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REPORT

ON SCIENTIST EXCHANGE PROGRAM

---ANALYSIS OF URANIUM SERIES NUCLIDES IN ROCKS AND MINERALS

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POWER REACTOR AND NUCLEAR FUEL
DEVELOPMENT CORPORATION, CHUBU WORKS

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1992

REPORT

ON SCIENTIST EXCHANGE PROGRAM

Research Subject : Analysis of Uranium Series Nuclides in Rocks and Minerals

Research Period : Sep.28,1992 to Dec. 26,1992

Research Place : PNC- Chubu Works,Japan

Assigned Section : Exploration and Mining Technology Development Section

Assignee's Tittle : Analytical Chemistry Engineer

Assignee's Division : Analysis Center

Organization : Beijing Research Institute of Uranium Geology,CNNC

Country : People's Republic of China

First and family name: Dongfa Guo

Signature:

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Forward

The research report is the result of Scientist Exchange Program between POWER REACTOR AND NUCLEAR FUEL DEVELOPMENT CORPORATION(PNC) under SCIENCE AND TECHNOLOGY AGENCY OF GOVERNMENT OF JAPAN(STA) and CHINA NATIONAL NUCLEAR CORPORATION (CNNC) . Author stayed at PNC Chubu Works for 3 months,mainly proceeding his research subject " Analysis of Uranium Series Nuclides in Rocks And Minerials " and its related techniques such as chemical analysis of uranium and thorium , data processing using personal computer and so on. During his stay with the staffs of PNC Chubu Works, especially with the members of Exploration and Mining Technology Development Section, author's research schedule was proceeding smoothly without any troubles. And with the helps and guidances of advisors, he was able to make his experiments successfully and exchange some ideas on analytical techniques . So,the program will benefit his coming work in China.

Meanwhile, author has visited PNC's facilities , Hiroshima Peaceful Memorial Museum , Toyota Motor Corporation and other places . These visits helped author's understanding greatly with Japanese people,Japan and her advanced modernized science and technology and her contribution to the world. Author never forget Hiroshima,where he got a great deal of knowledges about Hiroshima's catastrophe at the atomic bomb explosion 47 years ago. So ,the nuclear technology and nuclear energy for peaceful use are of the most importance.

Author believes that the further co-operation between PNC and CNNC will be increasing through mutual visiting appointments,benefiting for each other and contributing to the peaceful use of nuclear energy. He is aslo sure that the established closed relationship between Japan and China and the friendship between Japanese people and Chinese people will be deepening through this kind of exchange program.

Abstract

This report mainly described the analysis of uranium series nuclides in samples of rocks and minerials ,giving detailed procedures about them. The related analytical methods and techniques included alpha spectrometry for U-238,U-234,Th-232 and Th-230, which employed anion exchange and TBP- tetrachloromethane extraction methods separating uranium and thorium from matrix and electrodeposition method preparing source disks; gamma spectrometry for Pb-210,Pb-214,Bi-214,Th-234 and Ra-226; oxine-cholorform spectrophotometry for total U, in which the TBP-kerosene extraction technique was used to separate uranium from other elements; Arsenazo III for total Th,where the anion exchange method was essential to separate thorium from other elements; their data processing techniques using Apple Macintosh Plus personal computer system as well .

Meanwhile,some comparisons of analytical methods between PNC and CNNC were presented. And through the comparisons,some advantages and disadvantages of them were discussed herewith. Besides, as a report of Scientist Exchange Program under STA,something about nuclear industry involving uranium exploration and nuclear power electricity were mentioned.

Keywords Scientist Exchange Program, Analysis , Nuclides ,Uranium, Thorium, Alpha,Gamma,Spectrometry,Chemical,Spectrophotometry, Anion Exchange,Extraction, Separation,Computer.

FINAL SCHEDULE FOR STA PROGRAM (Guo Dongfa)

DATE	CONTENTS
Sep. 28 (Mon.)	Lv. Beijing and Ar. Tokyo
Sep.29 (Tue.)	Explanation on procedure in PNC Head Office
Sep 30 (Wedn.)	Lv. Tokyo and Ar. Toki Explanation on procedure in PNC Chubu Works
Oct. 1 (Thur.)	Introduced general information about daily life and visited the facilities of the lab.
Oct.2 (Fri.)	PNC anniversary Holiday
Oct. 3 (Sat.)	Holiday
Oct. 4 (Sun.)	Holiday
Oct. 5 (Mon.)	Making schedule of research and understanding the facilities of the laboratory
Oct. 6 (Tue.)	Making detail and concrete schedule of research and discussing with Mr. Ochiai and Mr.Okita
Oct. 7 (Wedn.)	Finish the schedule and type it
Oct. 8 (Thur.)	Prepare samples and be familiar with procedure of alpha spectrometry(15 samples)
Oct. 9 (Fri.)	Seal samples for gamma spectrometry(10 samples)
Oct. 10 (Sat.)	Holiday
Oct. 11 (Sun.)	Holiday
Oct. 12 (Mon.)	Chemical procedure for alpha spectrometry
Oct. 13 (Tue.)	"
Oct. 14 (Wedn.)	"
Oct. 15 (Thur.)	"
Oct. 16 (Fri.)	"
Oct. 17 (Sat.)	Holiday
Oct. 18 (Sun.)	Holiday
Oct. 19 (Mon.)	Chemical procedure for alpha spectrometry
Oct. 20 (Tue.)	"
Oct. 21 (Wedn.)	"
Oct. 22 (Thur.)	Measurement of U-238,U-234 ,Th-230 and Th-232 with alpha- spectrometer
Oct. 23 (Fri.)	"
Oct. 24 (Sat.)	Holiday
Oct. 25 (Sun.)	Holiday
Oct. 26 (Mon.)	Measurement of U-238,U-234 ,Th-230 and Th-232 with alpha- spectrometer
Oct. 27 (Tue.)	"

Oct. 28	(Wedn.)	"
Oct. 29	(Thur.)	"
Oct. 30	(Fri.)	"
Oct. 31	(Sat.)	Holiday
Nov. 1	(Sun.)	Holiday
Nov. 2	(Mon.)	Measurement of U-238,U-234 ,Th-230 and Th-232 with alpha- spectrometer
Nov. 3	(Tue.)	Cultural holiday
Nov. 4	(Wedn.)	Measurement of U-238,U-234 ,Th-230 and Th-232 with alpha- spectrometer
Nov. 5	(Thur.)	"
Nov. 6	(Fri.)	"
Nov. 7	(Sat.)	Holiday
Nov. 8	(Sun.)	Holiday
Nov. 9	(Mon.)	Total U analysis by wet chemical method
Nov. 10	(Tue.)	"
Nov. 11	(Wedn.)	"
Nov. 12	(Thur.)	"
Nov. 13	(Fri.)	"
Nov. 14	(Sat.)	Holiday
Nov. 15	(Sun.)	Holiday
Nov. 16	(Mon.)	Total Th analysis by wet chemical method
Nov. 17	(Tue.)	Visit to TOYOTA Motor Corporation
Nov. 18	(Wedn.)	Total Th analysis by wet chemical method
Nov. 19	(Thur.)	"
Nov. 20	(Fri.)	"
Nov. 21	(Sat.)	Holiday
Nov. 22	(Sun.)	Holiday
Nov. 23	(Mon.)	National holiday
Nov. 24	(Tue.)	Total Th analysis by wet chemical method
Nov. 25	(Wedn.)	Gamma spectrometry
Nov. 26	(Thur.)	"
Nov. 27	(Fri.)	"
Nov. 28	(Sat.)	Holiday
Nov. 29	(Sun.)	Lv. Toki and Ar. Hiroshima
Nov. 30	(Mon.)	Visit Hiroshima Memorial Park and so on, Lv. Hiroshima and Ar. Kyoto
Dec. 1	(Tue.)	Visit , Lv.Kyoto And Ar. Tsuruga
Dec. 2	(Wedn.)	Visit Fugen Nuclear Power Plant , Monju Construction Office , Japan Atomic Power Company Exhibition Center, Atom Plaza PNC ; Lv. Tsuruga and Ar. Toki
Dec. 3	(Thur.)	Gamma spectrometry
Dec. 4	(Fri.)	"
Dec. 5	(Sat.)	Holiday

Dec. 6 (Sun.)	Holiday
Dec. 7 (Mon.)	Gamma spectrometry
Dec. 8 (Tue.)	"
Dec. 9 (Wedn.)	"
Dec. 10 (Thur.)	"
Dec. 11 (Fri.)	"
Dec. 12 (Sat.)	Holiday
Dec. 13 (Sun.)	Holiday
Dec. 14 (Mon.)	Visit to open laboratory of SEIKO(OSAKA)
Dec. 15 (Tue.)	Report making
Dec. 16 (Wedn.)	"
Dec. 17 (Thur.)	"
Dec. 18 (Fri.)	"
Dec. 19 (Sat.)	Holiday
Dec. 20 (Sun.)	Holiday
Dec. 21 (Mon.)	Report making
Dec. 22 (Tue.)	Report to PNC Chubu Works
Dec. 23 (Wedn.)	Holiday
Dec. 24 (Thur.)	Lv. Toki and Ar. Tokyo
Dec. 25 (Fri.)	Report to PNC Head Office
Dec. 26 (Sun.)	Lv. Tokyo and Ar. Beijing

CHAPTER 1 INTRODUCTION

1.1 At a glance of nuclear power electricity and uranium exploration in Japan

Japan ,as a supereconomical nation, consumed more than 700 billion kwh electricity in 1990[1] . But her resources of energies are very limited , so her energies are mainly imported from overseas , more than 80% of her total consumed energies[1] . For electricity, the distribution of energies can be seen in Fig.1.1-1 (The data from literature[1]) . Obviously, nuclear power electricity has paid an important role in Japan. Now, there are 42 reactors in operation,12 reactors under construction , 1 reactor under application. The total output capacity reaches 46353 MW (see Table 1.1-1). Therefore, the consumption of uranium is also quite large. Fig1.1-2 (The data from literature[2]) shows the

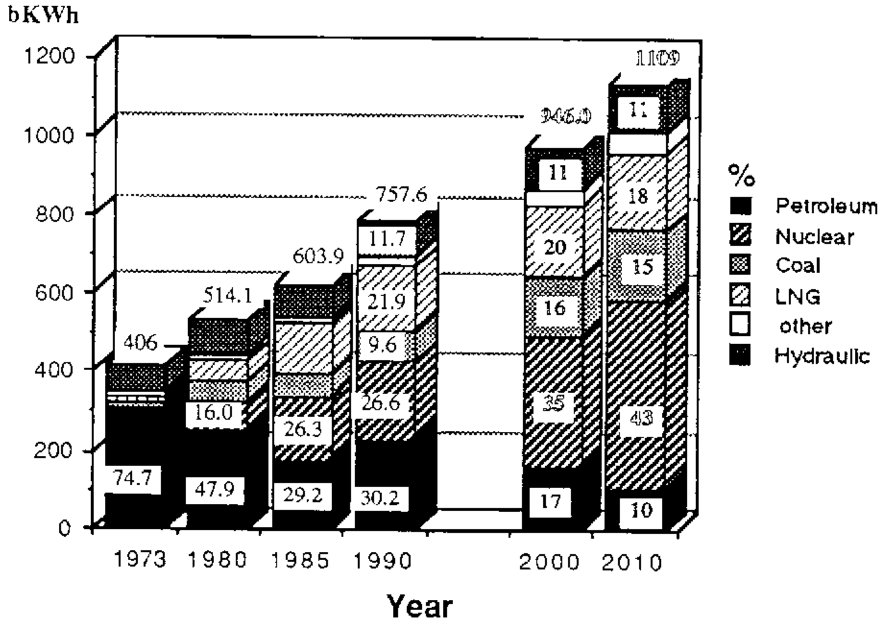


Fig.1.1-1 Distribution of Electricity Power

demand for uranium in main developed countries including Japan in recent and near future years . Unfortunately, Japan has still not enough her own uranium resource. There are only about 7700 ton(U_3O_8) available totally. The shortage of uranium has to be imported without exception. However, the supply of uranium has been unstable in recent years. From Fig1.1-3 , it can be seen that the production has been less than the demand of uranium since around 1985. In order to ensure the stable supply of uranium in long term,Japan has to do something using her advanced science and technology , excellent management and strong economical support,which provide the possibility for developing some more advanced high-tech nuclear reactors such as ATR and FBR that utilize

Table 1.1-1 Nuclear Power Ecectricity Output Capacity in Japan

NO.	OUTPUT POWER(10MW)	RUNING DATE(Y-M)	COMPANY
1	16.6	1966-7-25	JAPC
2	110	1978-11-28	JAPC
3	35.7	1970-3-14	JAPC
4	116	1987-2-27	JAPC
5	57.9	1989-6-22	HOKKAIDO
6	57.9	1991-4-12	HOKKAIDO
7	52.4	1984-6-1	TOHOKO
8	46	1971-3-26	TOKYO
9	78.4	1974-7-18	TOKYO
10	78.4	1976-3-27	TOKYO
11	78.4	1978-10-12	TOKYO
12	78.4	1978-4-18	TOKYO
13	110	1979-10-24	TOKYO
14	110	1982-4-20	TOKYO
15	110	1984-2-3	TOKYO
16	110	1985-6-21	TOKYO
17	110	1987-8-25	TOKYO
18	110	1985-9-18	TOKYO
19	110	1990-9-28	TOKYO
20	110	1990-4-10	TOKYO
21	54	1976-3-17	CHUBU
22	84	1978-11-29	CHUBU
23	110	1987-8-28	CHUBU
24	34	1970-11-28	KINKI
25	50	1972-7-25	KINKI
26	82.6	1976-12-1	KINKI
27	82.6	1974-11-14	KINKI
28	82.6	1975-11-14	KINKI
29	87	1985-1-17	KINKI
30	87	1985-6-5	KINKI
31	117.5	1979-3-27	KINKI
32	117.5	1979-12-5	KINKI
33	118	1991-12-18	KINKI
34	46	1974-3-29	CHUKOKU
35	82	1989-2-10	CHUKOKU
36	56.6	1977-9-30	SHIKOKU
37	56.6	1982-3-19	SHIKOKU
38	55.9	1975-10-15	KYUSHU
39	55.9	1981-3-30	KYUSHU
40	89	1984-7-4	KYUSHU
41	89	1985-11-28	KYUSHU
42	16.5	1979-3-20	PNC-FUGEN(ATR)
	3340.4	Runing now	42 Reactors
	1212.4	Under construction**	12Reactors
	82.5	Under application	1 Reactor
Total 4635.3			55 ReactorS
	**28	Under testing	PNC-MONJU(FBR)

