correlation Curve

4.3 Gross beta counting by Geiger–Müller Counters

4.3.1 Principle of GM Counters[2,4]

The detection technique is one of Gas Ionization Detection. This method is based on the ionizing effect of radioactive radiation. When radioactive radiation spreads through a gaseous medium, it causes part of the gas molecules to become ionized. These gas ionization creates a positive ion and an electron.If a suitable electric field is applied, the ions and electrons can be collected. As the voltage is increased to the GM region,the number of ions produced is independent of the type and energy of incident radiation.

Under the effect of the electric field between the electrodes, the electrons produced move towards to the anode wire and positive ions towards the cathode. The current in the counter is passed through an external resistance and the voltage pulse is amplified and recorded with a suitable device.Counting devices record only pulses whose amplitude exceeds a certain threshold value.A filling gas of 90% argon and 10% methane in GM tube is used because the low energy is required by argon to form ion-pairs. The beta radiation with the lowest possible energy of 0.02 MeV can penetrate through the mica windows of GM counters.

4.3.2 Experimental of β activity

The experiments were carried out in characteristics determining the quality of a GM counters. They are cmp-voltage characteristic,efficiency and resolving time.Also the beta activity was measured in JRR-2 thermal shield water during reactor shut down operation

4.3.2.1 Quality determination of GM counters

A. The cpm-voltage characteristic of a GM counters

The number of recorded pulses per unit time (cpm) is a function of the voltage applied to the electrodes of the counter. In the plateau region, the counting rate grows moderately with increasing potential. Good quality GM counters have a plateau lenght of at least 150 V and a gredient or plateau slope less than 5% per 100 V. The working voltage at a shorter plateau is selected in the middle of the plateau lenght,and for a longer one ,in the first third.

Procedure:

The ^{238}U standard source of 448 dps (26,880 dpm) was counted for one minute with increasing the potential. These responses are collected by Aloka model JDC-R74-8387 Universal Scaler. The cpm-voltage characteristic of GM counters is obtained by plotting the counting rate against the voltage and the result shows in Figure G. The quality of this GM counters is still good operation because the result of plateau slope is less than 5%,that is 2.2% per 100V.

B. Resolving times

It is given by dead time and should be in the range of 150-400 μSec. The two methods were investigated for measurement of resolving time.One had been seen from

oscillographic recording of Sr-90 paired-source that shows in Figure H. The resolving time is given at 200 μSec. The another one is the paired-source method.

Procedure:

The paired-source method was performed by using two pairs of background and 0.5 μCi Sr-90 paired-source and working voltage was selected at 1100 V.The averange activity (n_b) of background paired-source was counted for 1 minute, then counting one pair of background-Sr-90 source (n_1). Alternating the position of the pair of background-Sr-90 source and counting the activity (n_2), then following by counting the paired-source of Sr-90 ($n_{1,2}$). The resovling time was calculated by equation :

$$\tau = n_1 + n_2 - n_{1,2} - n_b / (n_{1,2})^2 - (n_1)^2 - (n_2)^2$$

Results:

	counting rate(cpm)				cps
	1	2	3	average	
n_b	28	32	23	28	0.46
n_1	17073	16969	17306	17116	285
n_2	12799	12829	12808	12812	214
$n_{1,2}$	27694	27776	27738	27736	462
τ	415 μSec				

Although this result is not given in the range of 150-400 μSec, the good quality of this GM tube is acceptable with another method.

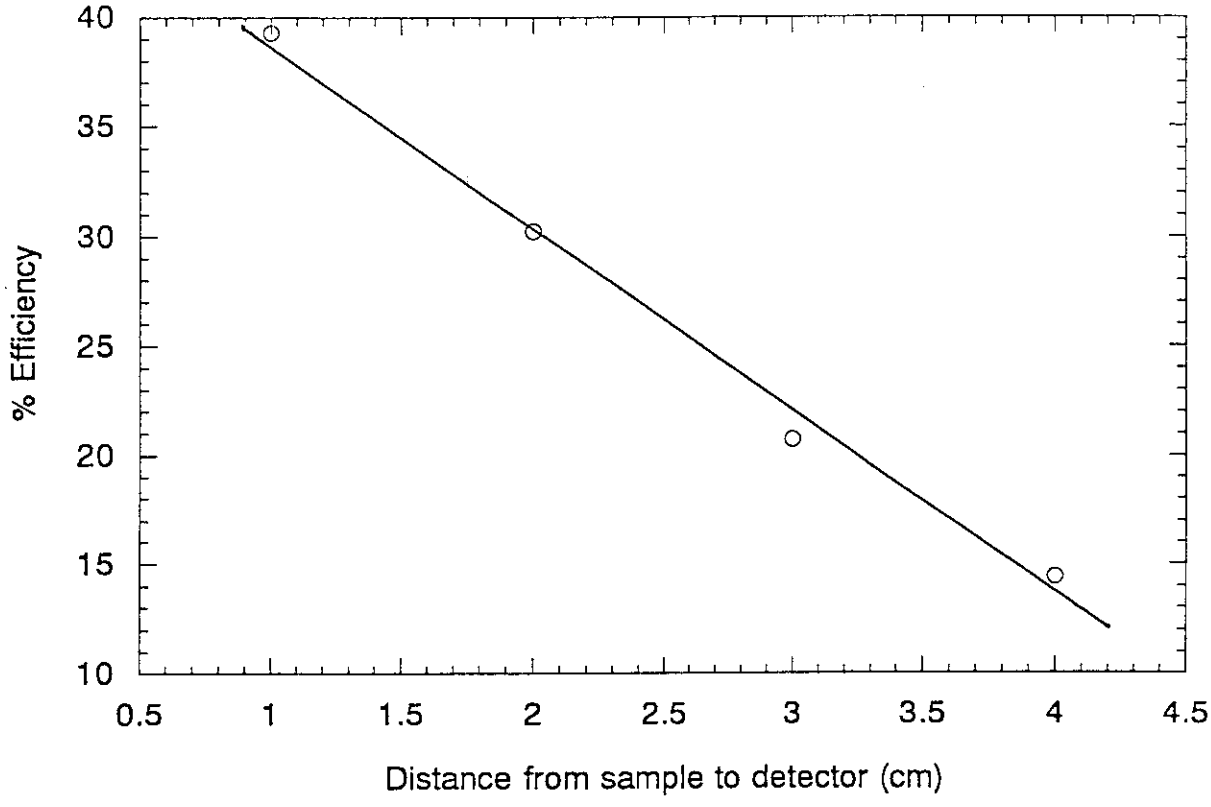
C. The efficiency of GM counters (η)

This is defined as the equation :

$$\eta = \frac{(\beta\text{-ray STD source,cpm})-\text{b.g.(cpm)}}{(\beta\text{-ray STD source,dpm})} \times 100$$

The efficiency is reverse proportional to the distance of sample to detector. The ^{238}U standard source of 448 dps (26,880 dpm) was counted for 1 minute in the distance range of 1 to 4 cm. The result is obtained as below.

Distance (cm)	Efficiency
1	39.30
2	30.25
3	20.71
4	14.40



4.3.2.2 Beta activity measurement

The JRR-2 thermal shield water was carried out as sampler during reactor shut down. One millilitre of sample was pipetted into stainless steel panchet, dried the sample with IR-lamp,following by measuring the sample. The beta activity is obtained lower than detection limit,that is 1.26 Bq/ml. The determination of detection limit by GM counter was treated in the same equation of that liquid scintillation counter.

This measurement is concerned not only with the coolant of reactor, but also with the purification system of each reactor. The inlet and outlet of this system has been compared the results of beta activity in order to investigate the quality of the used resin. Also in the spent fuel pool, the water has been analyzed to get data of beta activity.

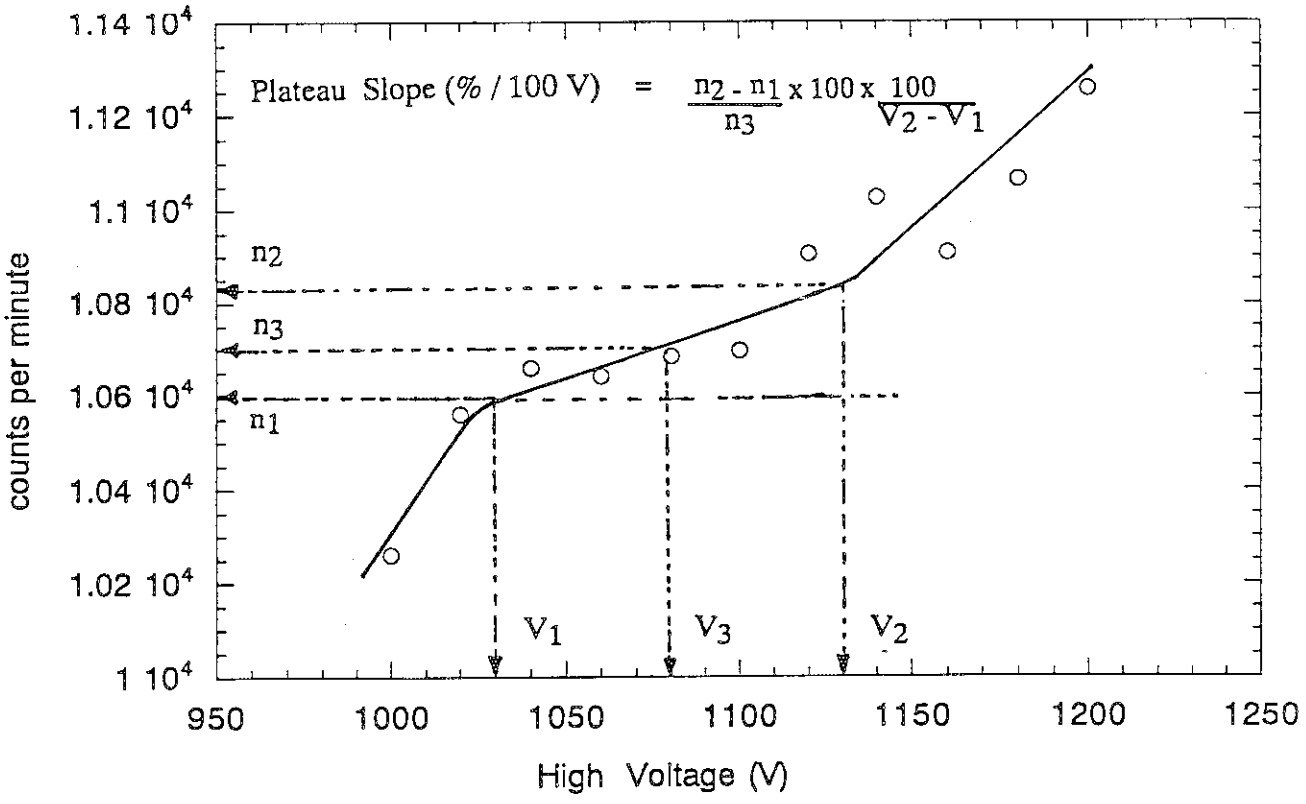


Fig.G The cpm – voltage characteristic of GM Counter

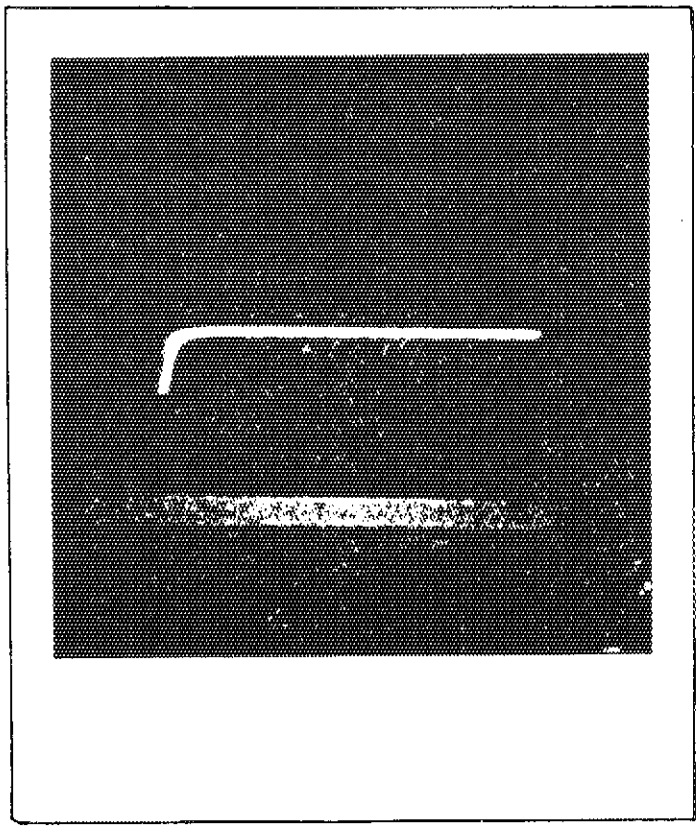


Fig.H Oscillographic recording of resolving time

4.4 Heavy water analysis by Infrared Spectrometry

4.4.1 Principle of Infrared Spectrometry [5,6]

Infrared (IR) spectrometry deals with the interaction of infrared radiation with matter. The IR region is considered to line in the wavelength range from 770 nm to 1,000 μm ; the corresponding wave number range is from 12,900 to 10 cm^{-1}.This IR region is subdivided into three subregions. The near -IR region extends from 12,900 to 4,000 cm^{-1}, the mid-IR region from 4,000 to 200 cm^{-1}, and the far-IR region from 200 to 10 cm^{-1} .