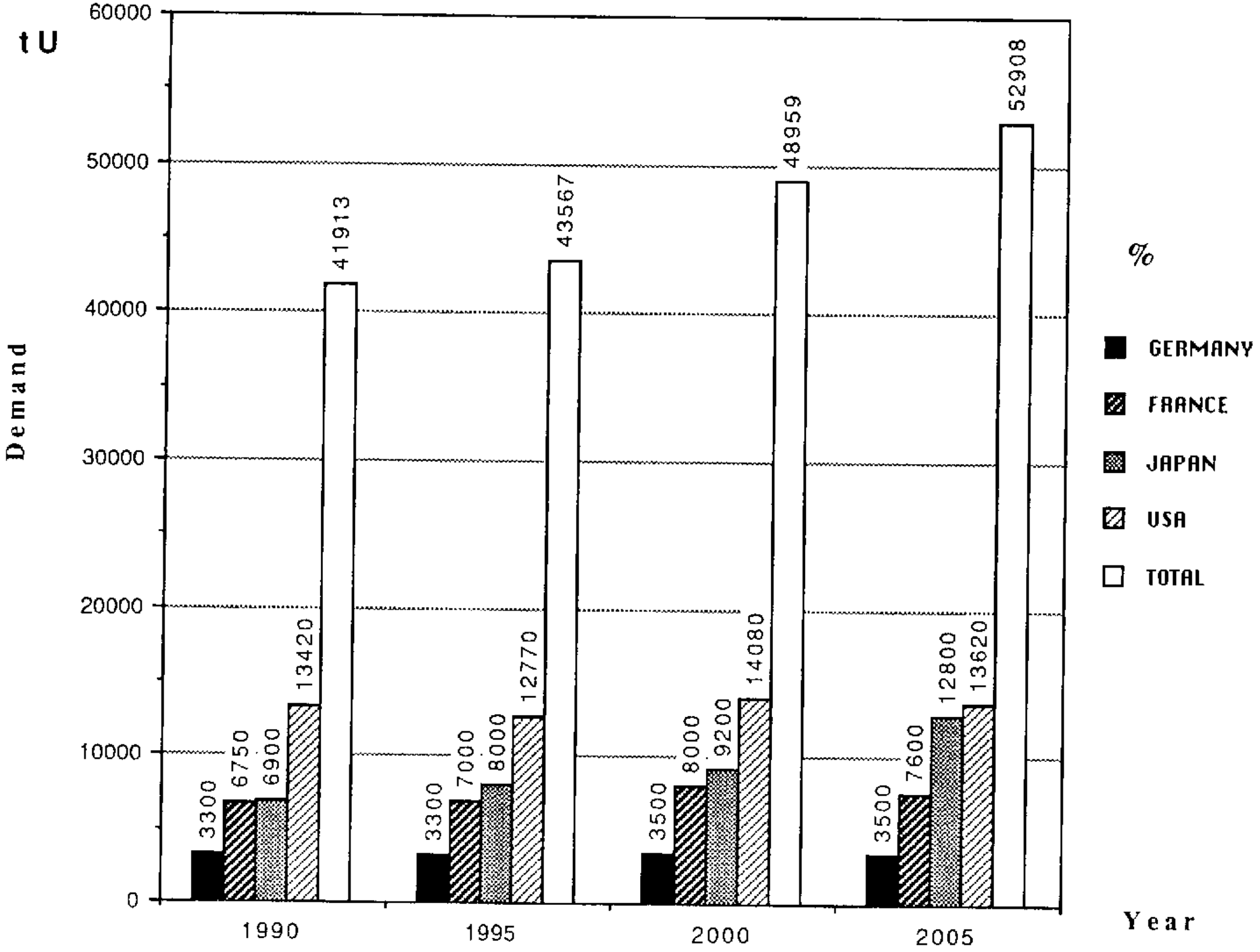


Fig 1.1-2 Demand of U in Main Developed Countries

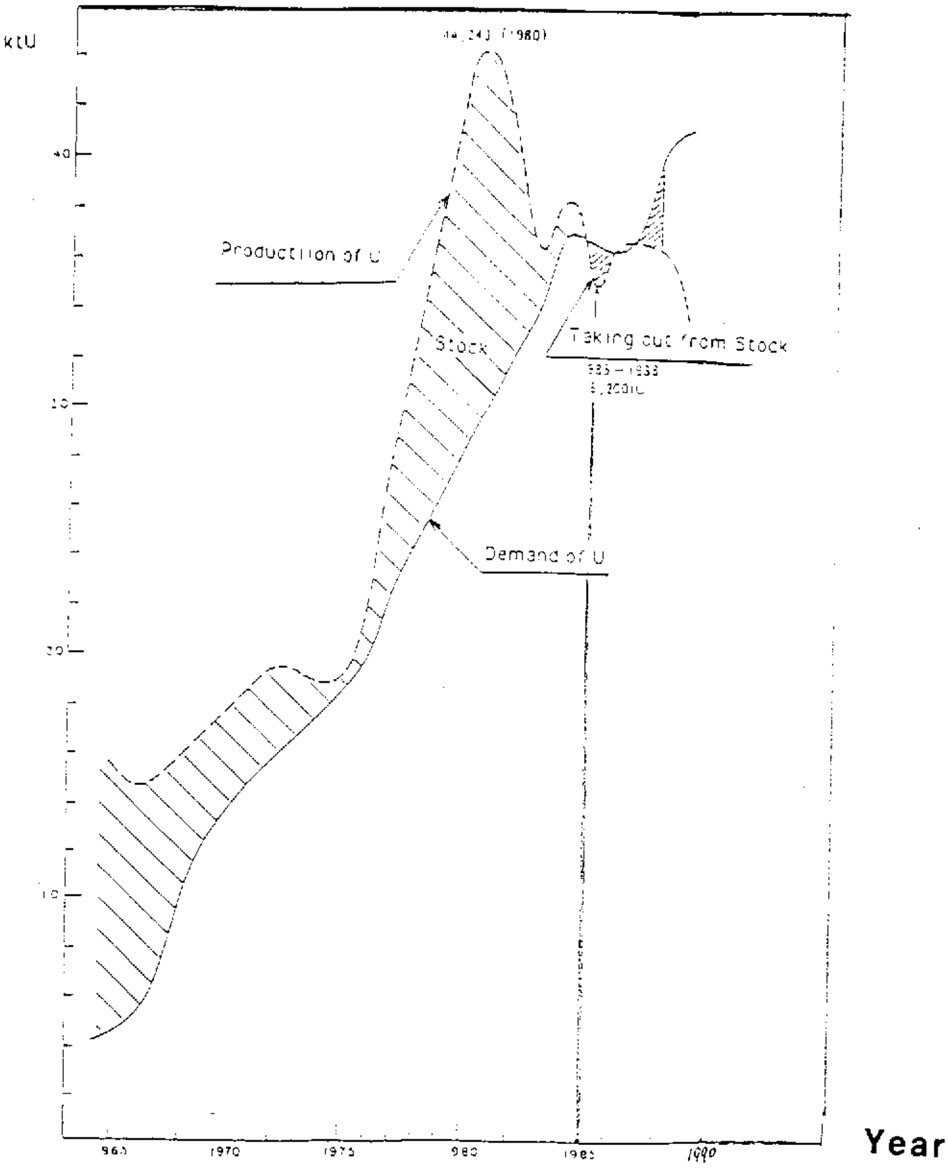


Fig 1.1-3 Production and Demand of U in the World

uranium resource effectively because of their employing economic nuclear fuels (UO_2 &MOX for ATR , U & Pu for FBR) which can be recycling usage after reprosessing. That is what PNC is doing, and a way for solving the shortage of uranium resource. The more information about PNC and its activities can be found in the literature[3]. Of course, another way is looking for more uranium resource around the globe,co-operating with other nations. This work is being done at PNC-Chubu Works,which is mainly responsible for uranium exploration in the overseas of Japan. Table 1.1-2 shows the main activities of uranium expolration in recent and near future at PNC-Chubu Works. Due to author's research subject metioned previously, it is necessary to introduce its analytical techniques for geological matertials herewith,which is an important part of uranium exploration technology. For more information about PNC Chubu Works ,the reference of this report can be looked up.

Table 1.1-2 Main Activities of Uranium Exploration at PNC-Chubu Works

Country	Project Name	Result
Canada	Priucesd Mery	Ore deposit found
	Dawn Lake	Ore deposit found
	Waterfound River	Good mineralization displayed
	Christie Lake	Good mineralization displayed
Australia	King River	Early stage exploration
	Plateau	Early stage exporation
	Rudall	Early stage exploration
Niger	Techili	Small ore deposit found
Zimbabwe	Kariba Lake	Small but high grade ore deposit found
China	Jiang Chang	Not yet found
Brazil	Rio Fresco	Not yet started,under negotiation

1.2 Analytical laboratories for geological materials at PNC-Chubu Works

There are 6 analytical laboratories for analysis of geological materials such as rocks,minerals and water. Table 1.2-1 shows the 6 labs and their main facilities employed. Table1.2-2,Table1.2-3 and Table1.2-4 show the details about their analytical items. In all these methods ,each has its special features according to different purposes. But for uranium exploration,the analyses of uranium,thorium and their nuclides are very important. So, author's research work focused on these techniques during his stay in PNC-Chubu Works.

Table 1.2-1 Labs Show at PNC-Chubu Works

Lab	Main Facilities	Reference
Rocks & Minerals Analysis Lab	General	see Table 1.2-2
Trace Elements Analysis Lab	General	see Table 1.2-3
Water Analysis Lab	General,IC,HPLC	see Table1.2-4
Instruments Lab	ICP-AES,AAS,UV-SP	
XRF Lab	XRF , XRD	
Rocks & Minerals Testing Lab	Alpha,Gamma,EPMA	

Table1.2-2 Analytical Items at Rocks & Minerals Analysis Lab

Item	Methods	Key Words
U	Beta-gamma counting Spectrophotometry Fluorophotometer	Made by Aloka TBP, Extraction,Oxine-cholorform, . Extraction by Ethyl Acetate . K_2CO_3 ,NaF, Na_2CO_3 Mixed Flux . Fluorescence at 540 nm
Th	Spectrophotometry	Anion Exchange,ArsenazoIII
U-238,U- 234 Th-232,Th-230	Alpha Spectrometry Alpha Spectrometry	Chemical, Anion Exchange, TBP,Extraction,Electrodeposition Am-241, Alpha spectrometer
Th-234 Pb-210,Pb-214 Bi-214,Ra-226	Gamma Spectrometry Gamma Spectrometry Gamma Spectrometry	Sealing,20g,High Pure Ge, Liquid Nitrogen, Gamma Spectrometer
SiO_2	XRF	Glass bead, Calibration Curve Method,BG Correction,Automatic Determination
Al_2O_3 ,MnO_2	XRF	
TiO_2 ,CaO_2 ,MgO	XRF	
Na_2O ,K_2O	XRF	
Total Fe	XRF	
$FeO.Fe_2O_3$	Chemical Method	FeO: $KMnO_4$ Titration Fe_2O_3: Calculation from total Fe and FeO
H_2O (±)	Chemical Method	Weight Loss Method

Table 1.2-3 Analytical Items at Trace Element Analysis Lab

Item	Methods	Key Words
Ag Au	AAS AAS	Based on JIS** ** (Japan Industrial Standards)
V,Mo,Zn ,Cu REEs	ICP-AES ICP-AES	Standard Solution ,Calibration Curve, Automatic Determination
P_2O_5	Chemical Method	Phosphorous Molybdate Method
CO_3^{2-}	Chemical Method	NaOH Absorption and HCl Titration
SO_4^{2-}	Chemical Method	Gravimetric Method
F^-	Chemical Method	Distillation and Lanthanum ALC method

Table1.2-4 Analytical Items at Water Analysis Lab

Item	Methods	Key Words
F^-, NO_3^- Br^-, SO_4^- Cl^-, PO_4^{3-}	Ion Chromatograph	. Made in Yokogawa Japan . Automatic and Simultaneous Analysis .High Sensitivity
Fe^{2+}/Fe^{3+} S^{2-}	High Performance Liquid Chromatograph	. Made in Shimadzu Japan . High Sensitivity . Automatic Analysis
Hazardous Elements (Hg,Pb,Cd,Cr)	AAS	Standard Methods
Ra	Ionization Chamber	$BaSO_4$ Coprecipitation . Sealed in Curie Flask
Organic Carbon	Total Organic Carbon Analyser	. Made in Shimadzu Japan . High Sensitivity . Automatic Analysis

Chapter 2 Analysis of Uranium Series Nuclides in Rocks and Minerals

2.1 General introduction

2.1.1 Uranium and thorium decay series

There are many literatures[4,5] introduced uranium and thorium decay series,two of the three natural radioactive decay series. Here, only giving a few figures and tables[4],shown in Fig2.1-1 & Table2.1-1 and Fig2.1-2 & Table2.12, respectively.From these ,it can be seen that long half life nuclides U-238,U-234 and Th-230 in U-series and Th-232 in Th-series; mediate half life nuclides Ra-226 and Pb-210 in U-series and U-232,Ra-228 and Th-228 in Th-series as well as other short half life nuclides in both series are included. Since these nuclides are unstable, alpha or beta particles or gamma ray are emitted during their decaying as the law of radioactivity[4], in which the energies of them are characterized by different nuclides. This is the physic foundation of radioactive measurement of nuclides.

2.1.2 Modes of radioactive decay

As metioned above, the modes of radioactive decay are classfied alpha decay,beta decay and gamma ray emission . Simply say, **alpha decay** is the ejection from the nucleus of two netrons and two protons bound together as a He nucleus; **beta decay** is the emission of the positive or negative electrons from nuclei ; and the **gamma emission** is a kind of electromagnetic radiation that a nucleus in an excited state gives up its excitation energy and return to the ground state . For more information about this , the literature[4] can be referred to. Fig2.1-3 & Fig2.1-4 [4] show the alpha decay and an example of fine structure of alpha particle spectra ; and Fig2.1-5[3] displays the alpha energies and intensities of natural nuclides . Fg2.1-6 [4]shows the beta decay spectrum. Table 2.1-3[3] expresses the gamma rays over 100 kev emitted by the uranium decay series in equilibrium with its decay products.

2.1.3 Measurement of radiation

The characteristics of alpha,beta and gamma rays are quite different from one another , leading to different methods or techniques. But alpha and gamma rays are more useful in analysis, the basic diagram of an instrument for their measurement is shown Fig2.1-7. The basic description of function for each part can be referred to literature[4] .

THE RADIOACTIVE DECAY SERIES

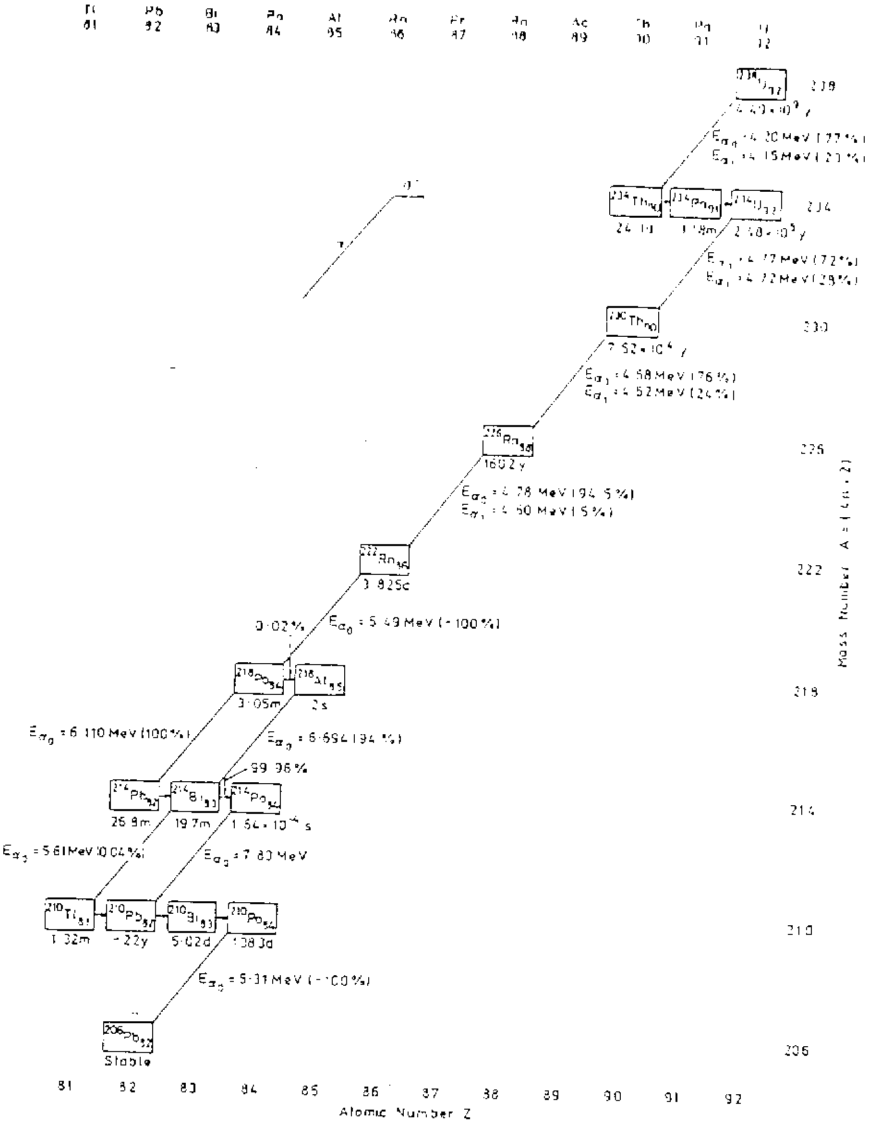
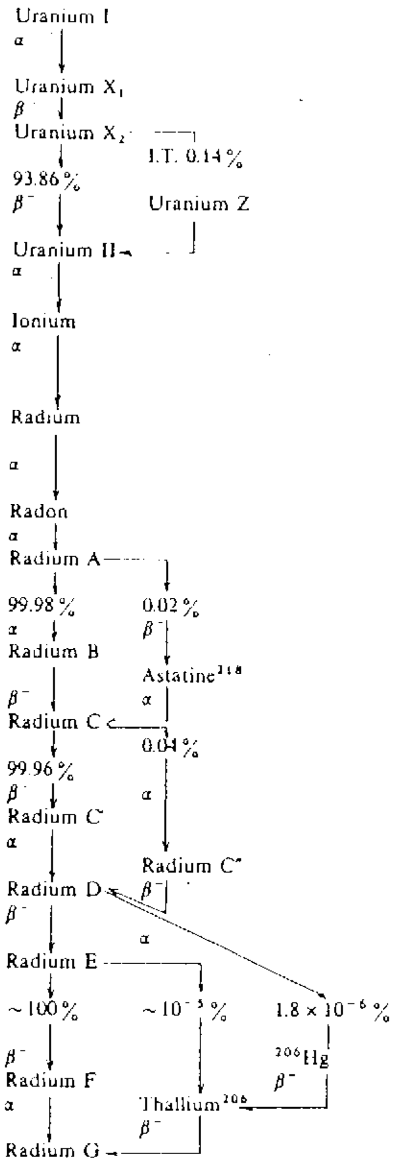


Fig 2.1-1 The uranium (4n+2) decay series

Table 2.1-1 The uranium(4n+2) decay series



Radioelement	Symbol	Half-life	Radiation	Alpha energy (MeV)	Abundance (per cent)	Beta end energy (keV)	Abundance (per cent)
Uranium I	^{238}U	4.468×10^9 y	α(β stable)	4.195 (α_0) 4.147 (α_1) 4.038 (α_2)	77 23 0 23		
Uranium X$_1$	^{234}Th	24.1 d	β⁻			191 ~103	81 19
Uranium X$_2$	^{234}Pa	1.18 m	β⁻			2290	98
Uranium Z	^{234}Pa	6.7 h	β⁻			530 1130 1300	66 13 ≤ 2
Uranium II	^{234}U	2.48×10^5 y	α(β stable)	4.768 (α_0) 4.717 (α_1) 4.600 (α_2)	72 28 0.3		
Ionium	^{230}Th	7.52×10^4 y	α(β stable)	4.682 (α_0) 4.615 (α_1) 4.476 (α_2) 4.437 (α_3)	76 24 0 12 0.03		
Radium	^{226}Ra	1602 y	α(β stable)	4.781 (α_0) 4.598 (α_1) 4.340 (α_2) 4.191 (α_3)	94.5 5.5 7×10^{-3} 1×10^{-3}		
Radon	^{222}Rn	3.825 d	α	5.486 (α_0) 4.983 (α_1)	~100 ~ 8×10^{-2}		
Radium A	^{218}Po	3.05 m	α and β⁻	6.110 (α_0)	(100)	330	(100)
Radium B	^{214}Pb	26.8 m	β⁻			1030 670	6 94
Astatine^{218}	^{218}At	2 s	α	6.70 (α_0) 6 65 (α_1)	94 6		
Radium C	^{214}Bi	19.7 m	α and β⁻	5.61 (α_0)	100	3260	(100)
Radium C′	^{214}Po	1.64×10^{-4} s	α	7.83 (α_0)	(100)		
Radium C″	^{210}Tl	1.32 m	β⁻			2300	(100)
Radium D	^{210}Pb	~22 y	β⁻ (α)	(3.7)	(1.8×10^{-8})	17 64	85 15
Radium E	^{210}Bi	5.02 d	β⁻ and α	4.93 (α_1) 4.89 (α_2) 4.59 (α_3)	60 34 5	1155	(100)
^{206}Hg	^{206}Hg	8.6 m	β⁻			1300	(100)
Radium F	^{210}Po	138.3 d	α	5.305	(100)		
Thallium^{206}	^{206}Tl	4.19 m	β⁻			1520	(100)
Radium G	^{206}Pb	—	stable				

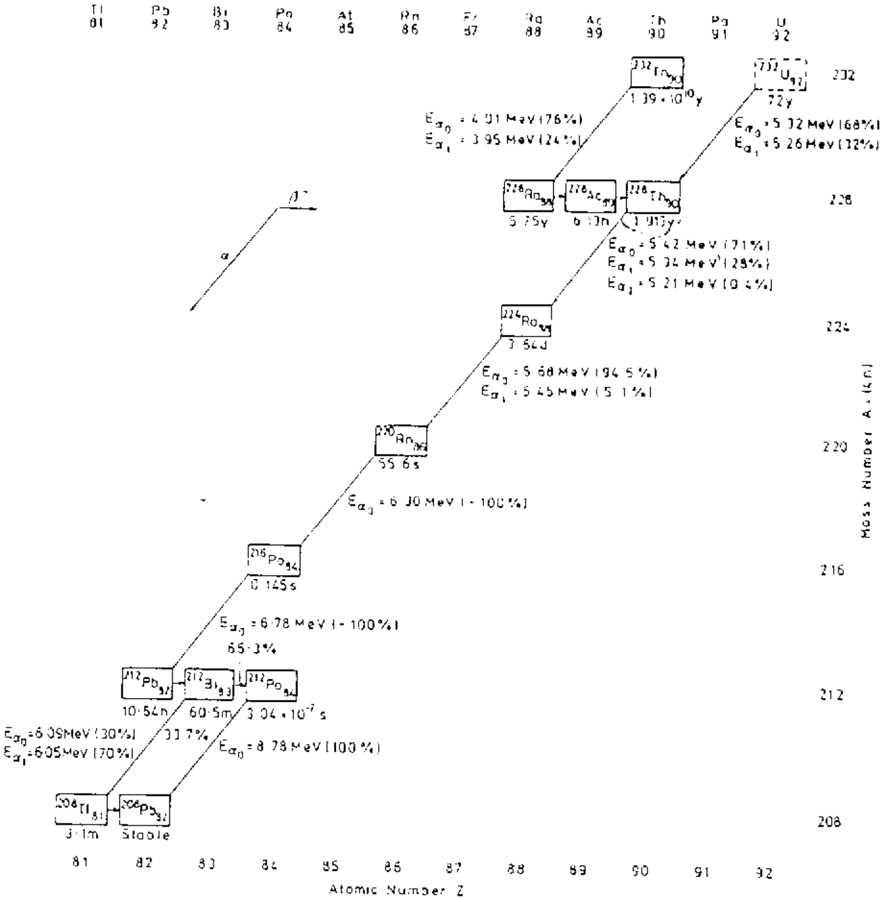


Fig 2.1-2/Table 2.1-2 The thorium(4n) decay series

Radioelement	Symbol	Half-life	Radiation	Alpha energy (MeV)	Abundance (per cent)	Beta end energy (KeV)	Abundance (per cent)
Thorium α ↓	^{232}Th	1.39×10^{10} y	α (β stable)	4.007 (α_0) 3.952 (α_1) 3.882 (α_2)	76 24 0.2		
Mesothorium 1 β^- ↓	^{228}Ra	5.75 y	β^-			55	100
Mesothorium 2 β^- ↓	^{228}Ac	6.13 h	β^-			2110	(100)
Radiothorium α ↓	^{228}Th	1.913 y	α(β stable)	5.421 (α_0) 5.338 (α_1) 5.208 (α_2) 5.173 (α_3) 5.137 (α_4)	71 28 0.4 0.2 0.03		
Thorium X α ↓	^{224}Ra	3.64 d	α(β stable)	5.684 (α_0) 5.447 (α_1)	94.5 5.5		
Thoron α ↓	^{220}Rn	55.6 s	α(β stable)	6.296 (α_0) 5.761 (α_1)	~ 100 ~ 0.[illegible]		
Thorium A α ↓	^{216}Po	0.145 s	α(β stable)	6.777 (α_0)	100		
Thorium B β ↓	^{212}Pb	10.64 h	β^-			580	(complex)
Thorium C 66.3 % β^- ↓ / 33.7 % α ↓	^{212}Bi	60.5 m	β^- and α	6.09 (α_0) 6.05 (α_1)	30 70	2250	(100)
Thorium C′ α ↓	^{212}Po	3.04×10^{-7} s	α(β stable)	8.780	100		
Thorium C″ β^- ↓	^{208}Tl	3.1 m	β^-			1800	(100)
Thorium D	^{208}Pb	—	stable				

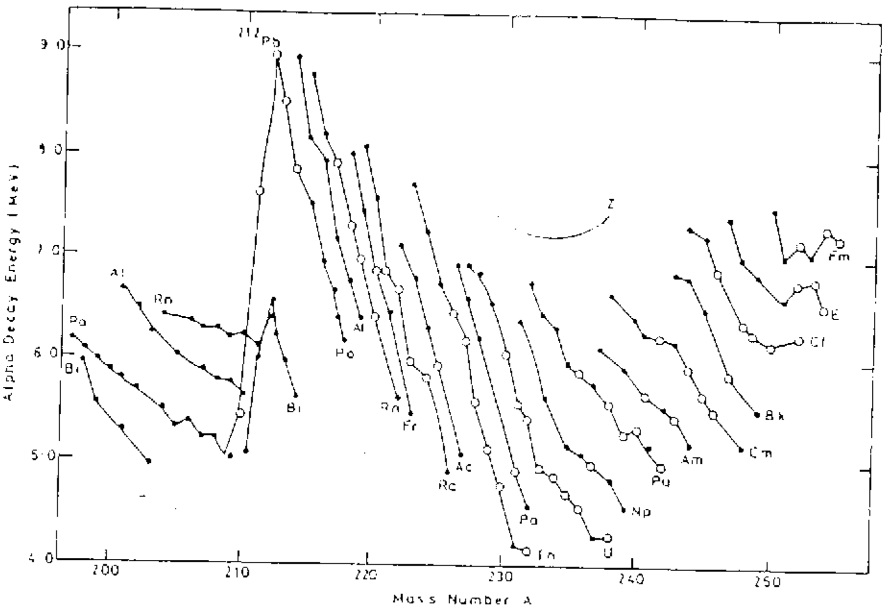


Fig 2.1-3 Energy released in the alpha-decay of heavy elements

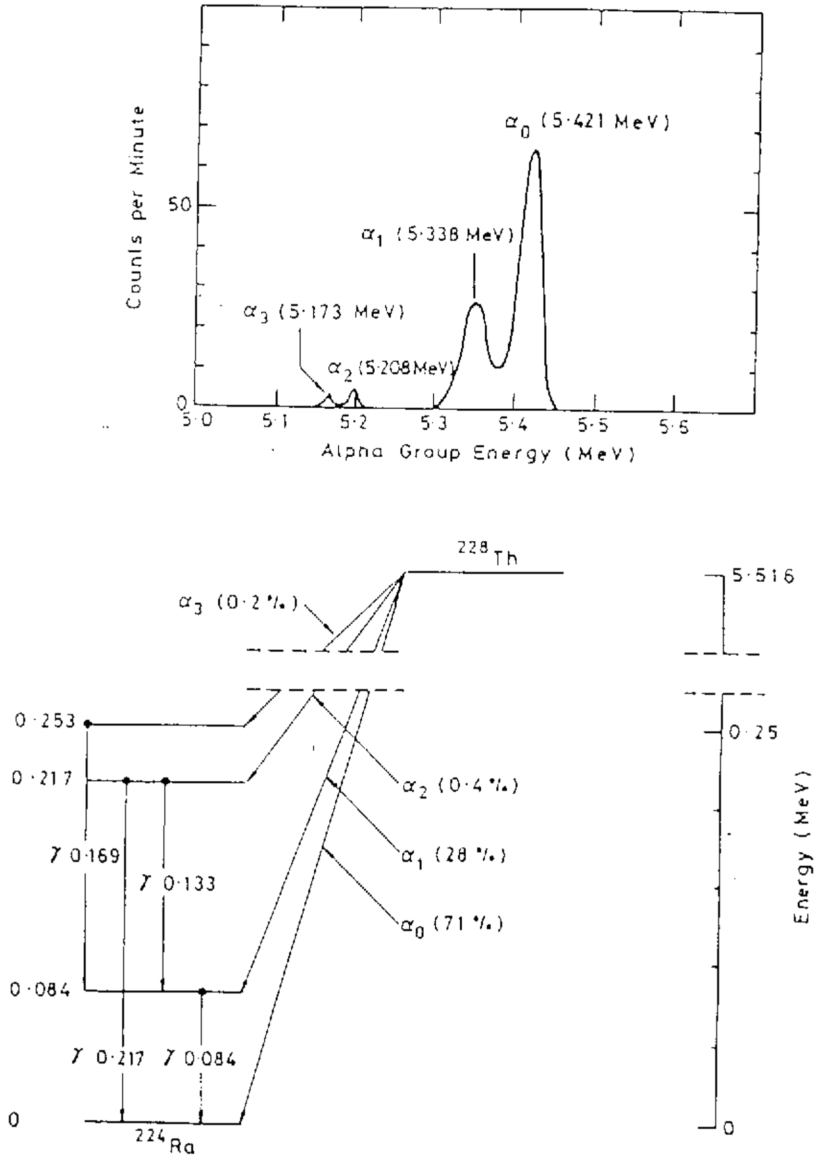


Fig 2.1-4 An example of fine structure of alpha particles spectra

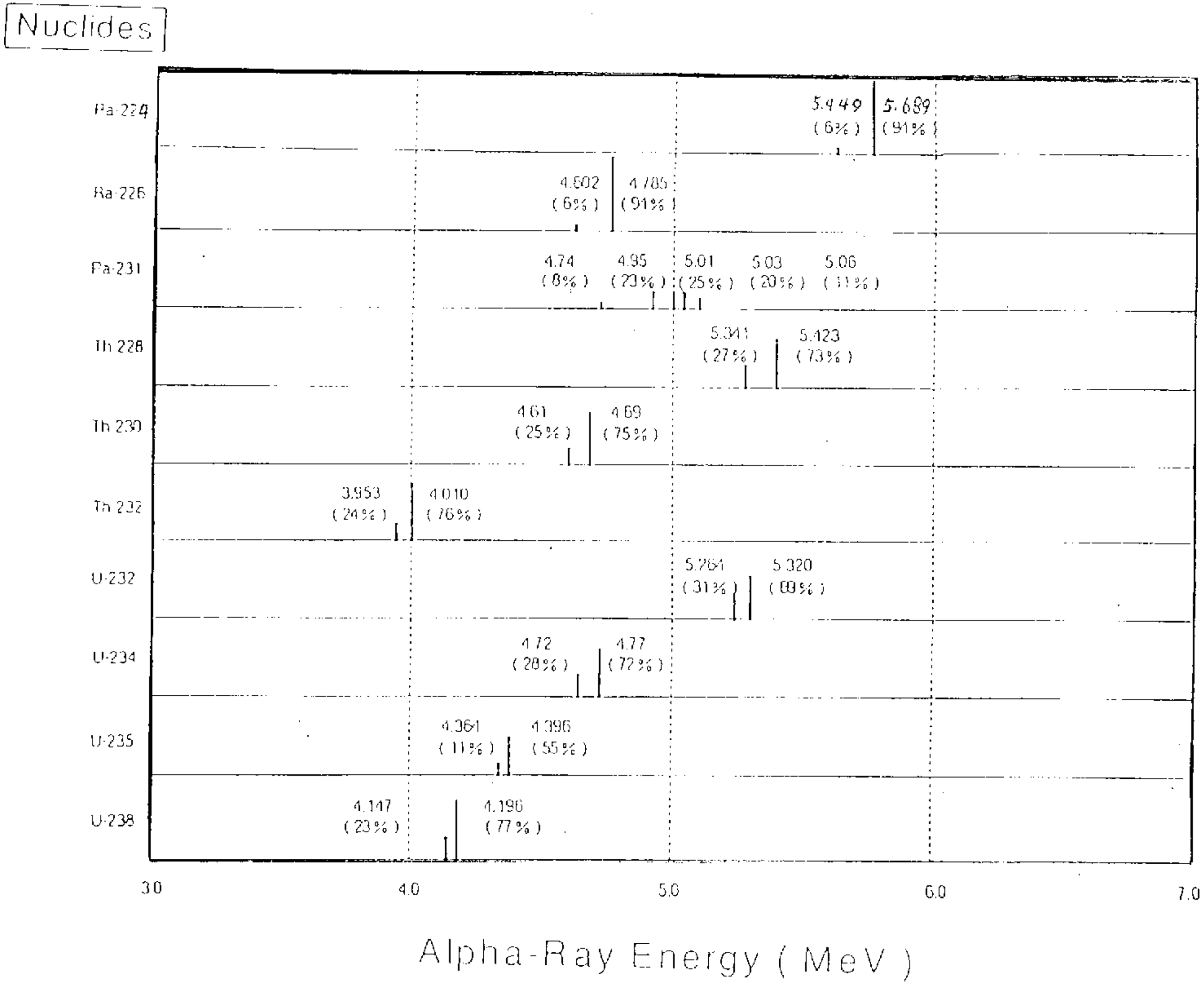


Fig 2.1-5 Alpha energy and intensity of natural nuclides

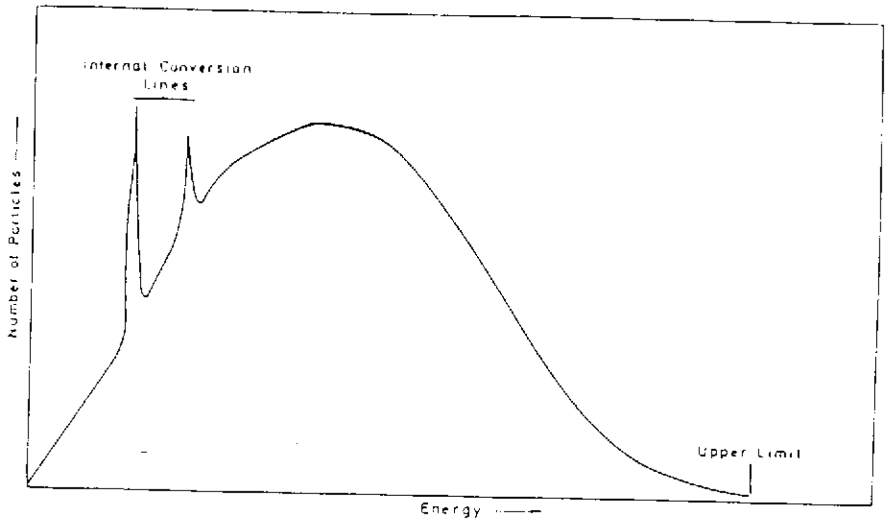


Fig 2.1-6 Beta decay spectrum

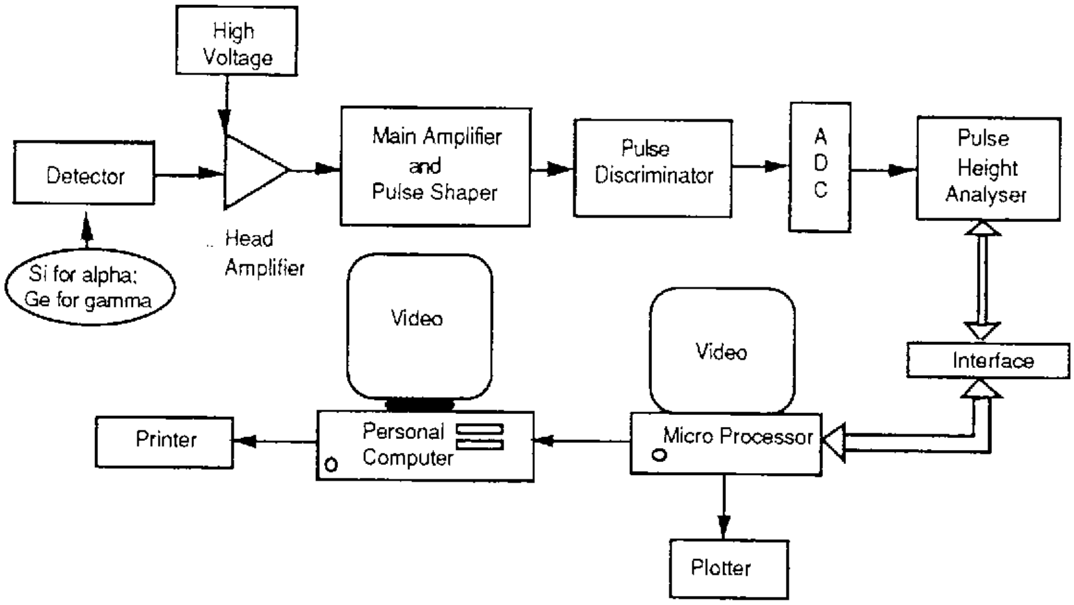


Fig2.1-7 Block diagram of alpha and gamma spectrometer

But this is a new model , some different from that . Especially ,the data processing system has been greatly improved and high pure Ge detector for high resolution gamma spectrometer makes the measurement more convenient , accurate and presice.

Table 2.1-3 Gamma rays over 100 kev emitted by equilibrium U-series

Isotope[c]	*γ-Energy (keV)*	*Intensity*[d]	*Isotope*[c]	*γ-Energy (keV)*	*Intensity*[d]
Th-234	113	0·42	Th-227	236	0·51
U-235	144	0·48	Pb-214	242	7·60
Ra-223	144	0·14	Th-227	256	0·28
Ra-223	154	0·24	Pb-214	259	0·80
U-235	163	0·22	Ra-223	269	0·61
U-235	186	2·52	Rn-219	271	0·45
Ra-226	186	3·90	Pb-214	275	0·70
U-235	205	0·22	Pb-214	295	18·9
Th-227	330	0·13	Pa-234M	1 001	0·83
Ra-223	338	0·12	Bi-214	1 052	0·33
Bi-211	351	0·60	Bi-214	1 070	0·26
Pb-214	352	36·3	Bi-214	1 104	0·16
Bi-214	387	0·31	Bi-214	1 120	15·0
Bi-214	389	0·37	Bi-214	1 134	0·25
Rn-219	402	0·29	Bi-214	1 155	1·70
Pb-211	405	0·18	Bi-214	1 208	0·47
Bi-214	406	0·15	Bi-214	1 238	6·10
Bi-214	427	0·10	Bi-214	1 281	1·50
Bi-214	455	0·28	Bi-214	1 304	0·11
Pb-214	462	0·17	Bi-214	1 378	4·30
Pb-214	481	0·34	Bi-214	1 385	0·80
Pb-214	487	0·33	Bi-214	1 402	1·50
Rn-222	511	0·10	Bi-214	1 408	2·60
Pb-214	534	0·17	Bi-214	1 509	2·20
Bi-214	544	0·10	Bi-214	1 539	0·53
Pb-214	580	0·36	Bi-214	1 543	0·34
Bi-214	609	42·8	Bi-214	1 583	0·73
Bi-214	666	1·40	Bi-214	1 595	0·30
Bi-214	703	0·47	Bi-214	1 600	0·34
Bi-214	720	0·38	Bi-214	1 661	1·16
Bi-214	753	0·11	Bi-214	1 684	0·24
Pa-234M	766	0·31	Bi-214	1 730	3·20
Bi-214	768	4·80	Bi-214	1 765	16·7
Pb-214	786	0·86	Bi-214	1 839	0·37
Bi-214	786	0·29	Bi-214	1 848	2·30
Bi-214	806	1·10	Bi-214	1 873	0·22
Bi-214	821	0·16	Bi-214	1 890	0·10
Bi-214	826	0·13	Bi-214	1 897	0·18
Pb-211	832	0·14	Bi-214	2 110	0·10
Bi-214	839	0·59	Bi-214	2 119	1·30
Pb-214	904	0·59	Bi-214	2 204	5·30
Bi-214	934	3·10	Bi-214	2 294	0·33
			Bi-214	2 448	1·65

---

[a] Photons with an intensity greater than 0·1%.