Beer's law provides the basis for quantitative IR methods. A general absorption law is expressed in equation (1), which is a combination of Beer's and Lambert's law.

$$I = I_0\, 10^{-kcd} \quad \text{.....(1)}$$

or $$kdc = \log_{10} I_0/I \quad \text{.....(2)}$$

and $$T = I/I_0 \quad \text{.....(3)}$$

or $$A = \log_{10} 1/T \quad \text{.....(4)}$$

that is $$kdc = A = \log_{10} 1/T \quad \text{.....(5)}$$

I and I_0 are the intensities of transmitted and incident radiation respectively, k is the extinction coefficient (absorptivity), c is the concentration of the substance in g/l and d is the thickness of the sample in cm., T is transmittance which is correlated with the concentration of substance.

Dispersive instruments with a monochromator are used in the mid-IR region for spectral scanning and quantitative analysis.The sample cell is placed in front of the monochromator to minimize the effects of infrared emission and stray radiation from the cell compartment. Optical null systems read out directly in transmittance on recorder. Optical diagram of IR spectrophotometer is shown in Figure I.

4.4.2 Heavy water analytical method [7]

The H_2O, D_2O and HDO molecules have characteristic and differing infrared radiation absorption properties which can be used for analytical purposes. An absorption band at 3,400 cm^{-1}(mid IR) of HDO was detected. When pure H_2O and D_2O are mixed, D-H exchange takes place according to the equilibrium reaction :

$$H_2O + D_2O \Leftrightarrow 2HDO$$

In Figure J. shows that, in the high heavy water concentration range more than 50 norminal % D_2O, it is chiefly present in the D_2O species more than in the HDO species. The percentage of transmittance increases at high concentration of D_2O because of decreasing of HDO species.

The high grade D_2O can be diluted with natural water to bring the standards within a concentration range analyzable.The transmission peak method is based on the

over 98 mol. % D_2O concentration range was done that covered the 4,000 to 3,200 cm^{-1}.

Equipment :

A JASCO Model A-102 , Diffraction Grating Infrared Spectrophotometer was used in experiment, and shows inFigure K. The sealed,fixed-thickness sample cell with sapphire windows and a reference cell; KRS-6 with 63 %T were employed. TlBr and TlI are as window material of this reference cell. Nichrome wire and thermocouple were installed as light source and detector respectively. To measure the transmittance,the sample solution was injected into the cavity of sealed sample cell by means of a small syringe and vaccuum pump, which is shown in FigureL.

Procedure :

The instrumentation was warmed up about 10 minutes. An adjusting of 0%T was done by closing the sample beam side to prevent the transmission of light from light source. To permit the light pass through the sample beam side 100%T by adjusting a " 100%T" knob,then followed by closing the sample beam and reference beam to detect at about 50%T with adjusting the "balance" knob. The IR energy was calibrated with polystylene film and is shown in FigureM.This spectral scanning was carried from 4,000 to 600 cm^{-1}. By pressing the "reverse" knob, a slit control motor was changed to begin at 4,000 cm^{-1},then measured the transmittance of reference cell (KRS-6) at sample beam side to record the result of 63 %T at 3,400 cm^{-1}.

The thickness of sample cell should be measured often for quantitative work since erosion of the window materials can cause thickness to change. It was determined by an interference fringe method. The transmittance spectrum of an empty sample cell was recorded against air in the reference beam, which covered the energy range from 4,000 to 2,800 cm^{-1}. The result is shown in FigureN. If n interference maxima or peak number are observed in a wavenumber region from $\bar{\nu}_1$ to $\bar{\nu}_2$, the cell thickness b can be calculate from

$$b = \frac{n\{1/(\bar{\nu}_1 - \bar{\nu}_2)\}}{2}$$

The result is note that 9 peak numbers are found in the region 3,760 to 3,200 cm^{-1}. The cell pathlength or thickness is thus 9/2 (1/560) or 0.08 mm.

Quantitative application of IR spectrometry are based on Beer's law. The calibration curve of standard had been done. A series of heavy water samples covering the 98.3 to 99.8 Mol% D_2O range were prepared from 99.87 wt% or 99.85 Mol% D_2O and natural water. These pure heavy water and natural water were weighed and calculated to wt% D_2O and converted into Mol% D_2O by equation :

$$\text{Mol\%} = \frac{924.625}{\frac{1027.91-1.0328}{\text{wt\%}}}$$

The HDO spectrum and calibration curve of heavy water is shown in FigureP.

The heavy water used as primary coolant in JRR-2 and as moderator and reflector in JRR-3M. The quality control of high purity of heavy water has been done for routine work continuously.In addition of installing the heavy water monitor in the analytical lines of JRR-2 and JRR-3M, the Anacon Infrared Analyzer,model 206 was designed for monitoring of stream constituents in liquid and gas streams. Water absorption bands in the near-IR region are detected at 1.4 and 1.93 microns.

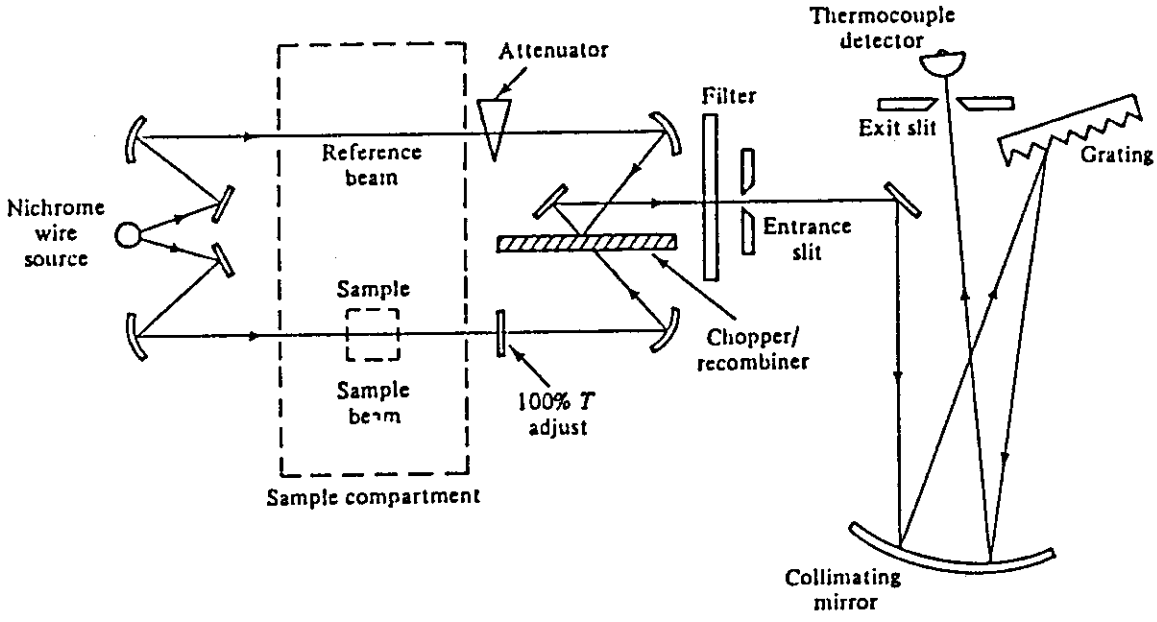


Fig.I Optical diagram of Beckman Acculab infrared spectro photometer. This system is of the optical null type. Radiation from the nichrome wire source is split into two beams and sent through the sample and the reference cells. The reference beam attenuator is controlled so that the reference beam intensity matches that of the sample beam. The tow beams are recombined and alternately pass through the monochro mator to a thermocouple detector. The recorder pen is mechanically linked to the reference beam attenuator.(Courtesy of Beckman Instruments, Inc.)

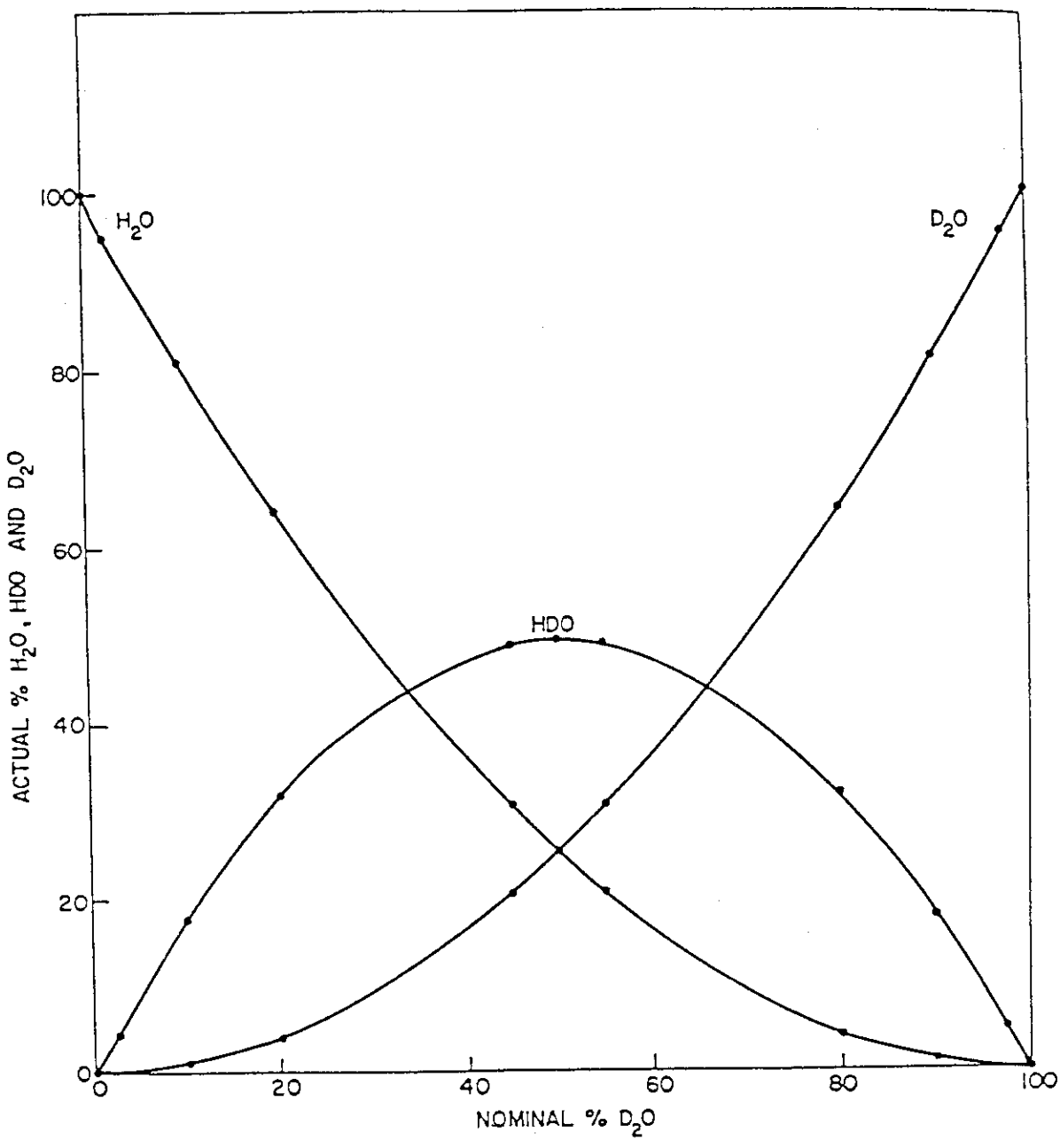


Fig.J Concentrations of H_2O, HDO and D_2O as a function of nominal D_2O concentration