[b] *Note*: the U-235 decay series is included, but all intensities are recorded relative to 100 decays of the longest lived parent U-238. Thus, for example for every 100 decays of U-238 there will be 16·7 gamma-rays, of energy 1765 keV, from Bi-214 and 0·83 gamma-rays from Pa-234.

[c] Decaying isotope.

[d] Decays per 100 decays of the longest lived parent.

2.1.4 Analysis of uranium series in rocks and minerals

The rocks and minerals uranium contained are complicated for the analysis of uranium series nuclides because of low radioactivity and existing a large amount of matrix and interference among nuclides. One method is not enough for all insterested nuclides, so generally, alpha spectrometry and high resolution gamma spectrometry are required. For alpha spectrometry, the chemical separation and preconcentraction must be performed. And for gamma spectrometry, without chemical procedure, the high resolution gamma spectrometer and data processing techniques are essential. In this work, U-238, U-234, U-232, Th-230 and Th-228 are determined by alpha spectrometry; Pb-210, Pb-214, Bi-214, Th-234, Ra-226 and also U-234 are measured by gamma spectrometry. Total U concentraction in sample is gotten by both alpha and gamma spectrometries and Total Th concentraction in sample is obtained from alpha spectrometry. Of course, the ratios between interested nuclides can also be calculated from above data.

2.2 Alpha spectrometry

2.2.1 Reagents

1. Spike Tracer Stock solution : Made in France.It has been corrected according to calibration of uraninite ore standard. The chemical conditions were as follows:

U-232 Activity = 93.75 Bq/g (Aug.3, 1990)
Volume =20 cm^3
Density = 1.054 g/cm^3
Media = 1.65 N HNO_3

Radioactivity Equilibrium with Th-228 .

Diluted solution:The spike tracer used in the experiment was the solution diluted (Aug.3, 1990) from the stock solution to 500 ml in 2N HNO3 media,which activity was calculated as follows:

$$A_{(U-232)} = 93.75 \times 1.054 \times 20 / 500 \qquad \text{......................} \ 2.2.1-1$$
$$= 3.95 \text{ Bq/ml}$$

The relation activity between U-232 and Th-228 was shown in follwing:

$$\frac{A_{(Th-228)}}{A_{(U-232)}} = \frac{[Th-228]}{[Th-228] - [U-232]}$$
$$= \frac{T_{(U-232)}}{T_{(Th-228)} - T_{(U-232)}}$$
$$= 1.027$$

..................2.2.1-2

Consequently, the activity of Th-228 in diluted spike tracer was

$$A_{(Th-228)} = 1.027 \times 3.95 = 4.058 \text{ Bq/ml} . \qquad \text{.................} 2.2.1-3$$

2. HNO_3 , 8N,(3+11)
3. HCl , 10 N, 6 N,(1+11)
4. HF
5. $HClO_4$
6. H_2SO_4 ,(1+19)
7. $HN_3.H_2O$ (1+1)

8. $NaNO_3$,(50%)

9. TBP-CCl_4 , (10%)

10. Thymol Blue (0.1% in alcohol)

11. Strong Anion Exchange Resin :

Product information was shown as follows:

Catalog Number: AG1x8
Ionic Form: Chloride
Dry Mesh Size: 100-200
Diameter(micron):106-180
Total Capacity(meq/ml): 2.6
Capacity(meq/ml): 1.2
Moisture Content(%):39-48
Density(gm/ml): 0.75

All reagents used in the experiment were analytical grade.

2.2.2 . Apparatus

1. General chemical analysis apparatus,but special exchange column,shown in Fig2.2.2-1 .

2. Electrodeposition system: shown in Fig2.2.2-2.

3. Alpha spectrometer : Made in SEIKO EG&G,Japan ,shown in Fig2.2.2-3 , in which there are 8 semiconductor radiation detectors whose specifications are as follows :(1). Active area(normal) 450 mm^2; (2) Alpha resolution at 5.486 Mev :N/A kev;(3).Noise width :15.7 Kev;(4). Shaping time constant : 0.5 us; (5). Sensitive thickness :100 microns ;(6) Operating bias :100 volts; (7) .Norminal resistivity :3.8 k; (8) Electrode thickness :Au 40.0 ugm/cm^2,Al 50.0 ugm/cm^2; and each two detectors shares a 1024-channel pulse height analyser and its related parts.

4. Am-241 standard source disk: Made in Amersham International plc,UK.

Detailed description is given in the APPENDIX A of this report.

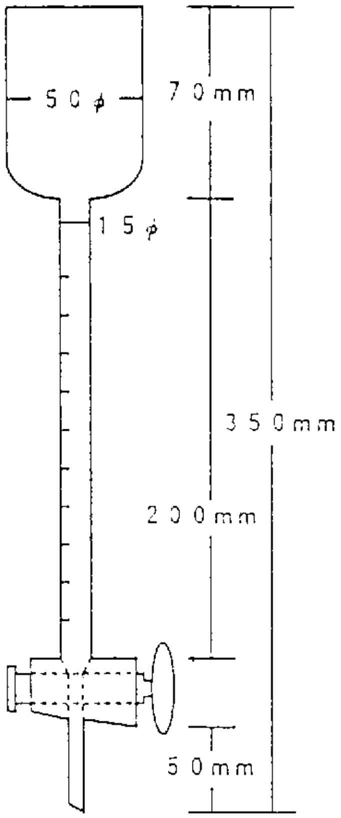
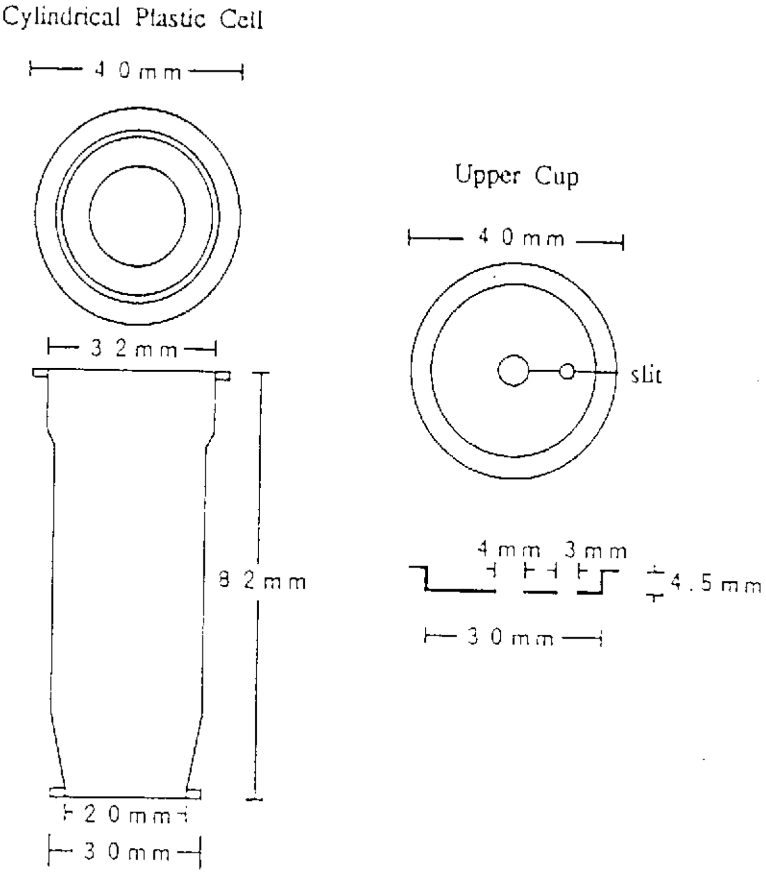
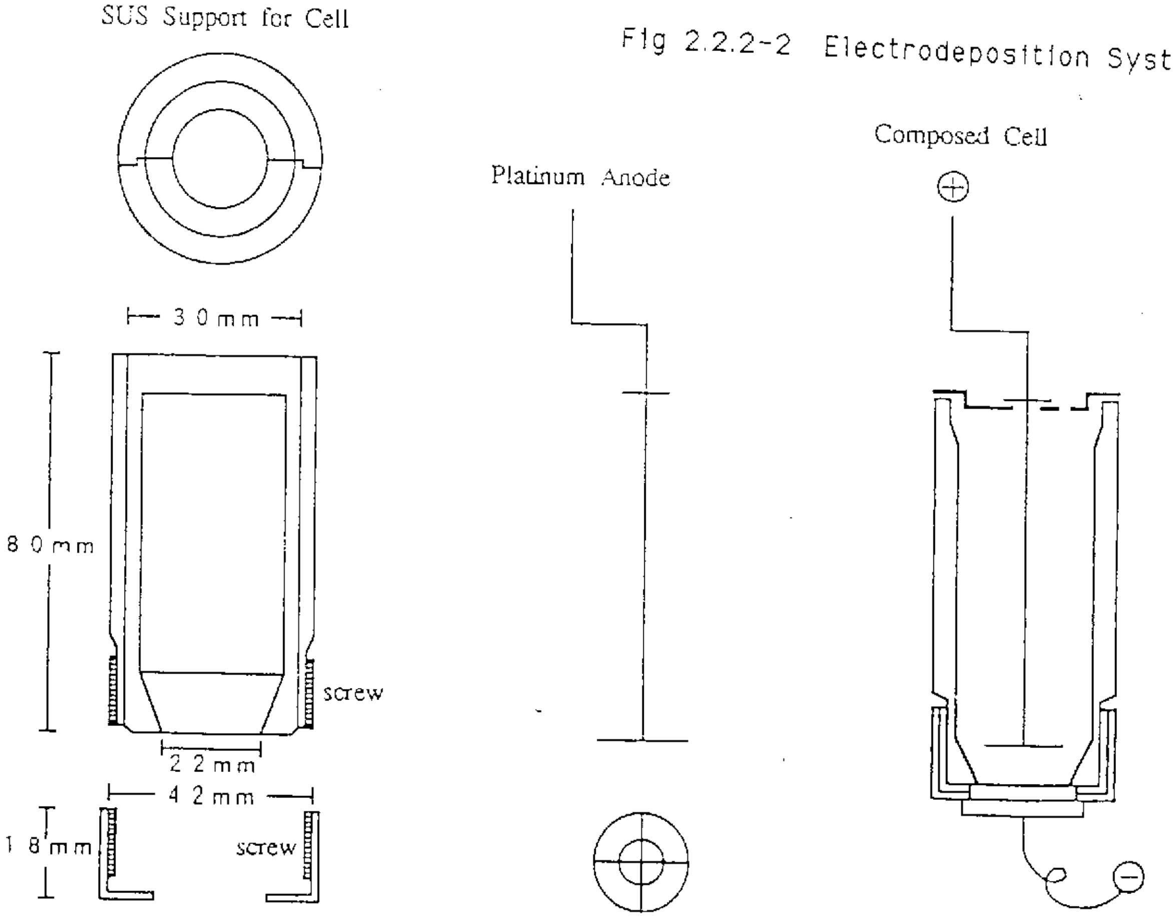


Fig 2.2.2-1 Ion Exchange Column Sizes



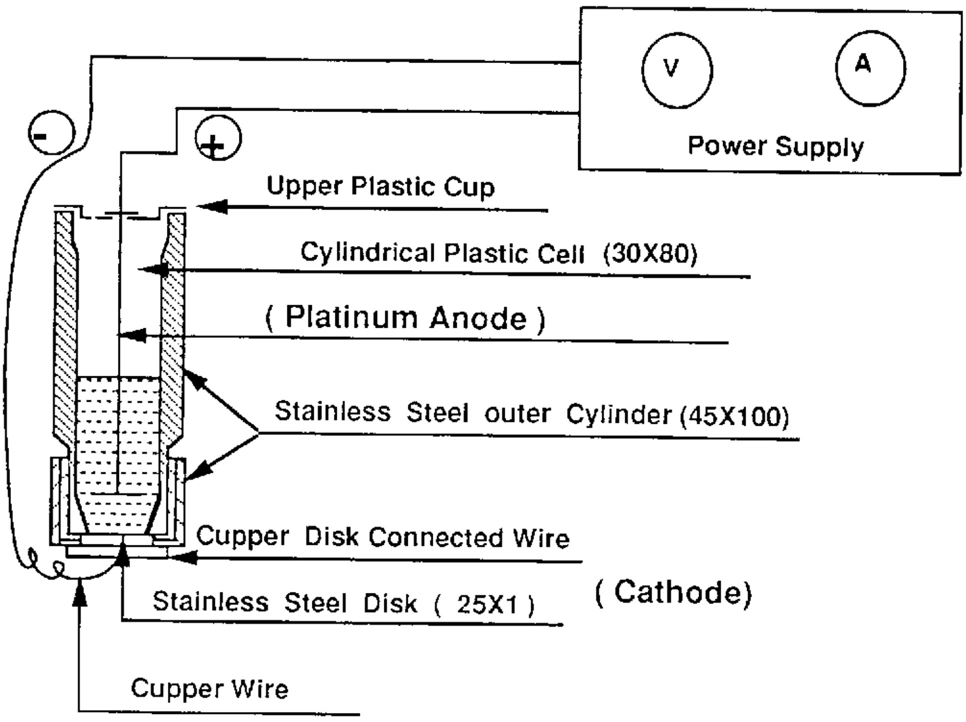
I. Disposable Plastic Cell

Fig 2.2.2-2 Electrodeposition System

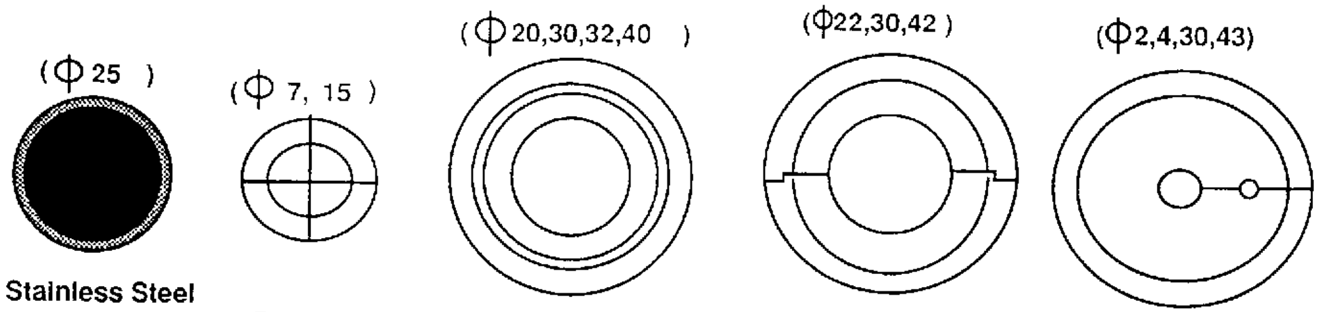


II. Assembly

III. System Cross Section View



a. Cross Section Diagram



Stainless Steel Disk Cathode

Pt Anode

Cylindrical Plastic Cell

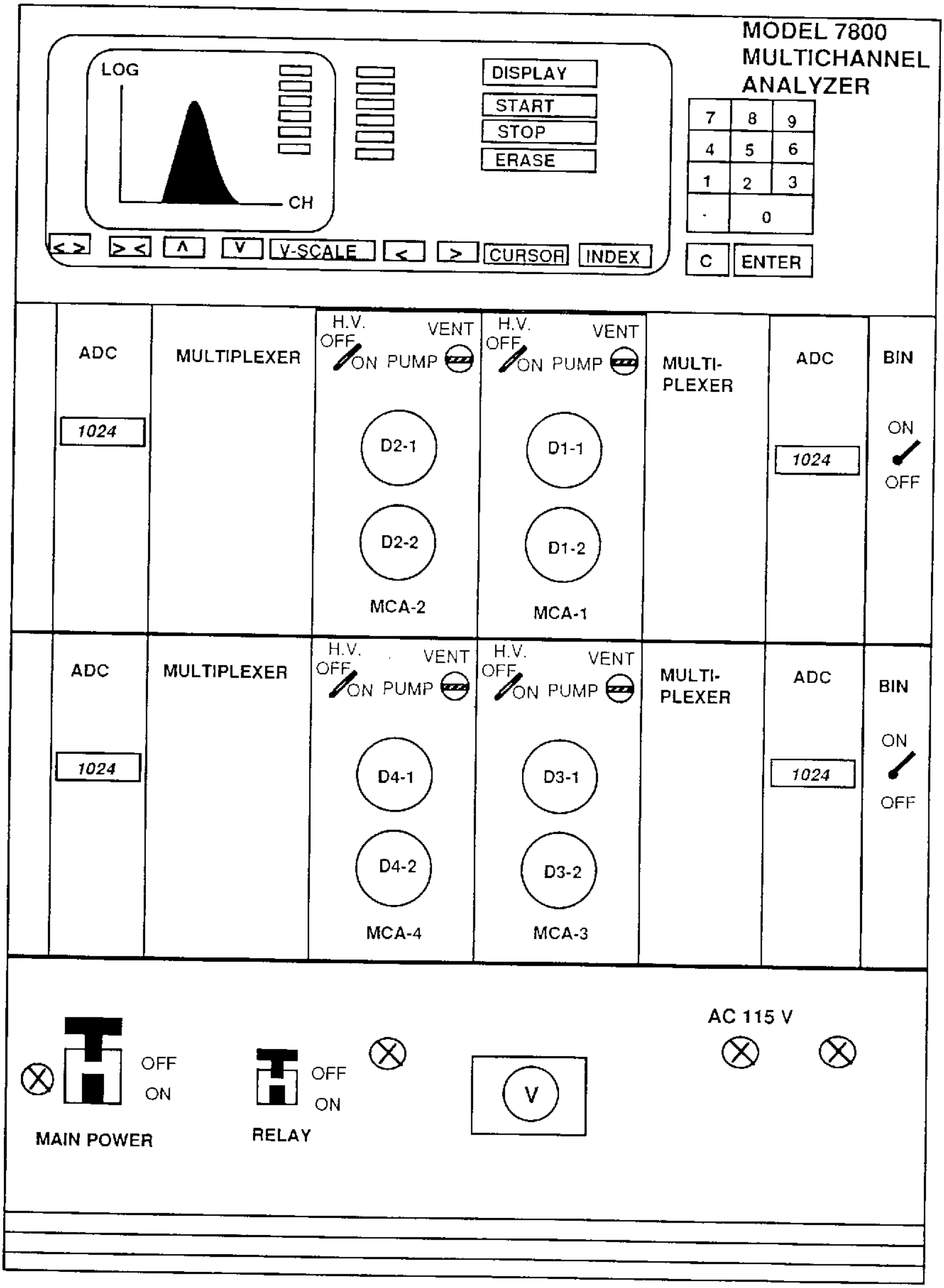
Stainless Steel Cylinder

Upper Plastic Cup

b. Outward View from Top

Fig 2.2.2-3 Alpha Spectrometer at PNC-Chubu Works

SEIKO EG & G (Outward View from Front)



NOTE:

MCA switch, PUMP switch, CUMP. ,switch in the back of it.