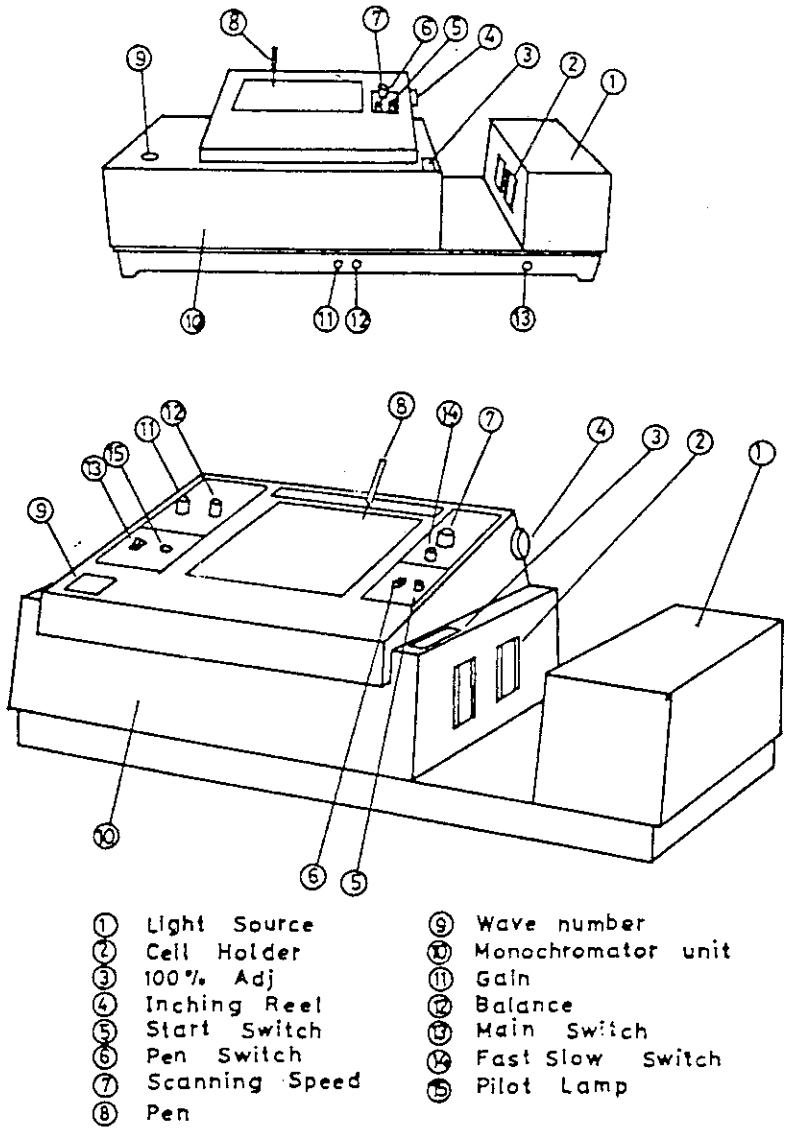


Fig.K Shows the functions of Diffraction Grating Infrared Spectrophotometer

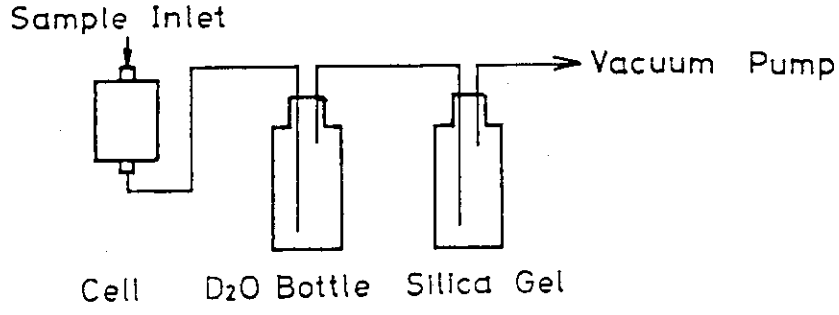


Fig.L The preparation of sample film in the sealed-sample cell

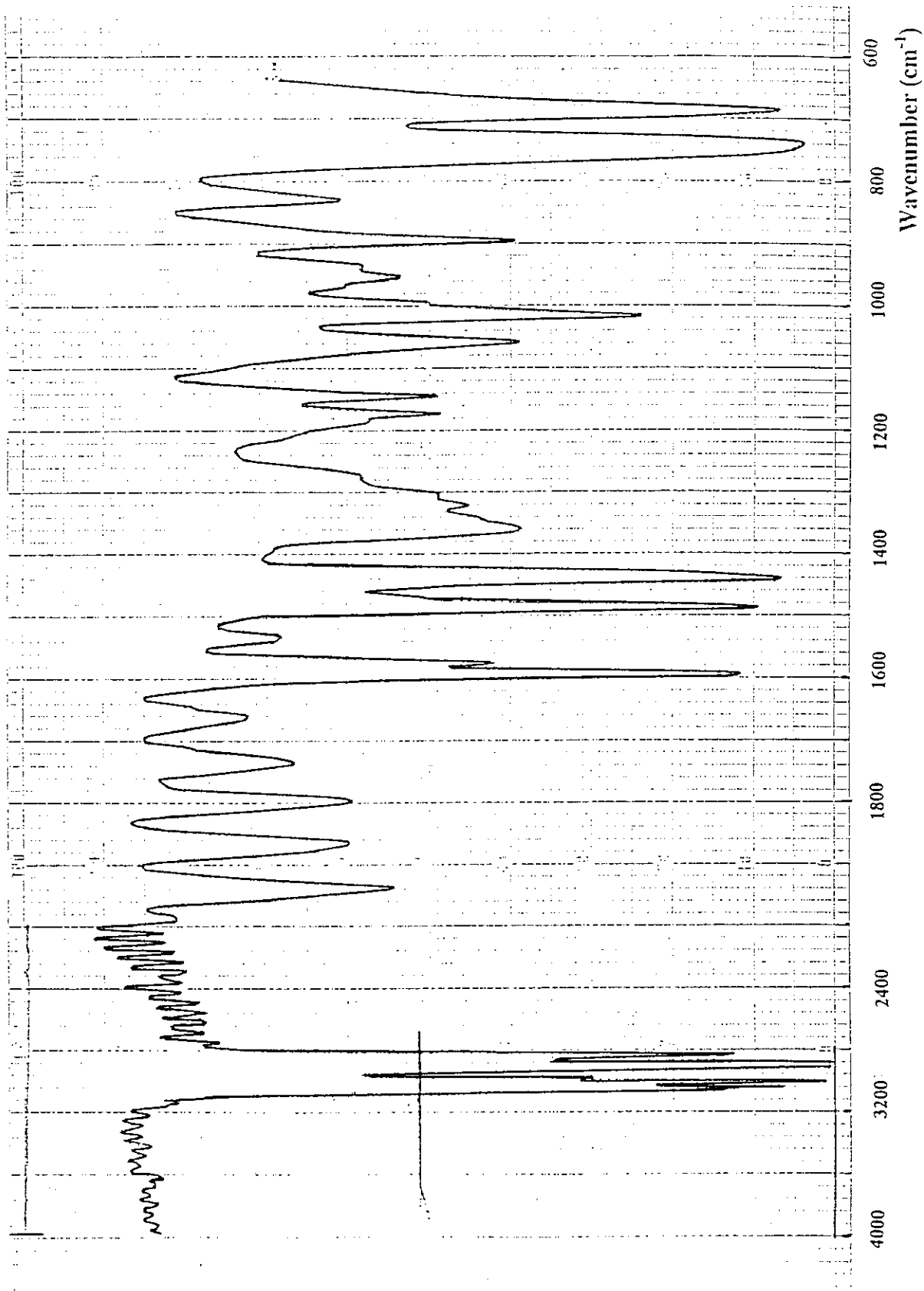


Fig.M The spectra of calibrated energy with polystylene film

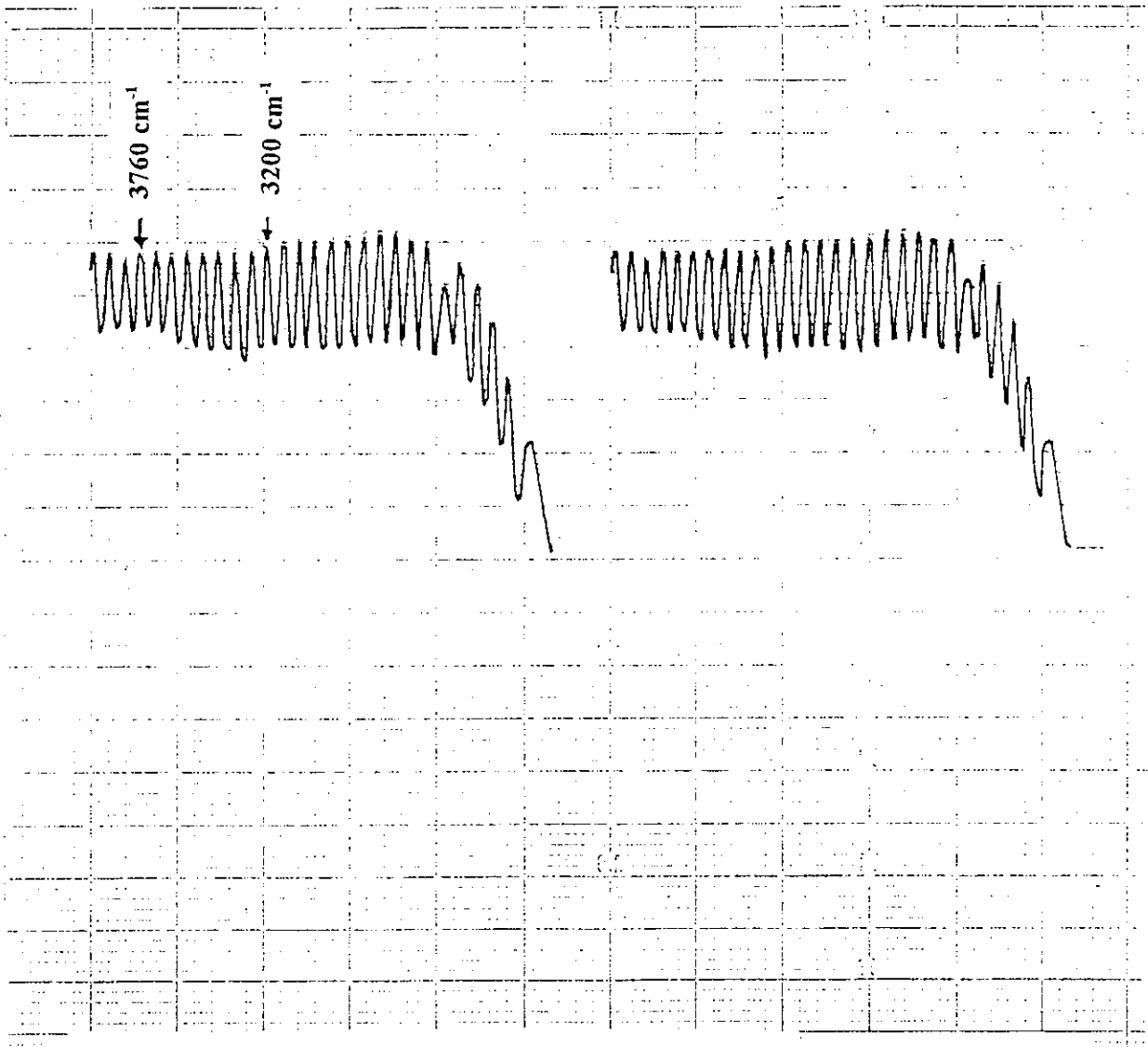


Fig.N Determination of cell thickness by Interference frige method

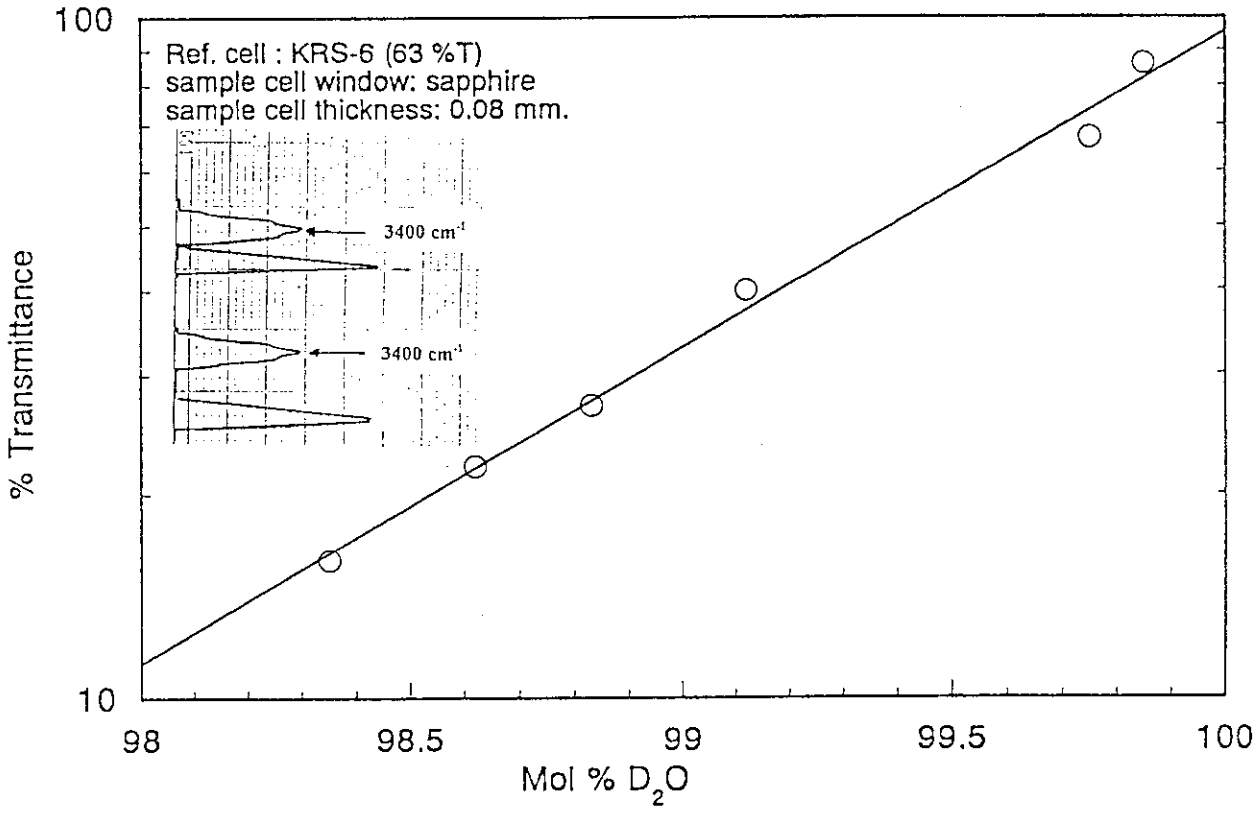


Fig.P Calibration curve of heavy water and Spectrum of HDO at 3400 cm^{-1}

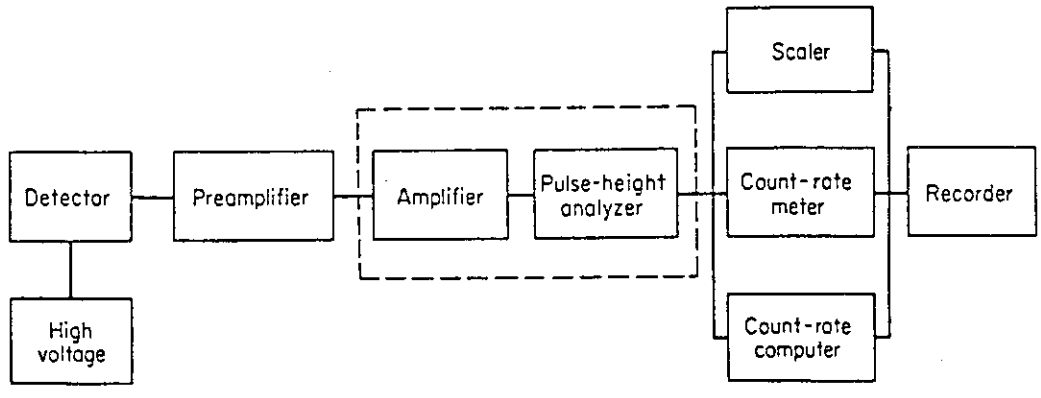
4.5 Gamma-ray measurement by γ -ray Spectrometer

4.5.1 Principle of Υ-ray Spectrometer [2,4]

Gamma-rays interact with matter in three processes : photoelectric effect, compton scattering and pair production. In practice, other effects such as annihilation,escape peak,backscattering,etc., contribute to pulse-height spectrum. Escape peaks occur only if the gamma energy exceeds about 1.2 MeV. Annihilation peaks are found only if the gamma transition is preceded by a β^+-decay or $E_\gamma \geq 1.2$ MeV,then the simultaneous emission of two 0.511 MeV gamma quanta occur.

For identification of an unknown gamma spectrum, the spectrometer is calibrated with the aid of a radionuclide of known gamma radiation energy value. The data in the calibration curve refer to the relationship between the energy of photopeak and the discriminator voltage in a multi-channel analyzer. For recording the half-life of decay of individual photopeaks according to their energy can identify the radionuclide exactly.

For this experiment, the gamma-ray spectra are collected by coaxial germanium detector which is semiconductor detector. A detector produces pulses proportional to the energy of the radiation source. After amplification,these pulses are sorted with the aid of pulse-height analyzer (MCA) in which pulse distribution is done through a differential discriminator. With the help of count-rate computer, we can obtain the radiation intensity which is recorded in recorder. The block diagram of a multi-channel pulse-height analyzer is shown as below.



4.5.2 Experiment of Υ-ray measurement

This experiments were carried out in energy calibration , determination of half-life and efficiency calibration of coaxial germanium detector (ϕ 3 inches) with Canberra model Series 80 Multichannel Analyzer. The gamma activity was measured in the primary cooling water of JRR-3M which was sampling at 2:00 p.m. on Nov. 7,1994.

4.5.2.1 Energy Calibration

A radionuclide of known gamma radiation energy value was calibrated with standard reference source no. 808957,Amersham of 100 ml. The curve represents the graphical correlation between γ-energy and channel number which was memorized in the computer. This curve was used to identify an unknown gamma spectrum in samples.

4.5.2.2 Efficiency Calibration

These calibration curves were performed by using standard reference source no. 808957, Amersham of 100 ml with the distance to detector between 2.5 to 10 cm.and using standard reference code QCD-1 (ring source type) with the distance of between 2 to 15 cm. The efficiency (η) is defined as the equation :

$$\eta = \frac{cps}{dps}$$

The correlation curve between gamma energy and efficiency of standard reference source no. 808957 and code QCD-1 were plotted in logarithmic coordinates as in Figure Q/1 and R/1 respectively. And the curves represent the graphical correlation between efficiency and distance of each standard source,are shown in Figure Q/2, Q/3 and R/2. These relative efficiency calibration curves are used for most of the gamma spectra in the energy range of between 50 to 2000 keV to determine the gamma activity in the samples.

4.5.2.3 Gamma activity measurement in primary cooling water of JRR-3M

Radiochemical separation method is necessary to determine the low activity of radionuclides. I-131, Tc-99m, Cr-51 in anion form can absorb on anion paper, while Na-24, Mn-54, Co-60,etc., absorb on cation paper.

Procedure:

The separation method of radionuclides was performed by using the cation-paper (NF-1,Na^+ form) and anion-paper (NF-3,Cl^- form) of Sumitomo Chemical Analyze Company. These " Expaper" of NF-1 and NF-3 were washed with 100 ml of pure water, then following with 200 ml of 2M HCl and 2M NaOH respectively,finally washing with pure water to maintain the pH of filtrate at 7.

The washed anion-paper was placed at first in the suction filter, then the cation paper and 0.45 μm of microfilter paper were followed on the anion paper. The primary cooling water of JRR-3M of volume100 ml was passed through this suction filter of flow rate about 10 ml/min. These cation-, anion-, filter paper were placed individualy in the plastic bag.All of these papers and filtrate after ion-exchanger were determined at the distance of 5 cm. to the detector. The efficiency curve of standard reference code QCD-1 was used for calculation of gamma activity in the sample.

Results:

The detected gamma spectra of cation, anion, microfilter paper and filtrate were obtained and shown in **Figure** S/1, S/2, S/3 and S/4 respectively. K-40 was background radionuclide which detected in such samples. Almost of Na-24 spectra (1368 keV,double escape peak of 1732 keV) and annihilation peak of 511 keV were found on the cation paper. A few activity of Na-24 (1368 keV) and almost activity of Tc-99m (140.5 keV) which is the daughter of impurity Mo-99 in aluminium cladding were detected on the anion paper. A few activity of Mn-54 (834.7 keV) and Na-24 (1368 keV) were contaminated on filter-paper.The Ar-41 spectrum (1293.5 keV) was found in filtrate because of non-absorption in all of papers. The gamma activity (A) was calculated by equation :

$$A\ (Bq/ml) = \frac{P}{t \times I \times \eta \times V}$$

and correlated with decay time by equation :

$$A_0\ (Bq/ml) = \frac{A}{e^{-\lambda t}}$$

which P = peak area (counts)
t = measuring time (sec)
I = gamma intensity (≤ 1)
V = volume of sample (ml)
λ = decay constance = $0.693/T_{1/2}$
t = decay time (sec)

The results are summarized in table as below.

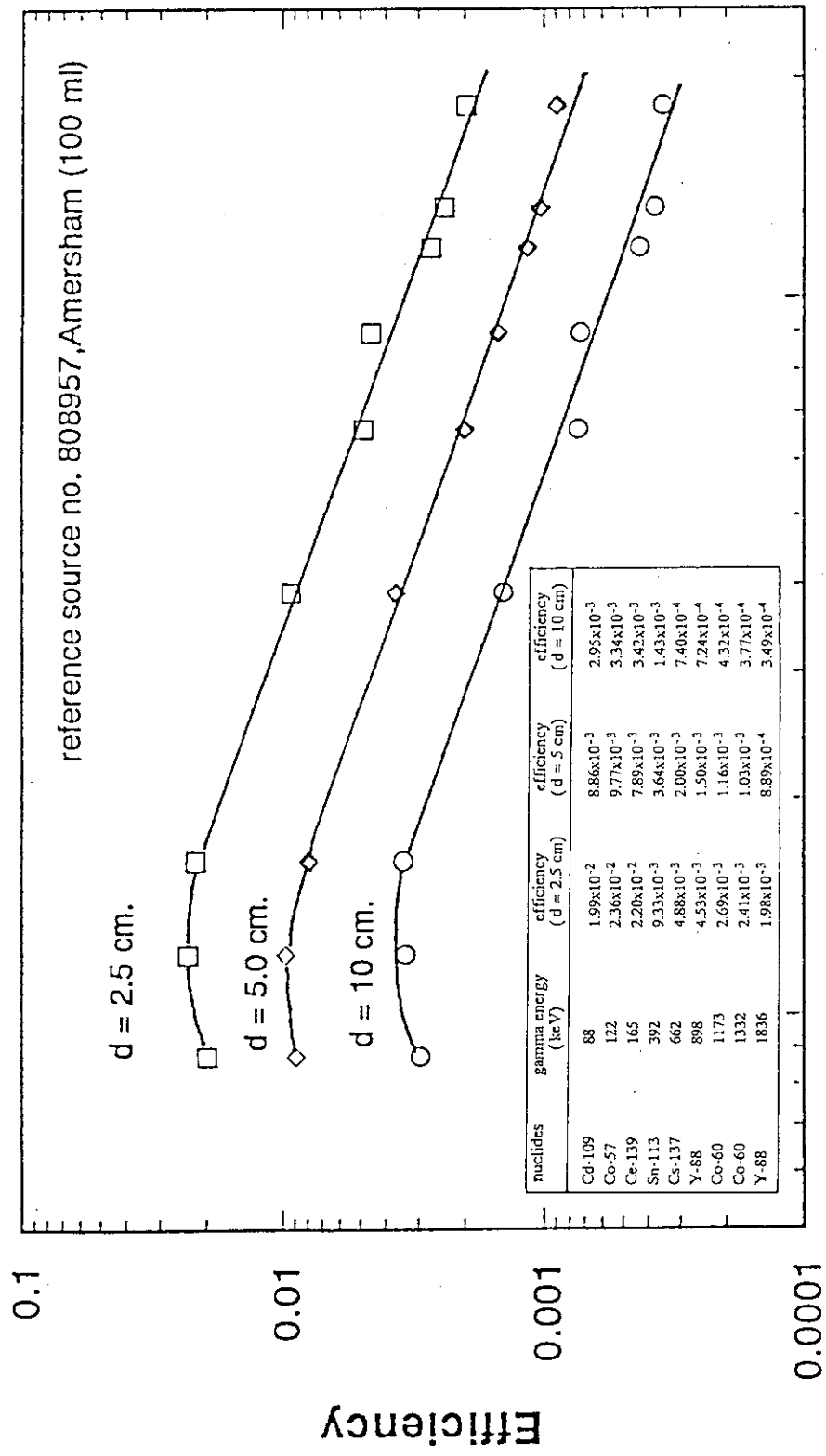
samples	identificated radionuclides	γ-activity (Bq/ml)
cation-paper	Na-24 (1368 keV)	503
anion-paper	Tc-99m (140 keV)	92
	Na-24	few
filter-paper	Mn-54, Na-24	few
filtrate	Ar-41	

Some radionuclides in the coolant samples of volume 100 ml can be determined the gamma activity directly with using the efficiency calibration curve of standard reference source no. 808957 (100 ml). This routine work was concerned with the primary heavy water coolant of JRR-2, primary water coolant, heavy water system and helium gas system of JRR-3M. Ar-41 radionuclide in the gaseous state can contribute in all of system in reactor. It may be detected W-187, Al-28, Na-24, Tc-99m, Mg-27, Cr-51, Mn-54 etc.,in primary water and heavy water system.