2.2.3 Chemical procedure

As described in 2.1.4, chemical treatment has to be performed for alpha spectrometry in order to separate and enrich uranium and thorium from other matrix elements. About this,there have been many methods[3,5,6] developed. However,the basic procedure is similiar , including sample decomposition, separation and preconcentration as well as source preparation. For sample decomposition , open mixed acids digestion and mixed ammonium salts flux[7] methods are usually used . In the experiment here(PNC-Chubu Works), the former was employed. And for separation and preparation , anion exchange , solvent extraction and extraction chromatograph methods are usually used. In the experiment here, the strong alkaline anion exchange resins (AG1x8) were used to separate (Cl-form) uranium fraction from thorium fraction and separate(NO_3^--form) thorium from other elements in thorium fraction ; TBP-CCl_4 extraction was used to separate uranium from other elements in uranium fraction. The separated U-contained solution and Th-contained solution were preconcentrated by means of evaporation. Finally, U-source disk and Th-source disk were prepared using electrodeposition technique ,which is the common mehtod for source preparation of uranium and thorium. The detailed chemical procedure was shown in Fig 2.2.3-1, in which some special descriptions were given as follows.

I. About samples and decomposition

Samples must be powdered to more than 200 mesh in order to decompose completely. The weight used(W) shoud be estimated according to the trace spiker activity(SPA) and the the estimated content of uranium(SC) such as from beta-gamma counting method as following formula:

$$W(g)=81 \times SPA(Bq) / SC(ppm) \quad .... 2.2.3-1$$

where, the coefficient "81" is the the uranium content of 1 Bq radioactivity intensity.

If somples contain more silica , the decomposition should be repeated 2 to 3 times, otherwise the result would be shifted out.

II. Preparation of exchange columns

1). Resin treatment

a). Commercial product AG1x8 resin 500 g was poured into 3-liter beaker and 2 L deionized water(later simply called water) was added into and mixed up as well as the upper clear water taken away.

b). 120 g NaOH was taken into 1 L water and mixed up to get NaOH solution,then poured into the frist beaker(a) loaded with resin and mixed up,then the upper clear water removed.

c). HCl(1+1) 2 L was added into the beaker(a) and then mixed up as well as the upper clear water removed.

d). 2 L water was added into the beaker(a) and mixed up and then the upper clear water removed. This procedure needs repeating 3 times.

e). Adequate water was added into the beaker(a) for storage.

2). Cl-form column

a). Prepare 10 columns and clean them. All pistons should be coated a layer of vaccum silicone grease.

b). Put a layer of glass wool into the bottom of each column and wash them with water several times.

c). Load the resin prepared in [1)] to the half line of each column and then wash down the resin from the upper side of the column with water.

d). Put a layer of glass wool on the upper side of the resin and tight it, then wash each column with water a few times.

e). Prepare HCl (10 M) 50 ml in 50 ml-beaker, then fristly, 5 ml of it was poured into the column,finally the left 45 ml was poured into the upper cup of the column. After the solution passing, the Cl-form column was ready to use just like the show of Fig2.2.3-1 .

3). NO_3^--form column

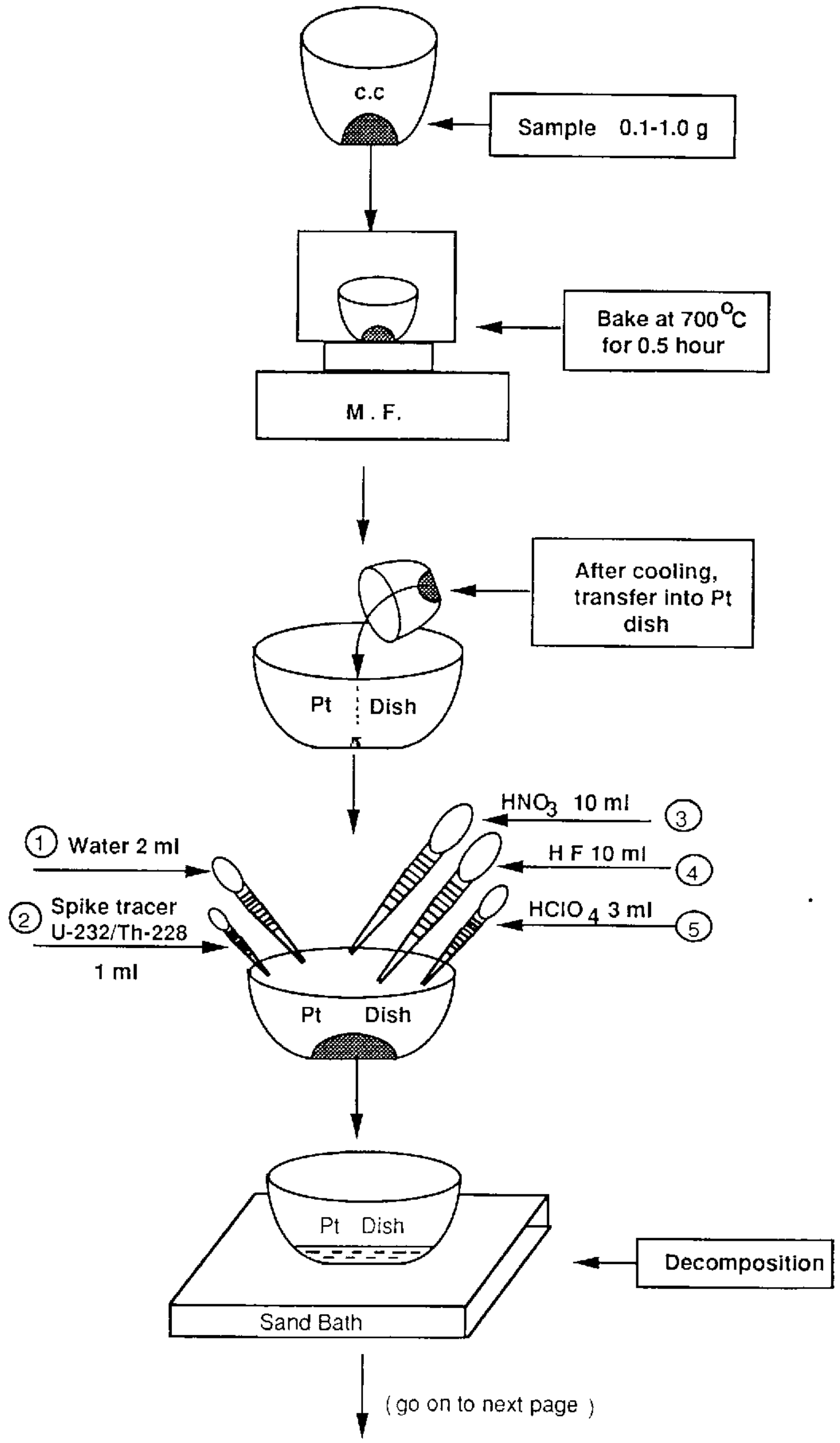
a). Repeat a)-d) procedure of the Cl-form column above.

b). Prepare HNO_3 (8 M) 50 ml in 50 ml-beaker, then fristly, 5 ml of it was poured into the column,finally the left 45 ml was poured into the upper cup of the column. After the solution passing, the NO_3^--form column was ready to use just like the show of Fig2.2.3-1 .

III. About electrodeposition

The electrodeposition system (shown in Fig2.2.2-1) shoud be assembled before use and disintegrated to wash after electrodeposition.The platinum anode shoud be set in the center of the cylindeical plastic cell, and the electric current shoud be checked and adjusted to preset value during the electrodeposition. But at the beginning, the electric current may be less than preset value,in this case, it is not necessary to adjust.

Fig 2.2.3-1 **Chemical Procedure for Alpha Spectrometry**



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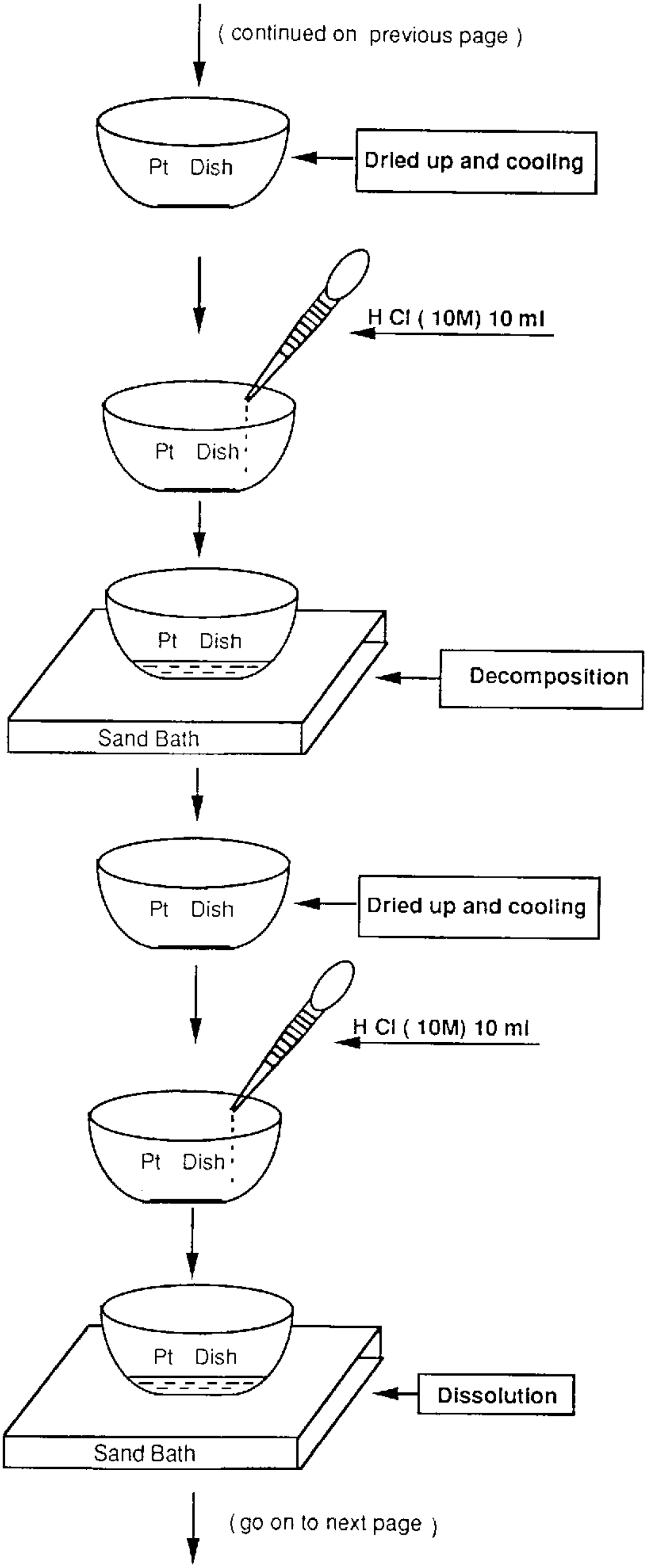
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Pt Dish
Dried up and cooling
H Cl (10M) 10 ml
Pt Dish
Pt Dish
Sand Bath
Decomposition
Pt Dish
Dried up and cooling
H Cl (10M) 10 ml
Pt Dish
Pt Dish
Sand Bath
Dissolution
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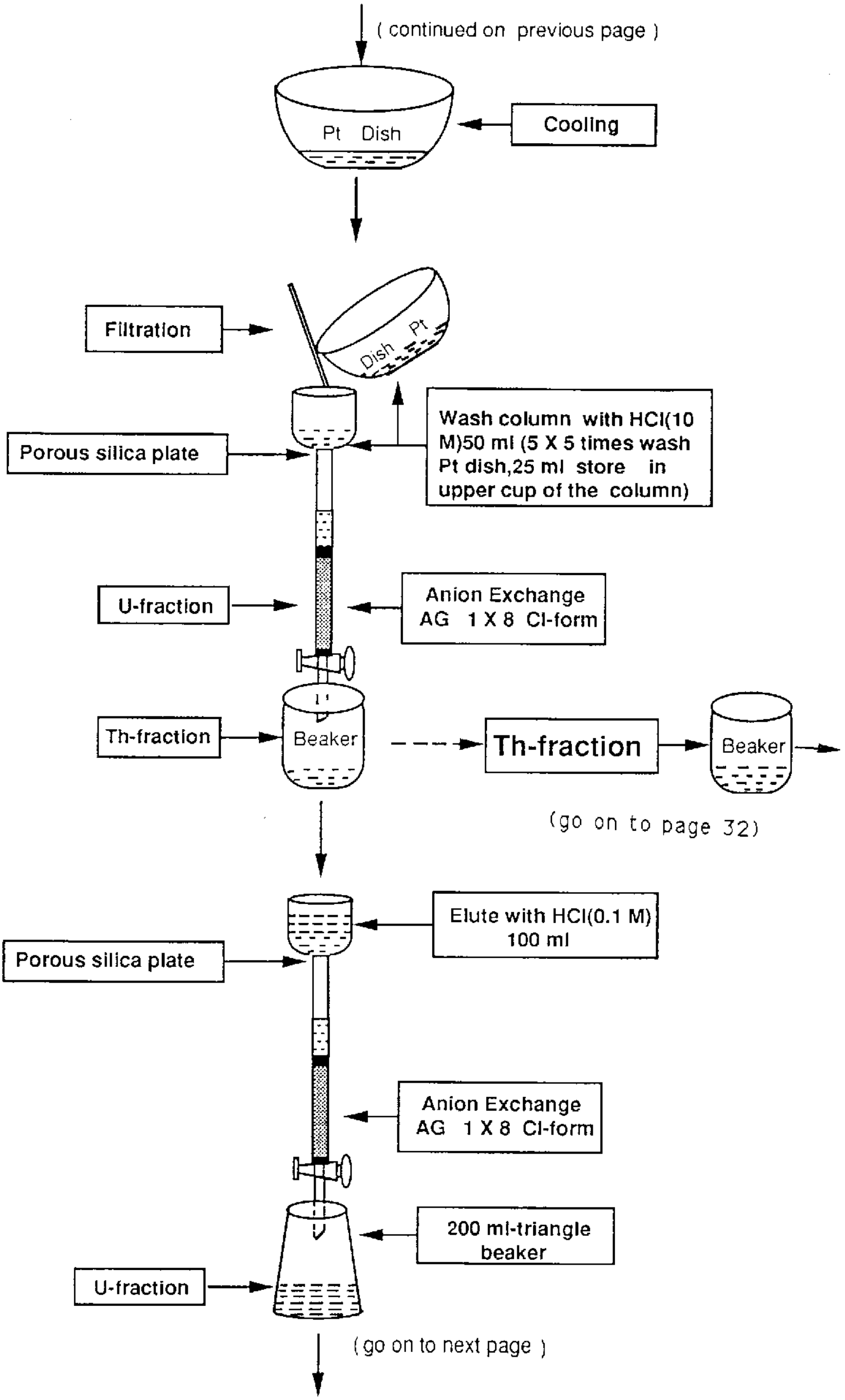

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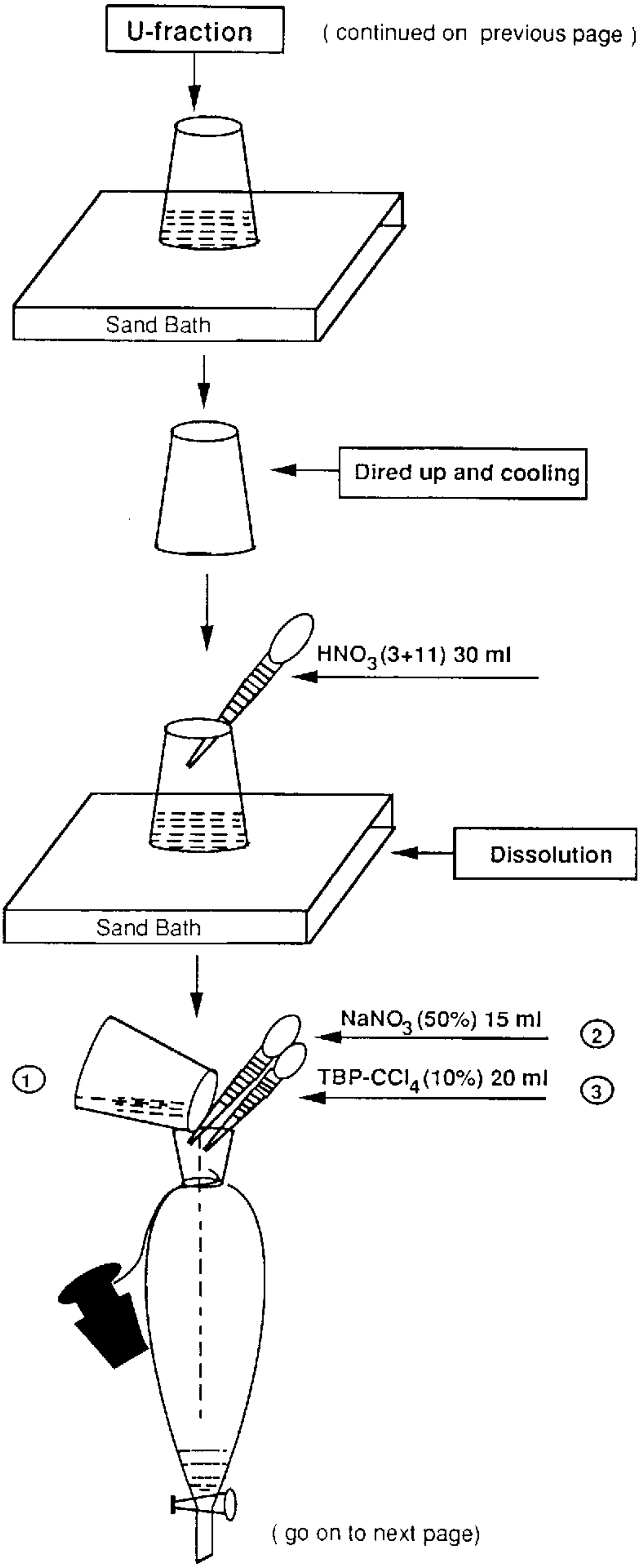