4.5.2.4 Determination of Half-Life

The half-life can be applied to identify the radionuclides exactly according to their energy. It is determined from the decay curve which represents the graphical correlation between activity and time, and is plotted in semilogarithmic coordinates. The half-life can be obtained from a straight line of decay curve in the case of a pure radionuclide sample.

The examples of determination of half-life was done by counting gamma spectrum related decay time. The radionuclides γ-energy of 140 and 1368 keV in anion-paper and cation-paper respectively were investigated. The result of decay curve is shown in **Figure** T ,that the radionuclides are proved as Tc-99m (140 keV with half-life of about 6 hours) and Na-24 (1368 keV with half-life of about 15 hours).



nuclides	gamma energy (keV)	efficiency (d = 2.5 cm)	efficiency (d = 5 cm)	efficiency (d = 10 cm)
Cd-109	88	1.99×10^{-2}	8.86×10^{-3}	2.95×10^{-3}
Co-57	122	2.36×10^{-2}	9.77×10^{-3}	3.34×10^{-3}
Ce-139	165	2.20×10^{-2}	7.89×10^{-3}	3.42×10^{-3}
Sn-113	392	9.33×10^{-3}	3.64×10^{-3}	1.43×10^{-3}
Cs-137	662	4.88×10^{-3}	2.00×10^{-3}	7.40×10^{-4}
Y-88	898	4.53×10^{-3}	1.50×10^{-3}	7.24×10^{-4}
Co-60	1173	2.69×10^{-3}	1.16×10^{-3}	4.32×10^{-4}
Co-60	1332	2.41×10^{-3}	1.03×10^{-3}	3.77×10^{-4}
Y-88	1836	1.98×10^{-3}	8.89×10^{-4}	3.49×10^{-4}

Fig.Q/1 The correlation curve between gamma energy and efficiency (coaxial HpGe detector)

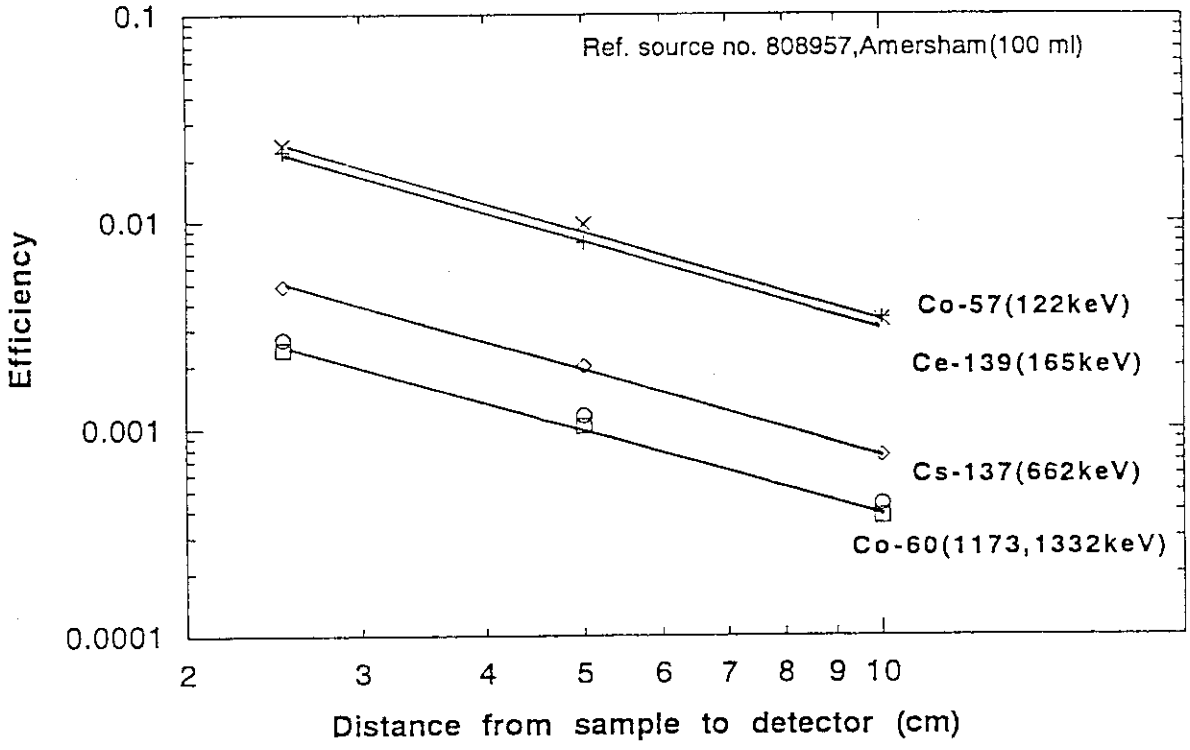


Fig.Q/2 The correlation curve between distance and efficiency

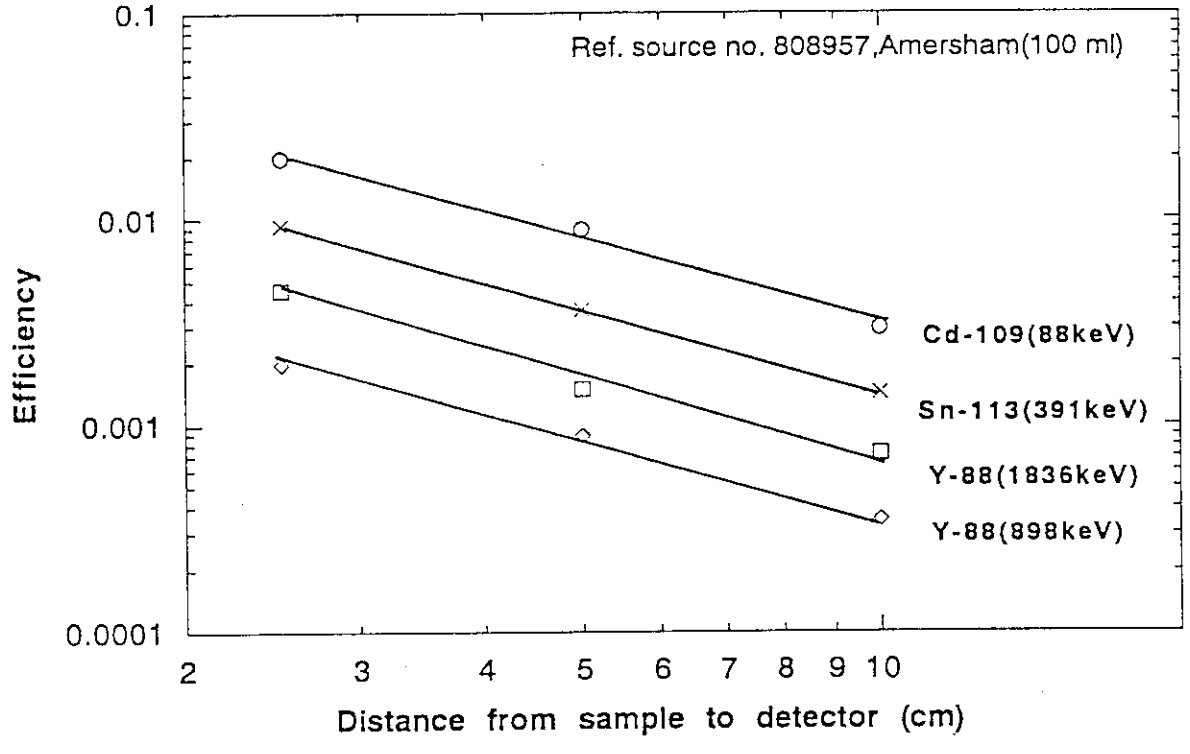
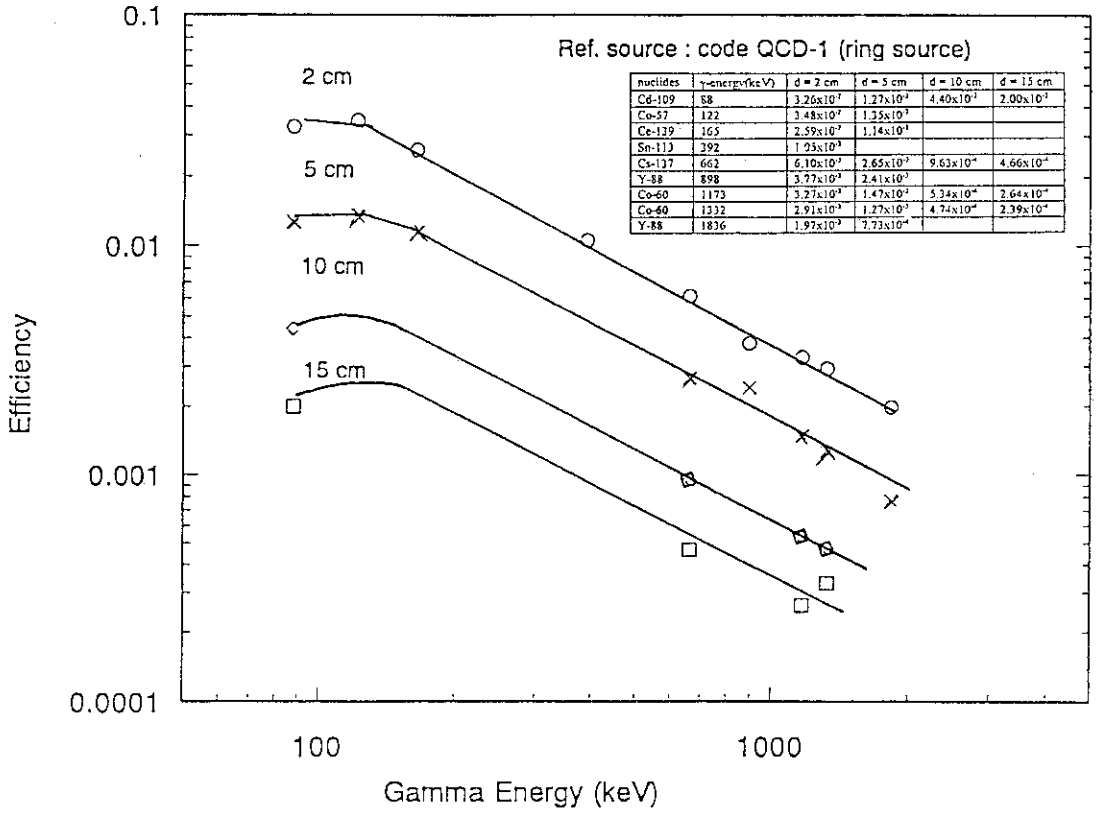
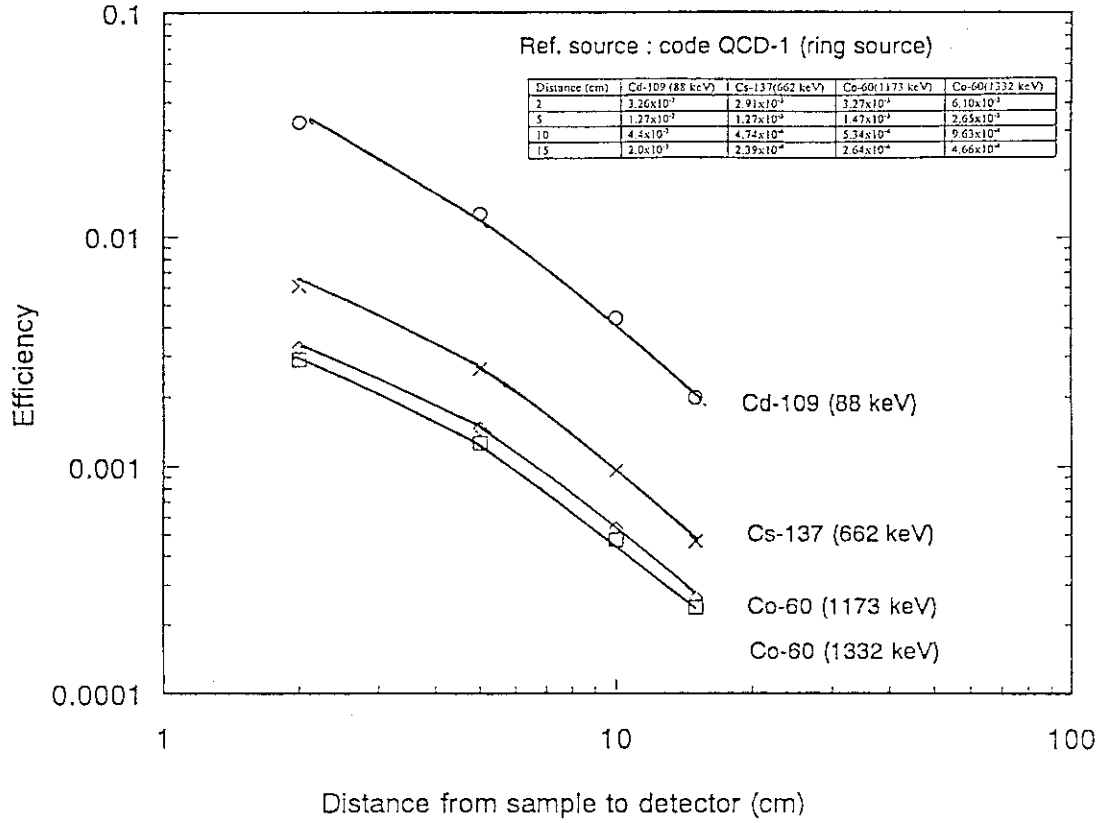