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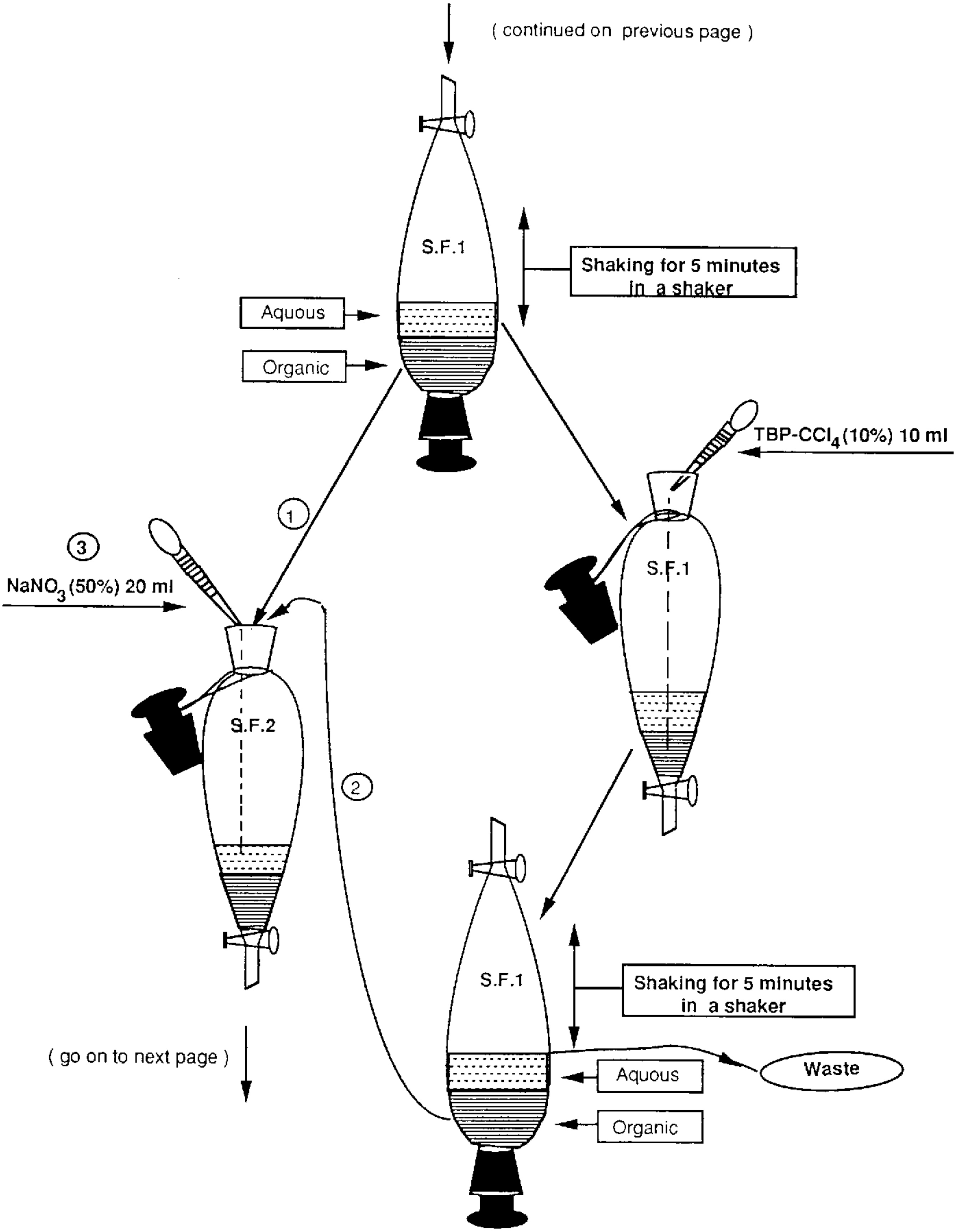

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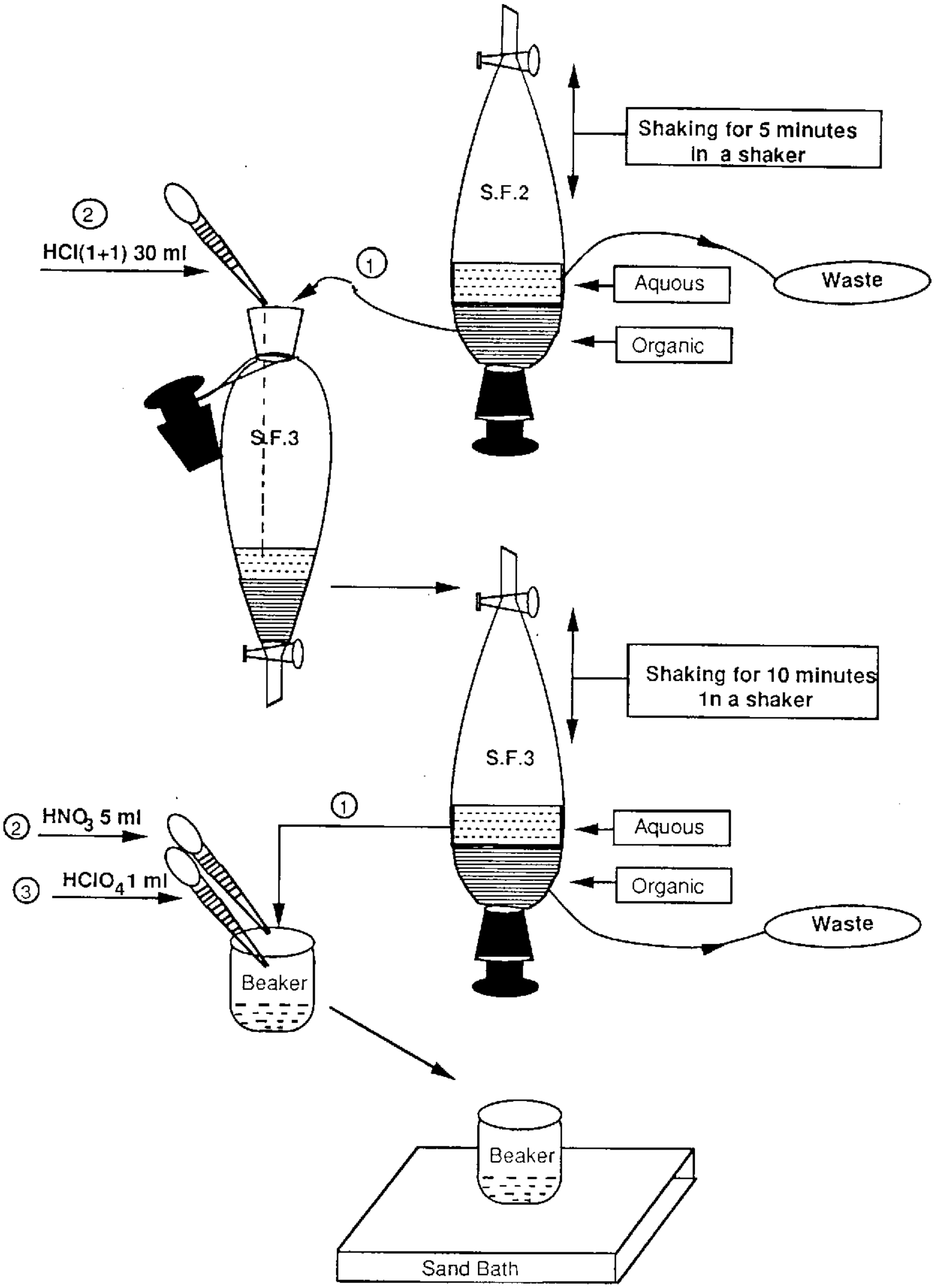

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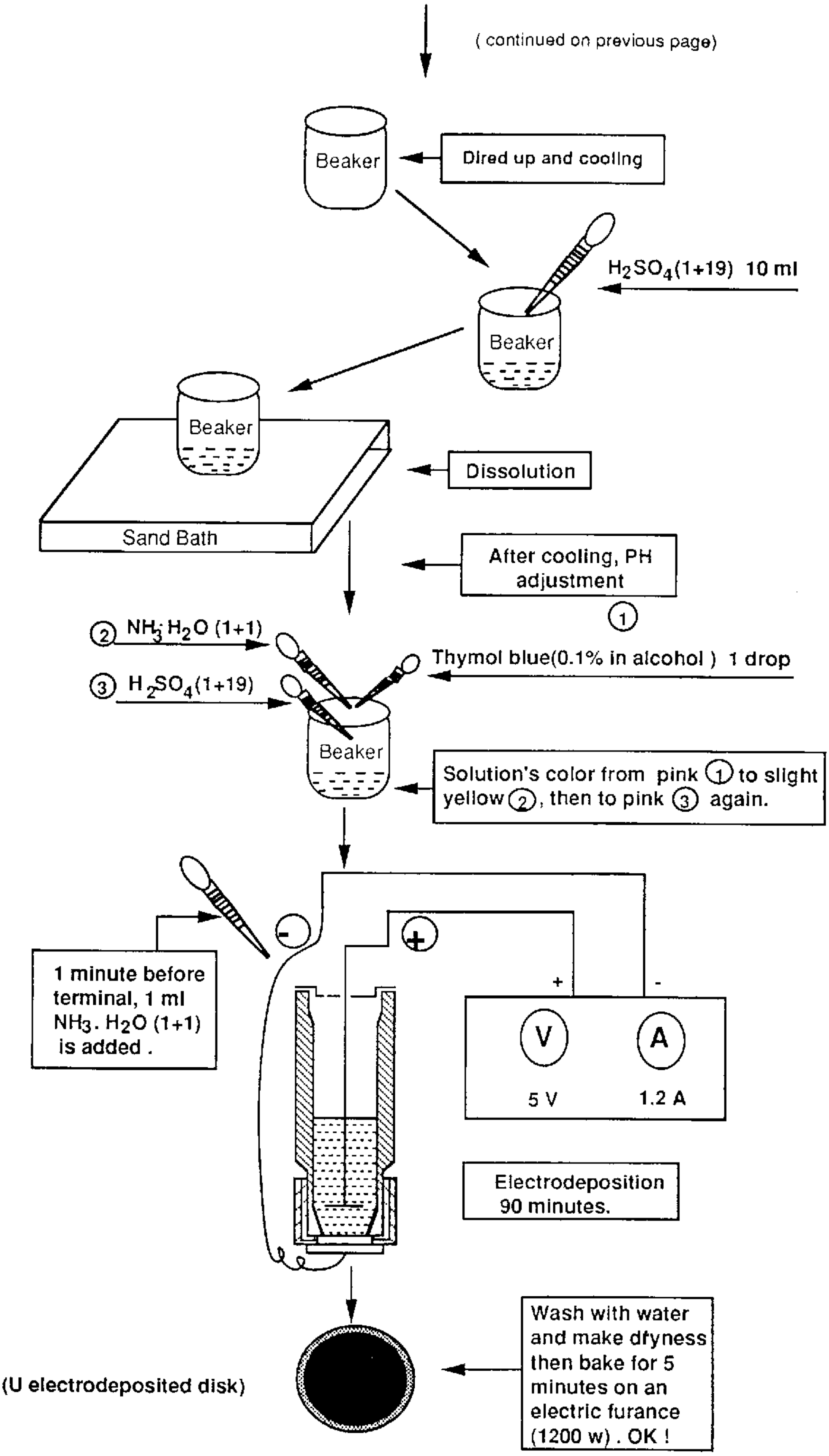

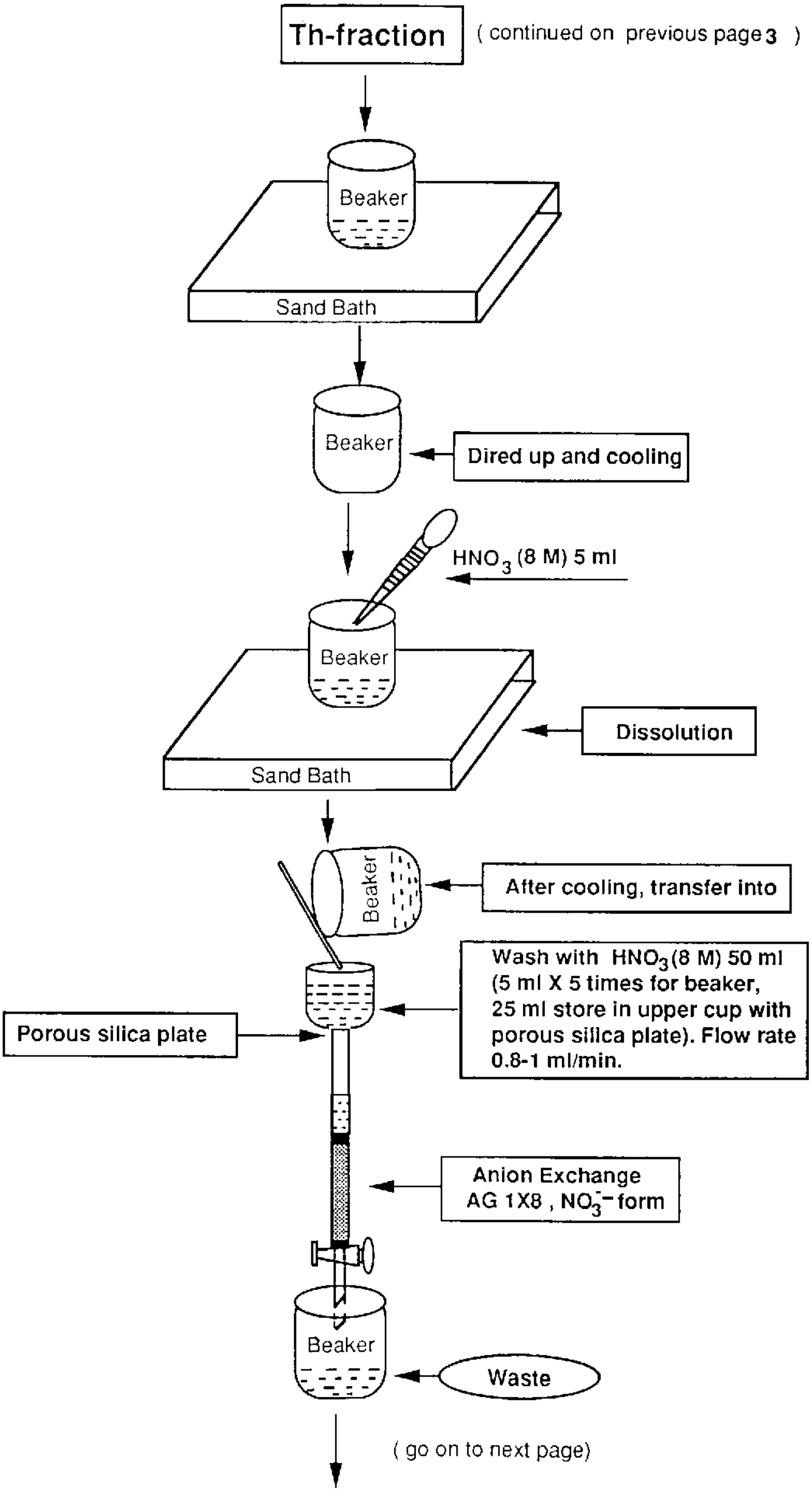

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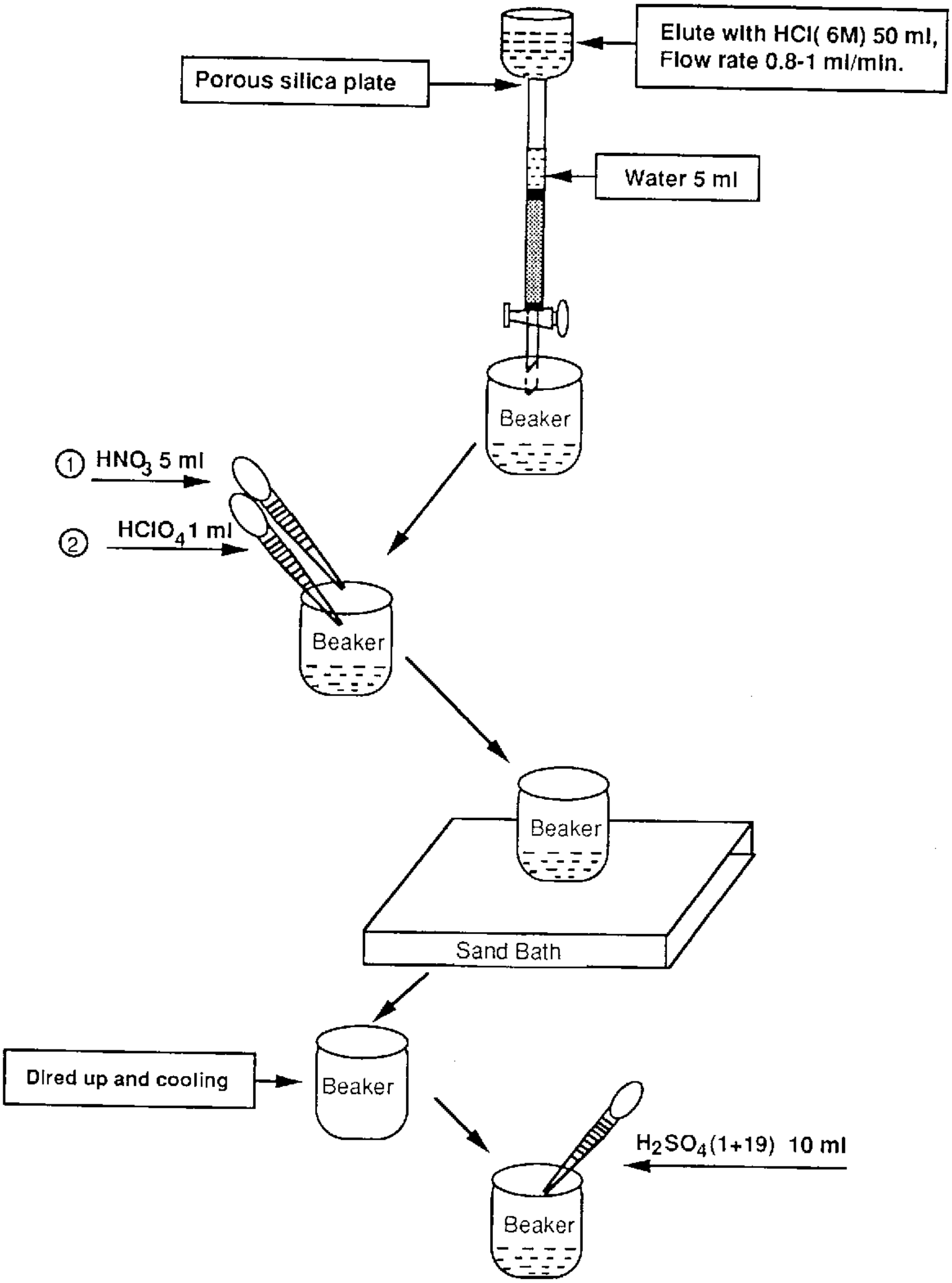