Fig.Q/3 The correlation curve between distance and efficiency



nuclides	γ-energy(keV)	d = 2 cm	d = 5 cm	d = 10 cm	d = 15 cm
Cd-109	88	3.26×10^{-2}	1.27×10^{-2}	4.40×10^{-3}	2.00×10^{-3}
Co-57	122	3.48×10^{-2}	1.35×10^{-2}		
Ce-139	165	2.59×10^{-2}	1.14×10^{-2}		
Sn-113	392	1.95×10^{-2}			
Cs-137	662	6.10×10^{-2}	2.65×10^{-2}	9.63×10^{-3}	4.66×10^{-3}
Y-88	898	3.77×10^{-2}	2.41×10^{-2}		
Co-60	1173	3.27×10^{-2}	1.47×10^{-2}	5.34×10^{-3}	2.64×10^{-3}
Co-60	1332	2.91×10^{-2}	1.27×10^{-2}	4.74×10^{-3}	2.39×10^{-3}
Y-88	1836	1.97×10^{-2}	7.73×10^{-3}		

Fig.R/1 The correlation between gamma energy and efficiency (coaxial HpGe detector)



Distance (cm)	Cd-109 (88 keV)	Cs-137(662 keV)	Co-60(1173 keV)	Co-60(1332 keV)
2	3.26×10^{-2}	2.91×10^{-2}	3.27×10^{-2}	6.10×10^{-2}
5	1.27×10^{-2}	1.27×10^{-2}	1.47×10^{-2}	2.65×10^{-2}
10	4.4×10^{-3}	4.74×10^{-3}	5.34×10^{-3}	9.63×10^{-3}
15	2.0×10^{-3}	2.39×10^{-3}	2.64×10^{-3}	4.66×10^{-3}

Fig.R/2 The correlation between distance and efficiency of Cd - 109, Cs - 137, Co - 60 nuclides