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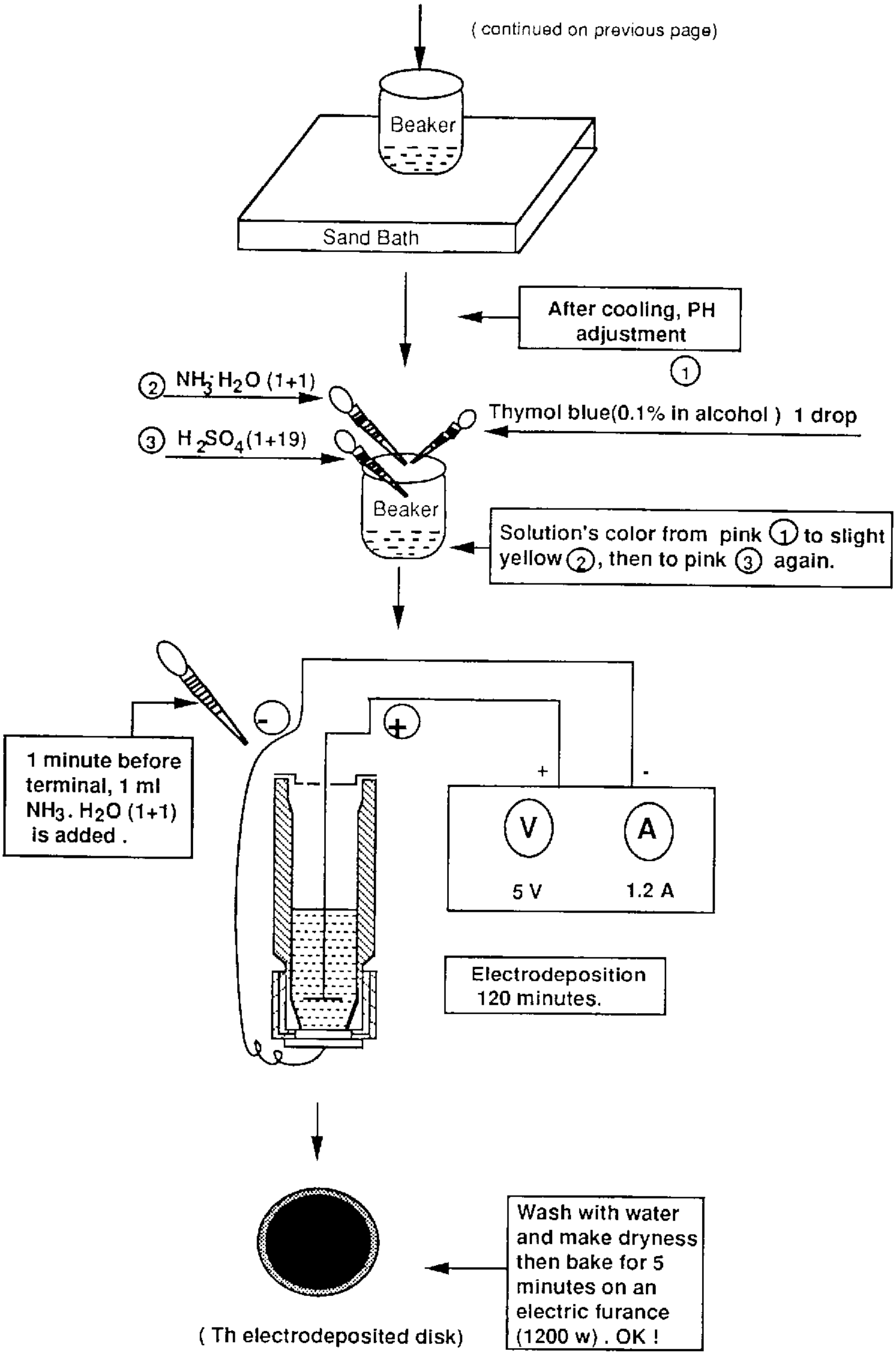


After cooling, PH adjustment

Thymol blue(0.1% in alcohol) 1 drop

Solution's color from pink ① to slight yellow ②, then to pink ③ again.

1 minute before terminal, 1 ml $NH_3 . H_2O$ (1+1) is added .

Electrodeposition 120 minutes.

Wash with water and make dryness then bake for 5 minutes on an electric furance (1200 w) . OK !

(Th electrodeposited disk)

2.2.4 Measurement

The measurement included measurement of background ,calibration of efficiency of detector using Am-241 standard source disk , measurement of sample and their data processing(In the later of this Chapter and Chapter 4 ,more details will be given). The procedure on it was shown in Fig2.2-5. In order to get correct results, the followings should be paid attention to.

1). Counting time

In order to maintain the counting error owing to the statistics at 1%, nuclide peaks in the alpha spectrum must contain 10000 counts. And the counting time required for such statistics depends on the activity of the source or the contents of uranium and thorium. So,for natural samples, the counting time should be at least 1000 minutes. Meanwhile, the blank source for background shoud be counted regularly for more than that time. Of course, the longer,the better.

2). Measurement of background

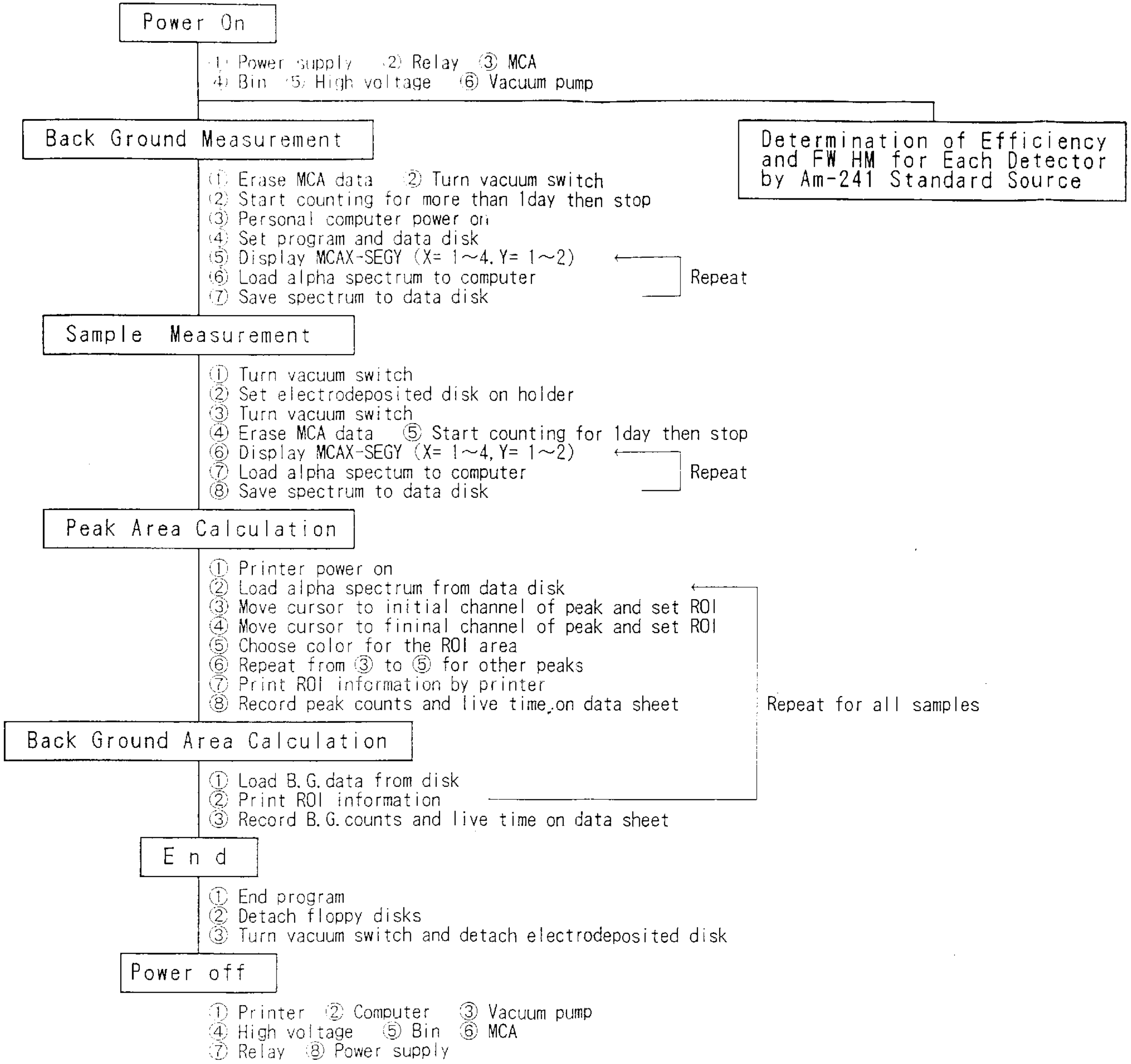
The measurement of background is essential,because the noise in the detector,ancillary electronic and incidental cosmic ray striking the detector will cause fixed background, and recoil nuclei drifting across the gap between the source and the detector will cause variable background. The most common recoil nuclei are those of U-232 spike daugnts,Th-228,Ra-224,Rn-220 and others when low activity samples are counted, blank sources are needed for the precise knowledge of variable background due to embedded recoil differ. For background measurement, the counting time should be at least 15 hours.In the experiment, the counting time for background was about 100 hours .

3). Calibration of efficiency of detector

Alpha spectrometry for quantitative anaysis must be known the intensity of alpha ray. But the spectrometer only records the counting ratios for each channel. If the full peak area needs to be calculated as the intensity of the alpha ray, the efficiency of the detector used must be konwn. Generally, a standard source , of which the energies and activities of nuclei are known, is employed to calibrate the detector(s). In the experiment, Am-241 standard source was used. From the measured spectrum, the efficiency of detector and its error as well as the resolution can be obtained.(In the later of this Chapter, more details can be seen).

4). Measurement of sample

When above procedure performed,the measurement of sample is quite simple. But the counting time must be enough just metioned above. The spectrum can be gotten automatically by the spectrometer.



Power On

① Power supply ② Relay ③ MCA
④ Bin ⑤ High voltage ⑥ Vacuum pump

Back Ground Measurement

① Erase MCA data ② Turn vacuum switch
② Start counting for more than 1day then stop
③ Personal computer power on
④ Set program and data disk
⑤ Display MCAX-SEGY (X= 1~4, Y= 1~2)
⑥ Load alpha spectrum to computer
⑦ Save spectrum to data disk

Repeat

Determination of Efficiency and FW HM for Each Detector by Am-241 Standard Source

Sample Measurement

① Turn vacuum switch
② Set electrodeposited disk on holder
③ Turn vacuum switch
④ Erase MCA data ⑤ Start counting for 1day then stop
⑥ Display MCAX-SEGY (X= 1~4, Y= 1~2)
⑦ Load alpha spectum to computer
⑧ Save spectrum to data disk

Repeat

Peak Area Calculation

① Printer power on
② Load alpha spectrum from data disk
③ Move cursor to initial channel of peak and set ROI
④ Move cursor to fininal channel of peak and set ROI
⑤ Choose color for the ROI area
⑥ Repeat from ③ to ⑤ for other peaks
⑦ Print ROI information by printer
⑧ Record peak counts and live time on data sheet

Repeat for all samples

Back Ground Area Calculation

① Load B.G. data from disk
② Print ROI information
③ Record B.G. counts and live time on data sheet

E n d

① End program
② Detach floppy disks
③ Turn vacuum switch and detach electrodeposited disk

Power off

① Printer ② Computer ③ Vacuum pump
④ High voltage ⑤ Bin ⑥ MCA
⑦ Relay ⑧ Power supply

Fig 2.2.4-1 Procedure of Measurement for Alpha Spectrometry

2.2.5 Analysis of alpha spectra and calculation

From the measurement, three kinds of spectra , background spectrum, Am-241 standard spectrum and samples spectra(an example shown in APPENDIX B) , were obtained and saved in the floppy disk of personal computer which connected with main system of alpha spectrometer . Using the software employed , the data of peaks of nuclei in the region of interest(ROI) of the spectrum displayed, such as counting time,peak number,start channel,stop channel,peak counts, int counts and net counts(that means the background has been minus from int counts), can be printed out . These data will be processed using another personal computer system (indepentent from alpha spectrometer). At PNC Cbubu Works, the Macintosh Plus was used. For more information about it, see Chapter 5.

1). Efficiency calculation

The efficiency (E) calculation is based on following formula:

$$E(\%)=(\ P_s/t_s - P_b/t_s)\quad \times\ (100/A)\ \times\ (100/B) \ldots\ldots\ldots\ldots 2.2.5\text{-}1$$

where, P_s is Peak Counts from Am-241 standard spectrum in Am-241 channels; t_s is Am-241 Counting Time(sec); P_b is Background Counts from background spectrum in Am-241 channels; t_b is Background Counting Time(sec);B is Branching Ratio; A is Activity of Am-241 standard on counted date , calculated as following:

$$A=A_0 . e^{-(\ln 2/T)\times t} \quad \ldots\ldots\ldots\ldots\ldots\ldots 2.2.5\text{-}2$$

where, A_0 is the Activity of Am-241 on certificated date ;
T is Half life(sec) ; and t is Time(sec) from certificated date to counted date. The error of efficiency(dE) is expressed as:

$$dE=E\ \times\ SQRT[\ (dN/N)^2 + (dA/A)^2\ ] \ldots\ldots\ldots\ldots 2.2.5\text{-}3$$

where, dA is the error of activity of Am-241; N is the net counting ratio and dN is its error expressed as:

$$N=P_s/t_s - P_b/t_s \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2.2.5\text{-}4$$

$$dN=SQRT\ (P_s/t_s{}^2 - P_b/t_s{}^2)\ldots\ldots\ldots\ldots 2.2.5\text{-}5\quad .$$

According to above expressions, the computer program,which can give the all data required , can be made using Microsoft Excel application software.

2). Relation between energy and channel

Still using Am-241 standard spectrum, there are 3 important alpha particles whose energies are shown in (Table 2.2.5-1). And from the spectrum, the peak channel number of each full energy peak can be read , then using the data to make a calibration curve between energy and channel. The calibration curve should be a linear curve which can be expressed as:

$$\text{Channel}=a+b\ \text{Energy} \quad \ldots\ldots\ldots\ldots 2.2.5\text{-}6.$$

Of course ,the equation can easily be obtained .

Table 2.2.5-1 Radionuclide and its energies

Radionuclide	energies(Mev)	Full energies(Mev)
Am-241	5.442(12.5%) ,5.484(85.2%)	5.463
Cm-244	5.783(23.6%) ,5.806(76.4%)	5.801
Pu-239	5.103(11%),5.142(15%),5.155(73%)	5.147

3). Resolution of detector

From the Am-241 standard spectrum ,the resolution od detector can be calculated as follows:

$$R(\%)= \frac{\Delta E}{E} \times 100 \quad \ldots\ldots\ldots 2.2.5\text{-}6$$

where , ΔE represents the energy of FWHM, E represents the energy in the largest distribution of alpha particles ,shown in Fig2.2.5-1

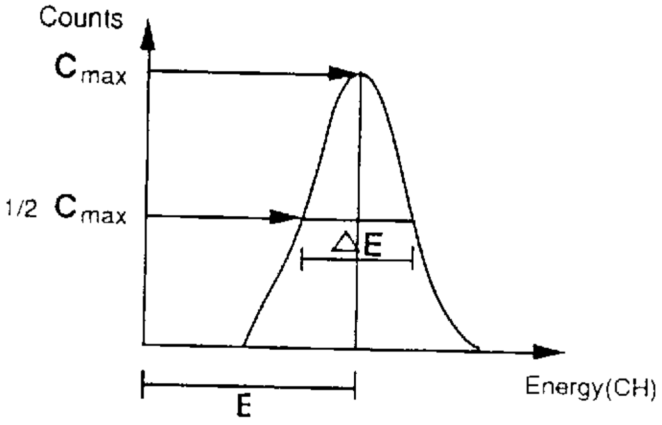


Fig 2.2.5-1 Resolution of Detector

4). Activities of nuclei and their errors

According to the relation between energy and channel [above 2)], the known energies' interested nuclei can be pasted in the alpha spectrum of sample and all required data just metioned above can be printed out. Then from those data, the following calculation formulae (from Formula 2.2.5-8 to 2.2.5-34), which are easy to be made a computing program using Microsoft Excel application software, can be operated in the Macintosh Plus personal computer system. And finally, the results can be displayed in the screen or printed out in the laserwriter. The symbols used in the formulae were listed in Table 2.2.5-2.