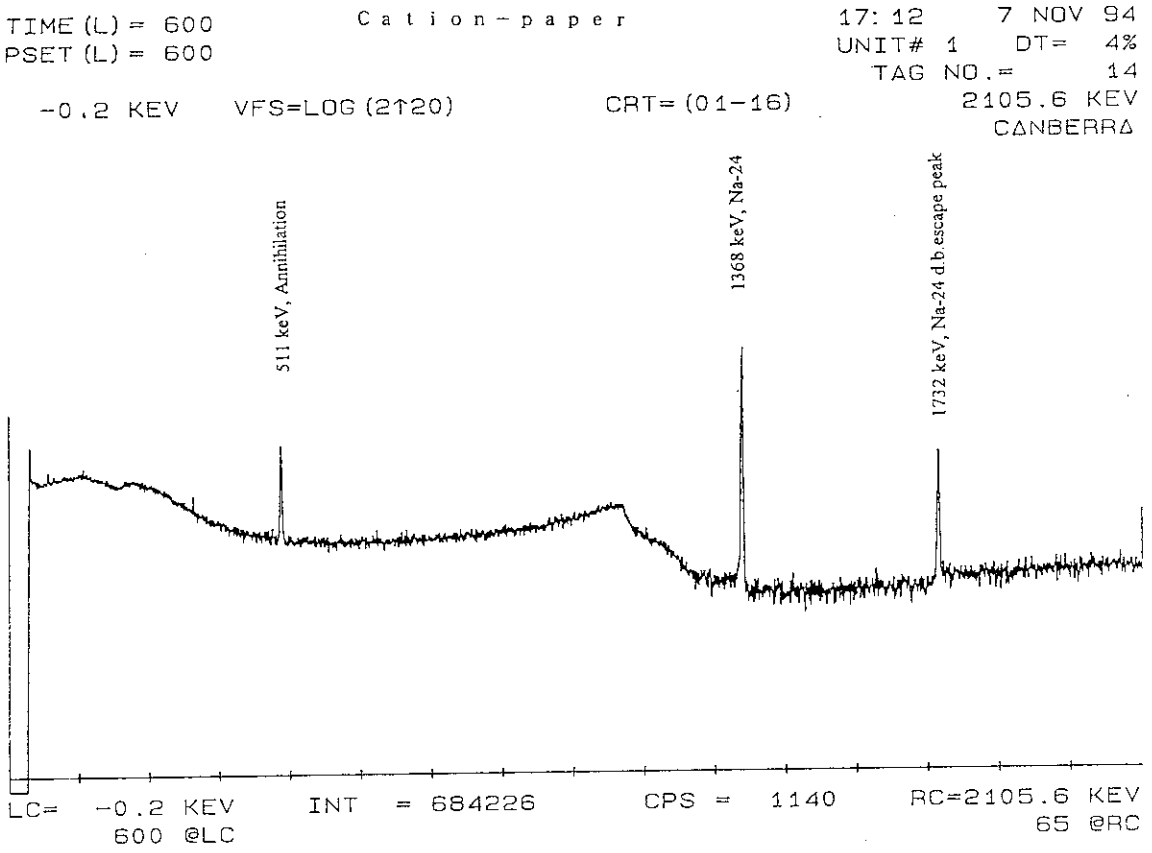


Fig.S/1 The gamma spectra detection on cation - paper

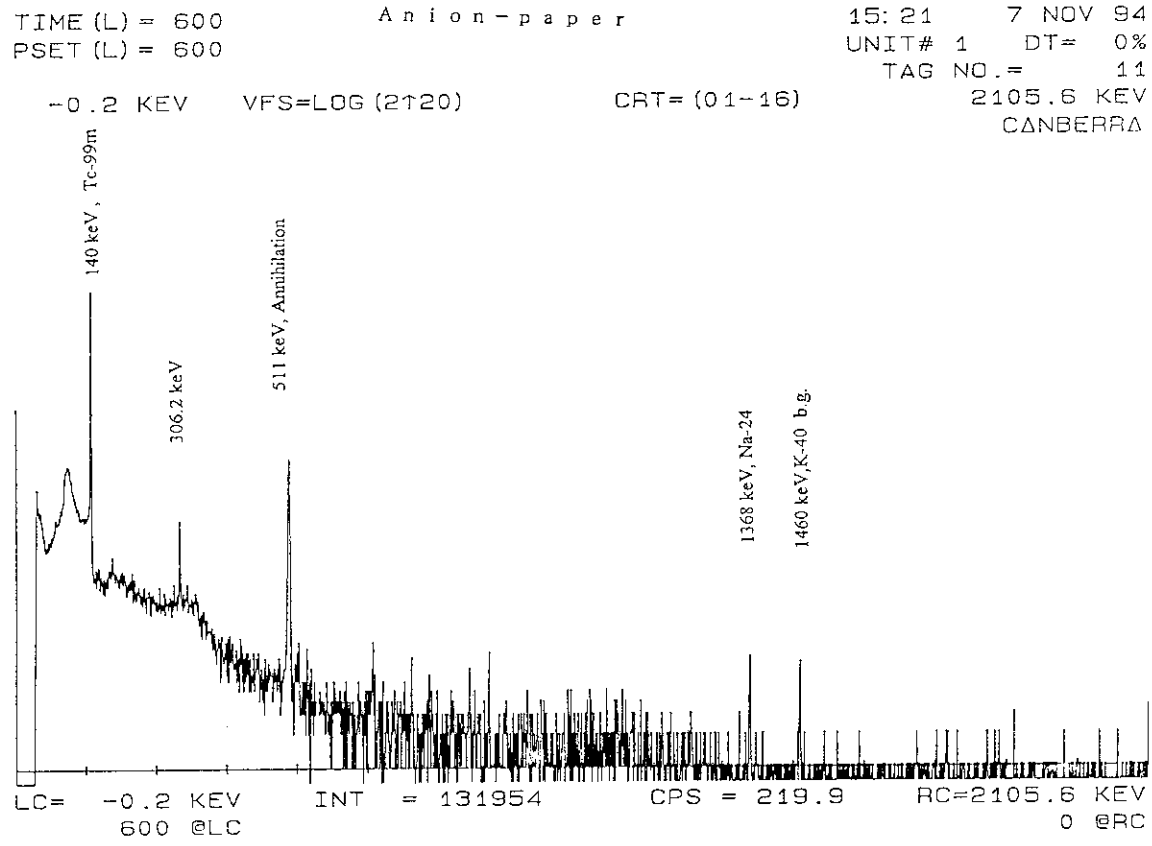


Fig.S/2 The gamma spectra detection on anion - paper

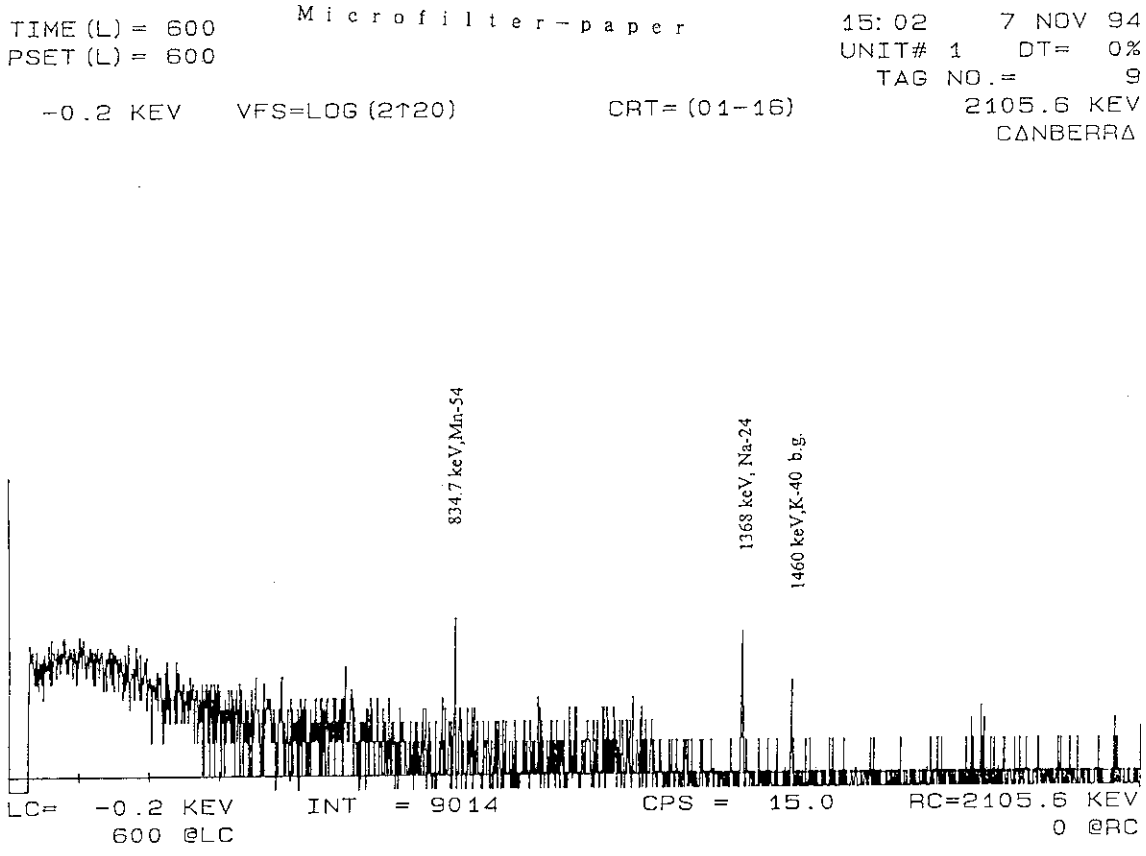


Fig.S/3 The gamma spectra detection on microfilter－paper

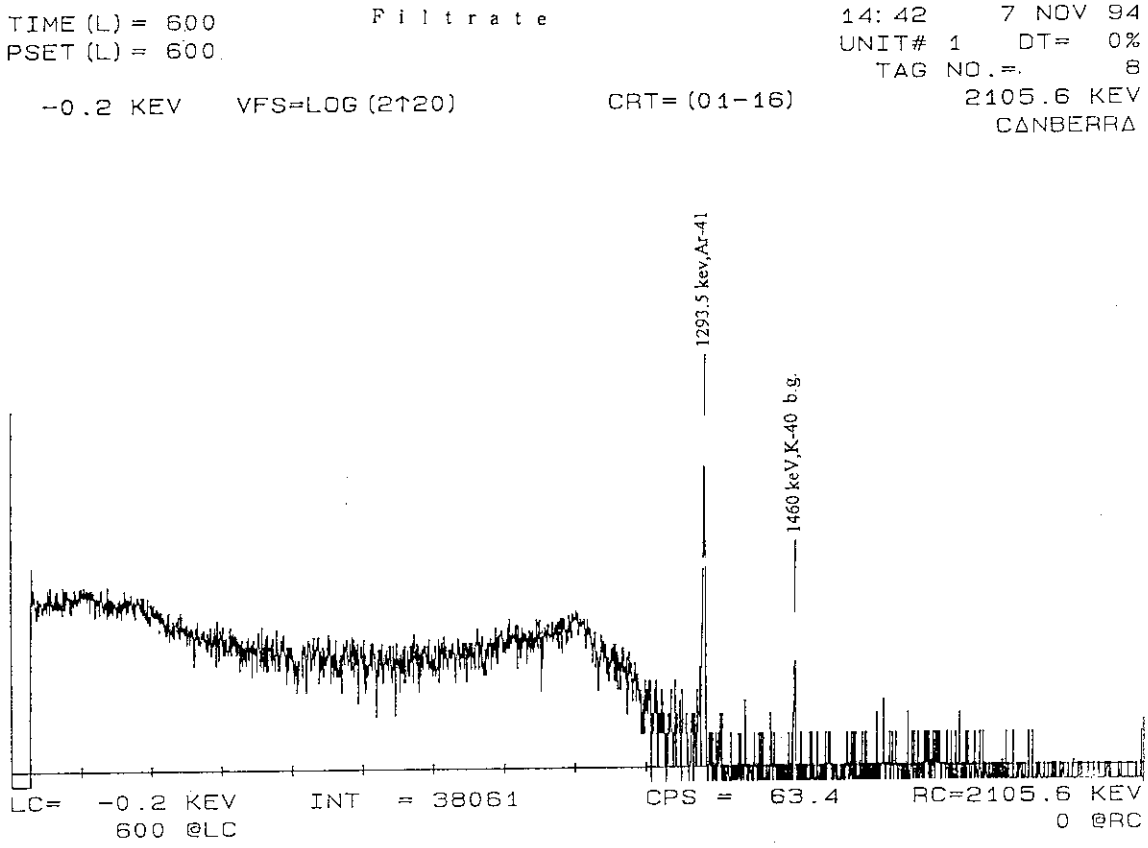


Fig.S/4 The gamma spectra detection in filtrate

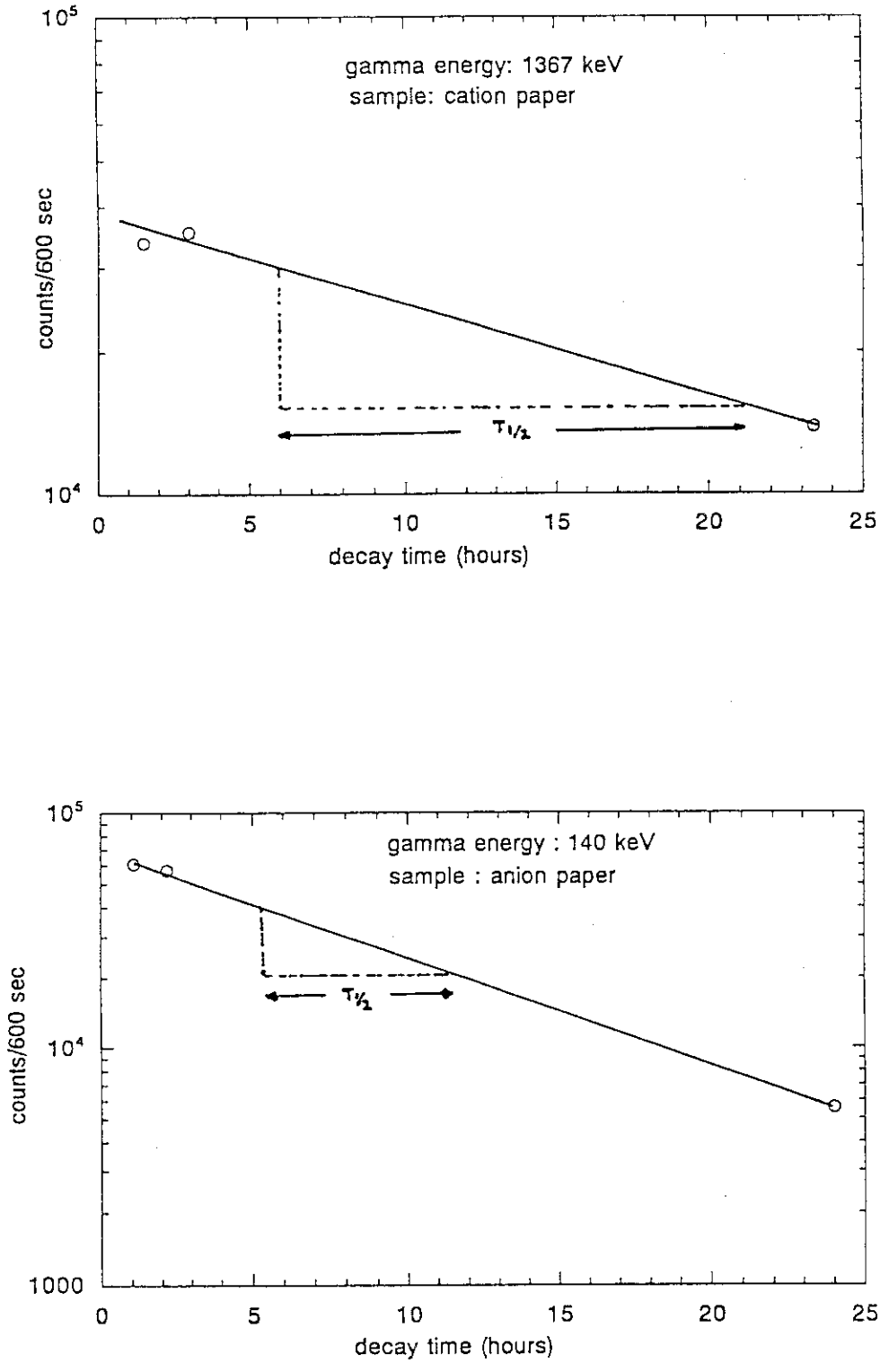


Fig.T Decay curve of gamma energy at 1367 and 140 keV

4.6 Ion analysis in secondary cooling water by Liquid Chromatography

4.6.1 General principles [9]

Liquid chromatography is useful for samples containing large molecules or ionic substances with low vapor pressure. The common features are : (a) a column packed with a stationary phase,and (b) a liquid mobile phase to elute the sample components through the column. One kind of chromatography which was interested in this experiment is ion-exchange method. The ionic constituents of the sample are selectively exchanged with the packed column.

4.6.2 Experimental section

The samples of river water supply and secondary water of JRR-2, JRR-3M were carried out. The secondary water was diluted in the factor of 1: 10 and no need dilution of river water before injection the samples into the column. The ion analysis was concerned with $H_2PO_4^-$, Cl^-, NO_2^-, Br^-, NO_3^- and SO_4^{-2} anions in this experimental conditions.

Equipment :

A YANAGIMOTO model L-5000 Liquid Chromatography with Shodex KD Degas, Shodex AO-30 Oven and Shodex CD-4 Conductivity Meter System used to acquire data for this study and is shown in FigureV.

Chemicals :

The standard contains mixed anions of 10 ppm $H_2PO_4^-$, Br^-, NO_3^- and SO_4^{-2}, 1 ppm of Cl^-, and 4 ppm of NO_2^-.

A 2.5 mM phthalic acid ,pH 4.0 was prepared by dilution 0.5 mM phathalic acid with pure water and used as mobile phase. It was filtered under vacuum with 0.45 μm microfilter and further degassed with placing in the supersonic-wave bath via vacuum filtration apparatus.

Procedure :

The Shodex IC I-524 A anion-exchange column with ambient temperature at 40°C was chosen. The 2.5 mM phthalic acid ,pH 4.0 was used as the mobile phase with a constant flow rate of 1.5 ml/min. The standard and samples were filtered with a 0.45 μm microfilter, and 100 μl of these standard and samples injections were performed. A Conductivity Meter System was used as detector. Retention data and peak area of each anion were recorded. A calculation method by pushing .Calib. knob, was performed with the standard peak. The concentration of ions in samples were obtained by using this calculation method.

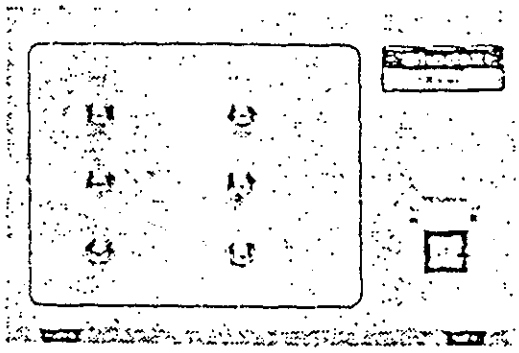
Results :

The chromatogram of standard is shown in Figure W and the results are summarized in table below.

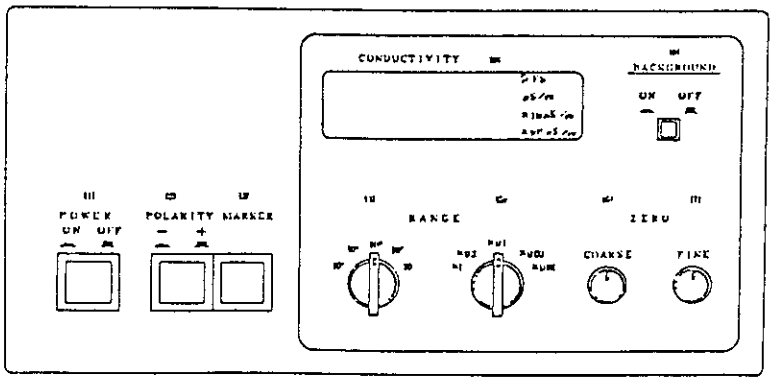
Sample	Sampling date	Conc. of ions (ppm)			
		PO_4^{-3}	Cl^-	NO_3^-	SO_4^{-2}
river water	Oct.24, 1994	N.D.	9.4	3.3	19.0
	Nov.15,1994	3.5	9.0	N.D.	15.0
JRR-2 secondary water	Nov.15,1994	N.D.	18.8	5.9	40.0
JRR-3M secondary water	Oct.24,1994	N.D.	56.6	35.9	112.2
	Oct.31,1994	N.D.	70.6	40.7	141.0
	Nov.7,1994	N.D.	70.7	37.0	139.8
	Nov.14,1994	N.D.	72.8	32.5	141.0
	Nov.15,1994	18.9	68.5	37.8	138.4

N.D. = not detect

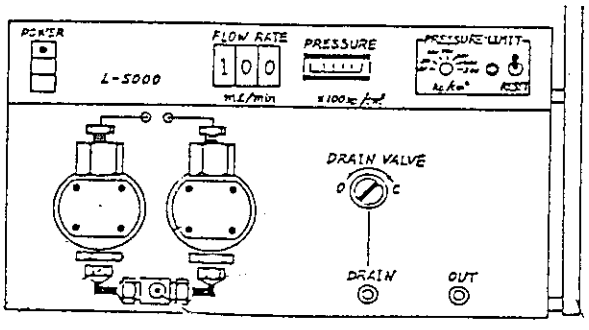
These data show that the concentration of dissolved anions PO_4^{-3}, Cl^-, NO_3^- and SO_4^{-2} in secondary cooling water are higher than in river water supply. However, the data values of secondary water are acceptable, no need to dilute the secondary water with river water.



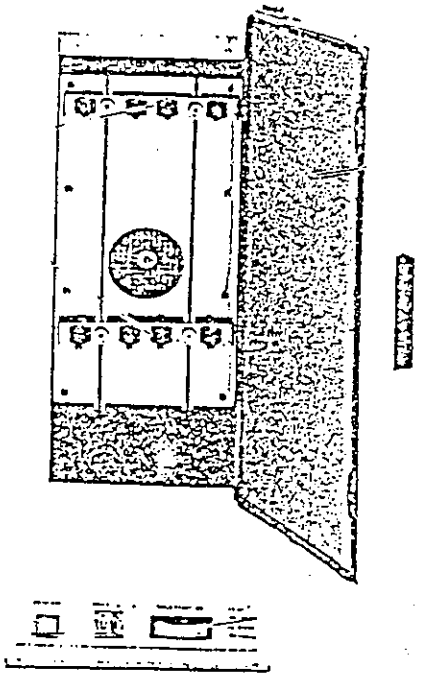
DEGAS SHODEX KD



CONDUCTIVITY METER SHODEX CD-4

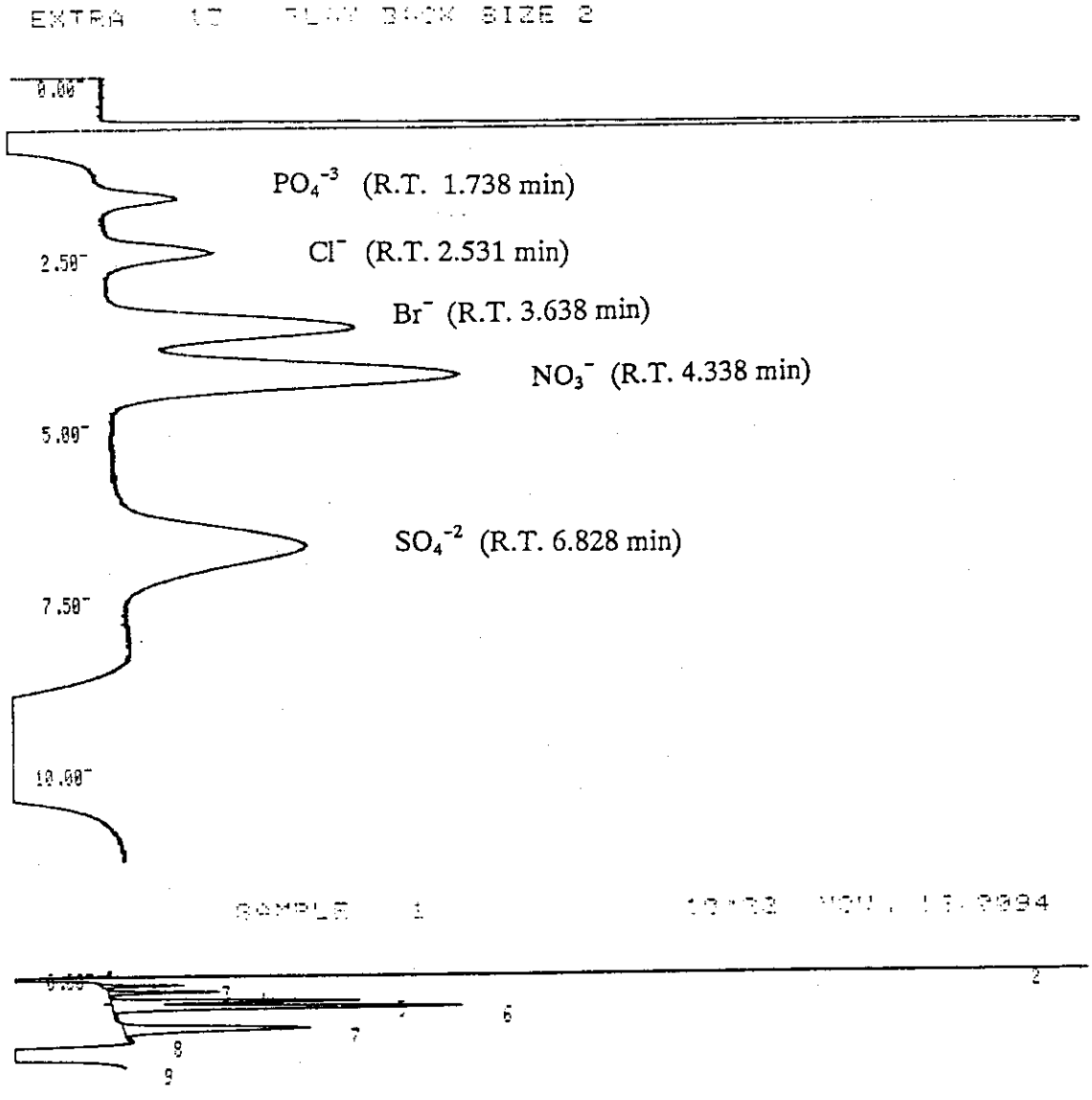


LIQID CHROMATOGRAPHY YANAGIMOTO L-5000



OVEN SHODEX AO-30

Fig.V The components of equipment with Liquid Chromatography



CAL. METHOD 00

	BF	PA	PP
	.100000E+03	.100000E+01	.100000E+01

NO.	NAME	RT	A OR H	MK	CONC.
1		0.000	50		0.0013
2		0.705	124475		54.6409
3		1.738	4335		1.9030
4		2.531	7092		2.1174
5		3.638	22975	M	10.0078
6		4.338	37964		17.5770
7		6.828	30757		13.5213
8		8.058	122		0.0575
9		11.285	34		0.0151
	TOTAL		227909		101.0000

Fig.W Shows the chromatogram of standard solution

4.7 Chemical analysis of corrosion products by AAS

4.7.1 Principles [9]

Atomic absorption spectrophotometer (AAS) in this experiment is used as a deuterium lamp for correction of non-atomic absorption. When a solution of the sample is introduced into a flame as an aerosol, a sequence of processes occurs as desolvation, vaporization , dissociation and atomization or ionization. These vapor atoms can absorb the spectral line from the radiation source, that the required spectral line can be isolated by monochromator. A photomultiplier is used as detector. The diagram of AAS is shown in **Figure** X. And the corresponding absorbance follows directly from the use of Beer's law and a combination of Lambert's law which is given by :

$$A = -\log T = kcd$$

which A is absorbance, T is transmittance, k is extinction coefficient, c is concentration and d is thickness of sample. The calibration curve of standard solution represents the graphical correlation between absorbance and concentration.

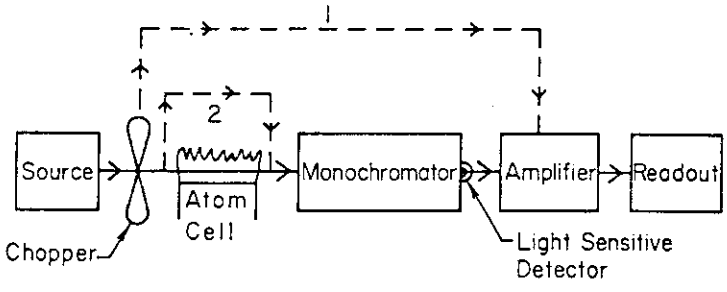


FIGURE X Block diagram of atomic absorption instrumentation.

4.7.2 Experimental section

The secondary cooling water piping system of JRR-2 is constructed of carbon steel. Although the system is treated with corrosion inhibitors, some corrosion products were performed. Quantitative determination of iron and dissolved salts(e.g. Ca, Na,K) is necessarily carried out to obtain information of the corrosion in the JRR-2 secondary circuit.

Procedure :

A series of standard solution was prepared by dilution of stock solution 1000 ppm. All determinations were made on SHIMADZU model AA-660 Atomic Absorption Spectrophotometer. The air-C_2H_2 was used as fuel. D_2 lamp was usedfor background correction if only iron analysis was performed.The operating conditions used in this study are summarized as table below.

conditions	Fe	Ca	K	Na
current (mA)	16	12	10	12
slit width (nm)	0.25	0.50	0.50	0.50
wavelength(nm)	248.3	422.7	766.5	589.0

A 241.47 mg of corrosion products sample was placed into Pt-crucible and the weight was measured exactly. This sample was allowed to dryness in an oven at 110°C for two hours, then weighed the sample to obtain the percentage of moisture in the sample. The percentage of ignition loss was determined by placing the sample in the muffle furnace at 600°C for one hour. This residue was dissolved with 15 ml of (1+1)HCl and heating at about 200°C. Fifteen millilitres of conc. HNO_3 was added and the solution again taken to dryness. Finally it was redissolved with 10 ml of (1+1)HCl.The residue was filtered with . Advantec toyo. filter paper no. 5c (0.10 mg ash) and placed in the Pt-crucible to ignite at 850 °C for two hours, to determine the SiO_2 by gravimetric method.While the filtrate was made up the volume into 250 ml with pure water, and added 10 ml 0f 10% $SrCl_2$. This sample solution was diluted in the factor of 1:100, then determinated Fe, K, Ca and Na by AAS.

Results :

The results were summarized as table below.

	total wt.(g)	%
moisture	0.01762	7.30
ignition loss	0.02638	10.92
Fe_2O_3	0.17713	73.35
SiO_2	0.00892	3.69
Na_2O	0.00516	2.14
others	0.00626	2.59
total	0.24147	100.00

The major oxide of iron was found in this sample,that the corrosion products were occured in the carbon steel piping of secondary circuit. A 10.92% ignition loss contains the corrosion inhibitor (polyphosphate base: Towercrin S-306) which was supplied in the secondary water, slime and algae .

Nitrogen and oxygen gas in the air can combine to form HNO_3 which can also cause corrosion products of aluminium piping or cladding in reactor.The pH control of water is necessary to carried out. Mg and Ca which combine with SO_4^{-2}, PO_4^{-3},CO_3^{-2} and SiO_2 can cause scaling formation.

4.8 Analytical method of ion-exchange resin capacity

The purposes of primary coolant purification system in research reactor are to remove dissolved, suspended solid and radioactive impuities that can maintain the coolant at its nominal pH value. When an ion-exchange resin loses its efficiency, a new resin cartrige will be replaced. It is necessary to confirm the capacity of this new resin.

The strongly acidic and strongly basic ion-exchanger are used for purification system in the primary coolant of JRR-2 and JRR-3M, and in the water pool of JRR-4. These cation and anion resins are in the form of H^+ and OH^-, and have approximately capacity of 1.9 and 1.3 meq/ml respectively.

4.8.1 Experimental section

If 10 % NaCl is passed through the mix-bed resin column, then the reaction will occure as following :

$$\underset{\text{cation-resin}}{R\text{-}H} + NaCl \rightarrow R\text{-}Na + HCl_{(l)}$$

or

$$\underset{\text{anion-resin}}{R\text{-}OH} + NaCl \rightarrow R\text{-}Cl + NaOH_{(l)}$$

The capacity of cation and anion resins were determined by titration the solution with NaOH and HCl respectively. The neutralized reactions are the same reaction as following :

$$HCl + NaOH \rightarrow NaCl + H_2O$$

The mixed of methyl orange and methlene blue in ethyl alcohol was used as indicator.

Procedure:

The wet volume of 10 ml of cation-resin was packed into the column (ϕ 1 cm.). The column was washed with 500 ml of pure water of flow rate about 6 ml/min, then followed by passing 30 ml of 10% NaCl of flow rate about 1 ml/min. The exact volume of resin was measured while the effluent was added 3 drops of mixed indicator and titrated with 0.9904N NaOH. For the anion-resin, it was carried out in the same treatment of cation-resin, but the effluent was titrated with 0.9310N HCl. These titrants had been standardized by using the same as indicator. The resin capacity is calculated by equation :

$$\text{Resin capacity (meq/ml-resin)} = \frac{(\text{ml of NaOH}) \times (0.9904\ \text{N NaOH})}{\text{resin volume (ml)}}$$

Results :

The results of capacity were summarized in table below.

resin		capacity	(meq/ml-resin)	
	1	2	3	average
cation	1.91	1.89	1.90	1.90
anion	1.11	1.08	1.08	1.09

The capacity of resin has the results approximately as the acceptable value.

5. Conclusion

Water chemistry is concerned with all types of reactor. The components and facilities of three research reactors (JRR-2,JRR-3M and JRR-4) were studied. In routine work proper water chemistry (water treatment and chemical control) determines for protection of corrosion and scale formation, and also for control the radioactive species (fission products, activation products). Primary coolant is based on high purity water in all reactors that is connected with water purification system. Furthermore, heavy water and helium system in all reactors require high purity in the system. Special analytical techniques such as Gas Chromatography, GM Counter, Liquid Scintillation Counter, IR-Spectrophotometry, Gamma-ray Spectrometry, Liquid Chromatography and Atomic Absorption Spectrophotometry were used for determining impurities in helium system,primary and secondary coolants. The capability of purification system in reactor can be investigated with analysis of resin capacity. Furthermore the operational controls are summarized as follows : pH value, temperature, conductivity, solid residue, radioactive species and ions-concentration. Some coolant samples were investigated and recieved high purity and low radioactivity. If the quantity of impurities are more than specific value, it will be diluted in the coolant system or changed a new resin in purification system. The circulating of secondary water with serving of chemical (polyphosphate based) can also prevent the scale formation in the heat exchanger cooling tube.

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