2.2.6 Results

The efficiencies of the detectors used were shown in Table2.2.6-1. The relation between energies and channels were given in Fig 2.2.6-1. And the analytical results of 15 rocks and minerals samples which were taken from China were listed in Table 2.2.6-2.

Table 2.2.5-2 Symbols used from Formula 2.2.5-8 to 2.2.5-34

Symbols (Index)		Explanation
$A_{\#\#\#}$		Activity (Bq/g)of nuclide "###"
$A_{\#\#\#/@@@}$		Activity (Bq/ml) of nuclide "###" on date "@@@"
B#T	#=U,Th	Background counting time of nuclei "#"
BUn	n=2,4,8	Background counts of U-23n
BRa4		Background counts of Ra-224
BThn	n=0,2,8	Background counts of Th-230,Th-232 and Th-228
BThT		Background counting time of Th-fraction
BUn	n=2,4,8	Background counts of U-23n
BUT		Background counting time(sec) of U-fraction
DTn	n=1	Certified date of spike tracer
	n=2	Sample weighing date
	n=3	U-Th separated date
	n=4	Counted date of Th-fraction
E$$$		Error of physic item "$$$"
R&&&		Ratio of physic item " &&&"
Thn	n=0,2,8	Peak counts of Th-230,Th-232 and Th-228
ThRn	n=0,2,8	Count rate of Th-230,Th-232 and Th-228
ThT		Counting time(sec) of Th-fraction
Th_{ppm}		Th content(ppm) in sample
Un	n=2,4,8	Peak counts of U-23n
URn	n=2,4,8	Counting rate of U-23n
U_{ppm}		U content(ppm) in sample
UT		Counting time(sec) of U-fraction
VOL		Added volume(ml) of spike tracer
WT		Sample weight(g)
Y#(%)	#=U,Th	Chemical yield of "#"

$$A_{U\text{-}232/DT3} = A_{U\text{-}232/DT1} \times e^{-\frac{\ln 2}{365.25 \times 71.79} \times (DT3-DT1)} \qquad .....2.2.5\text{-}8$$

$$A_{Th\text{-}228/DT2} = 1.027\, A_{Th\text{-}228/DT1} \times e^{-\frac{\ln 2}{365.25 \times 71.79} \times (DT2-DT1)} \qquad ...2.2.5\text{-}9$$

$$A_{Th\text{-}228/DT4} = A_{Th\text{-}228/DT2} \times e^{-\frac{\ln 2}{365.25 \times 1.913} \times (DT4-DT2)} \qquad ...2.2.5\text{-}10$$

$$UR8 = \frac{U8}{UT} - \frac{BU8}{BUT} \qquad ....2.2.5\text{-}11$$

$$UR4 = \frac{U4}{UT} - \frac{BU4}{BUT} \qquad ....2.2.5\text{-}12$$

$$UR2 = \frac{U2}{UT} - \frac{BU2}{BUT} \qquad ....2.2.5\text{-}13$$

$$ThR0 = \frac{Th0}{ThT} - \frac{BTh0}{BThT} \qquad ....2.2.5\text{-}14$$

$$ThR2 = \frac{Th2}{ThT} - \frac{BTh2}{BThT} \qquad ....2.2.5\text{-}15$$

$$ThR8 = \frac{Th8}{ThT} - \frac{Th2}{ThT} - \frac{5.5 \times Ra4}{94.5 \times ThT} - \frac{BTh8}{BThT} \qquad ......2.2.5\text{-}16$$

$$EThR8=\sqrt{\frac{Th8}{ThT^{2}}+\frac{Th2}{ThT^{2}}+\frac{5.5xRa4}{94.5xThT^{2}}+\frac{BTh8}{BThT^{2}}} \qquad \text{....2.2.5-17}$$

$$A_{U-238}=UR8\times A_{U-232/DT3}\times\frac{VOL}{UR2\times WT} \qquad \text{.......2.2.5-19}$$

$$A_{U-234}=UR4\times A_{U-232/DT3}\times\frac{VOL}{UR2\times WT} \qquad \text{......2.2.5-20}$$

$$A_{Th-232}=ThR2\times A_{Th-228/DT4}\times\frac{VOL}{ThR8\times WT} \qquad \text{.....2.2.5-21}$$

$$A_{Th-230}=ThR0\times A_{Th-228/DT4}\times\frac{VOL}{ThR8\times WT} \qquad \text{....2.2.5-22}$$

$$EThR8=\sqrt{\frac{Th8}{ThT^{2}}+\frac{Th2}{ThT^{2}}+\frac{5.5xRa4}{94.5xThT^{2}}+\frac{BTh8}{BThT^{2}}} \qquad \text{...2.2.5-23}$$

$$EA_{U-238}=A_{U-238}\times$$

$$\sqrt{\frac{U2\times BUT^{2}+BU2\times UT^{2}}{(U2\times BUT-BU2\times UT)^{2}}+\frac{U8\times BUT^{2}+BU8\times UT^{2}}{(U8\times BUT-BU8\times UT)^{2}}+\frac{EA_{U-232}}{A^{2}_{U-232/DT3}}}$$

$$\text{...........2.2.5-24}$$

$$EA_{U\text{-}234} = A_{U\text{-}234} \times \sqrt{\frac{U2 \times BUT^2 + BU2 \times UT^2}{(U2 \times BUT - BU2 \times UT)^2} + \frac{U4 \times BUT^2 + BU4 \times UT^2}{(U4 \times BUT - BU4 \times UT)^2} + \frac{EA_{U\text{-}232}}{A^2_{U\text{-}232/DT3}}}$$

........2.2.5-25

$$EA_{Th\text{-}230} = A_{Th\text{-}230} \times \sqrt{\left(\frac{EThR8}{ThR8}\right)^2 + \frac{Th0 \times BThT^2 + BTh0 \times ThT^2}{(Th0 \times BThT - BTh0 \times ThT)^2} + \left(\frac{EA_{U\text{-}232}}{A_{U\text{-}232/DT3}}\right)^2}$$

.........2.2.5-26

$$RAT48 = \frac{A_{U\text{-}234}}{A_{U\text{-}238}} = \frac{UR4}{UR8}$$

..................2.2.5-27

$$ERAT48 = RAT48 \times \sqrt{\frac{U8 \times BUT^2 + BU8 \times UT^2}{(U8 \times BUT - BU8 \times UT)^2} + \frac{U4 \times BUT^2 + BU4 \times UT^2}{(U4 \times BUT - BU4 \times UT)^2}}$$

............2.2.5-28

$$RTA04 = \frac{A_{Th\text{-}230}}{A_{U\text{-}234}}$$

.................2.2.5-29

$$ERTA04 = RTA04 \times \sqrt{\left(\frac{EA_{U\text{-}234}}{A_{U\text{-}234}}\right)^2 + \left(\frac{EA_{Th\text{-}230}}{A_{Th\text{-}230}}\right)^2}$$

...2.2.5-30

$$YU(\%) = \frac{10000 \times UR2}{EFU \times VOL \times A_{U-232/DT3}} \qquad \text{..........2.2.5-31}$$

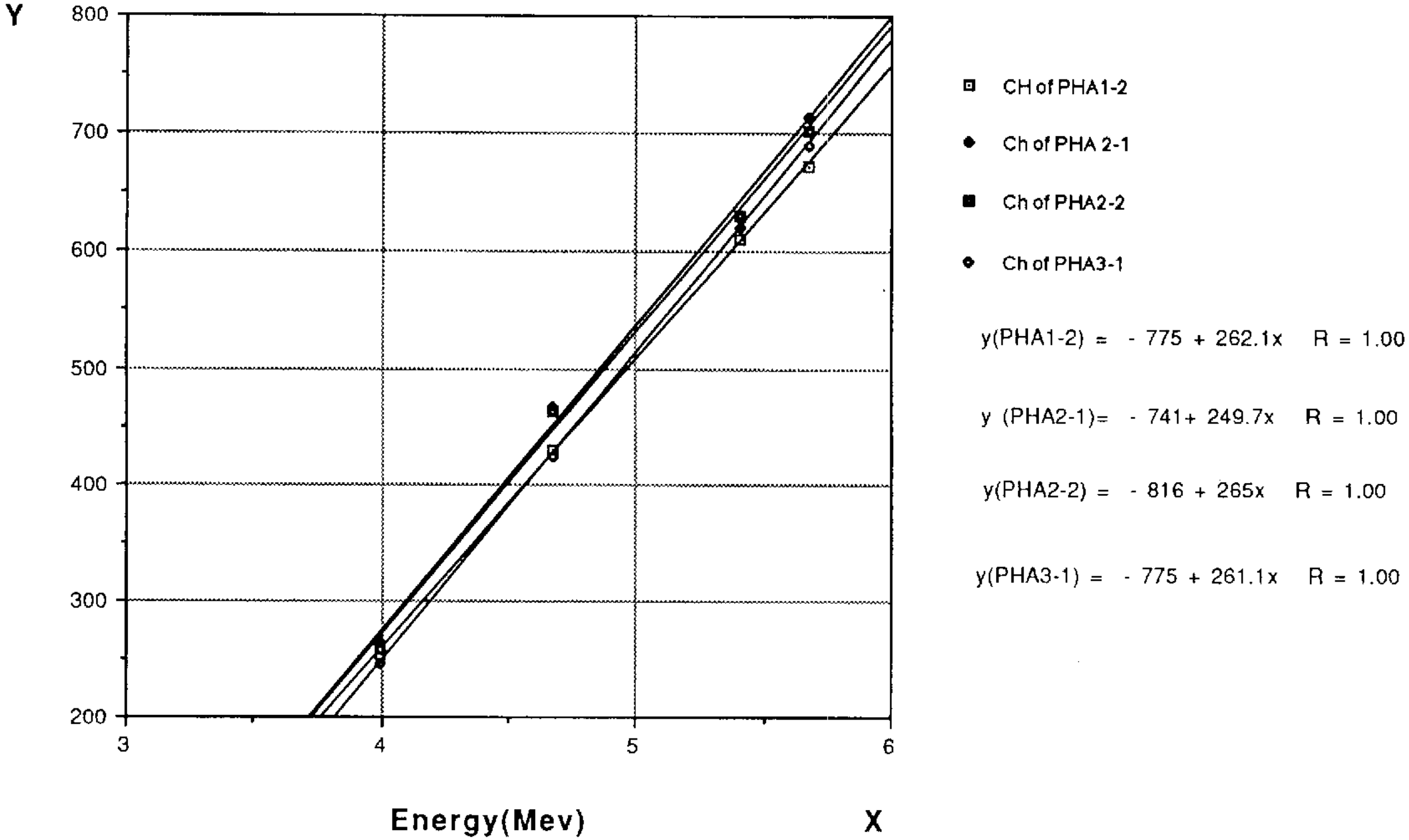
$$YTh(\%) = \frac{10000 \times ThR8}{EFTh \times VOL \times A_{Th-228/DT4}} \qquad \text{..........2.2.5-32}$$

$$U_{ppm} = 81 \times A_{U-238} \qquad \text{........................2.2.5-33}$$

$$Th_{ppm} = 247 \times A_{Th-232} \qquad \text{.......................2.2.5-34}$$

Table 2.2.6-1 Efficiency and Deviation of Detector Used in PNC Chubu Works

Date of measurement	10/26/92			Source:	Am-241	Half life(year):	433	
Date of certificate	2/7/83					Accuracy	2.00%	
Days of decay	3549	(day)		Real time(sec	120			
Activity of original(Ao)	38100	(dpm) =	635(Bq)	Live time(sec	120			
Activity of present(A)	37512	(dpm) =	626.2(Bq)					
dA/A	0.02							
dA	12.5	(Bq)						
Number of detector	Efficiency(E %)	Deviation(dE%)	Start CH	Stop CH	Peak CH	Peak Counts	INT Counts	NET Counts
PHA1-2	32.28	0.65	563	646	625	1325	23662	23636
PHA2-1	32.81	0.66	560	657	629	1226	24054	23972.3
PHA2-2	30.16	0.6	564	658	626	1027	22111	21984.3
PHA3-1	32.12	0.64	571	663	638	1202	23546	23468.5



y(PHA1-2) = - 775 + 262.1x R = 1.00

y (PHA2-1)= - 741+ 249.7x R = 1.00

y(PHA2-2) = - 816 + 265x R = 1.00

y(PHA3-1) = - 775 + 261.1x R = 1.00

Fig 2.2.6-1 Relation between energy and channel

Table 2.2.6-2 Calculated Alpha Data

Sample Name		1	2	3	4	5
		EJB20-85	EJB17-85	EJB21-85	GSS-4	GSD-11
Certified Activity of Spike Tracer	Bq/ml	3.95	3.95	3.95	3.95	3.95
Error of Certified Activity	Bq/ml	0.20	0.20	0.20	0.20	0.20
Certified Date	M-D-Y	8/3/90	8/3/90	8/3/90	8/3/90	8/3/90
Added Volume of Spike Tracer	ml	1.00	1.00	1.00	1.00	1.00
Sample Weight	g	1.00265	1.00751	1.00435	1.00369	1.00097
U-Th Separated Date	M-D-Y	10/13/92	10/13/92	10/13/92	10/13/92	10/13/92
Counted Data of U-fraction	M-D-Y	10/28/92	10/28/92	10/28/92	10/28/92	10/29/92
Counted Date of Th-fraction	M-D-Y	11/2/92	11/4/92	11/4/92	11/4/92	11/6/92
MCA NO & Efficiency of U-fraction	NO&%	32.28	32.81	30.16	32.12	32.28
MCA NO & Efficiency of Th-fraction	NO&%	32.28	32.28	32.81	30.16	32.12
Counting Time of U-fraction	Sec	157055	157043	157073	157045	87701
U-238 Peak INT Counts	Counts	2025	6185	8617	3033	3655
U-234 Peak INT Counts	Counts	2396	6471	9445	3236	3567
U-232 Peak INT Counts	Counts	165693	140281	137501	148486	91776
Background Counting Time	Sec	410988	410980	410979	410987	410988
B.G. INT Counts of U-238 Peak	Counts	88	23	50	21	115
B.G. INT Counts of U-234 Peak	Counts	136	86	145	61	140
B.G. INT Counts of U-232 Peak	Counts	858	801	822	1045	866
Counting Time of Th-fraction	Sec	239243	166741	166987	167680	167337
Th-232 INT Peak Counts	Counts	1131.5	1815.7	715	244.5	4036.8
Th-230 INT Peak Counts	Counts	731	1510.8	641	0	4768.3
Th-228 INT Peak Counts	Counts	259479	115350	34613	8997	182263.7
Ra-224 INT Peak Counts	Counts	234133.7	100846.7	33216	16352	175822.2
Background Counting Time	Sec	410988	410988	410980	410979	410987
B.G. INT Counts of Th-232 Peak	Counts	19	32.8	42	35.5	28.2
B.G. INT Counts of Th-230 Peak	Counts	32	15.5	105	0	-13.7
B.G. INT Counts of Th-228 Peak	Counts	1399	1387	1932	1145	771.8
B.G. INT Counts of Ra-224 Peak	Counts	1231.8	1140.8	1346	853	642
U-232 Activity on Counted Date	Bq/ml	3.87	3.87	3.87	3.87	3.87
Th-228 Activity on Separated Date	Bq/ml	3.97	3.97	3.97	3.97	3.97
Th-228 Activity on Counted	Bq/ml	3.89	3.89	3.89	3.89	3.88
U-238 Count Rate	cps	0.0127	0.0393	0.0547	0.0193	0.0414
U-234 Count Rate	cps	0.0149	0.0410	0.0598	0.0205	0.0403
U-232 Count Rate	cps	1.0529	0.8913	0.8734	0.9430	1.0444
Th-232 Count Rate	cps	0.0047	0.0108	0.0042	0.0014	0.0241
Th-230 Count Rate	cps	0.0030	0.0090	0.0036	0.0000	0.0285
Th-228 Count Rate	cps	1.0195	0.6423	0.1867	0.0437	1.0020
Error of Th-228 Count Rate	cps	0.0022	0.0021	0.0012	0.0006	0.0027
U-238 Activity in Sample	Bq/g	0.0464	0.1693	0.2412	0.0787	0.1531
Error of U-238 Activity in Sample	Bq/g	0.0026	0.0089	0.0125	0.0042	0.0082
U-234 Activity in Sample	Bq/g	0.0546	0.1765	0.2634	0.0836	0.1491
Error of U-234 Activity in Sample	Bq/g	0.0030	0.0092	0.0136	0.0045	0.0080
Th-230 Activity in Sample	Bq/g	0.0113	0.0542	0.0742	0.0000	0.1103
Error of Th-230 Activity in Sample	Bg/g	0.0007	0.0031	0.0049	#DIV/0!	0.0058
U-234/U-238 Activity Ratio		1.1771	1.0424	1.0921	1.0621	0.9743
Error of U-234/U-238 Activity Ratio		0.0363	0.0186	0.0163	0.0270	0.0231
Th-230/U-234 Activity Ratio		0.2075	0.3070	0.2818	0.0000	0.7396
Error of Th-230/U-234 Activity Ratio		0.0174	0.0237	0.0238	#DIV/0!	0.0555
Chemical Yield of U	%	84.38	70.28	74.91	75.94	83.70
Chemical Yield of Th	%	81.12	51.21	14.65	3.73	80.44
Concentration of U	ppm	3.76	13.71	19.54	6.37	12.40
Concentration of Th	ppm	4.41	16.03	21.39	29.99	22.97
Reference Result of U(China)	ppm	11.2	#4.6	#6.3	6.3	9.1
Reference Result of Th (China)	ppm	3.4	17.9	21.7	28	23.3

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Table 2.2.6-2 Calculated Alpha Data (Continued)

Sample Name		6	7	8	9	10
		GBW04324	EJB18-85	EJB22-85	EJB19-85	Y1-04
Certified Activity of Spike Tracer	Bq/ml	3.95	3.95	3.95	3.95	3.95
Error of Certified Activity	Bq/ml	0.20	0.20	0.20	0.20	0.20
Certified Date	M-D-Y	8/3/90	8/3/90	8/3/90	8/3/90	8/3/90
Added Volume of Spike Tracer	ml	1.00	1.00	1.00	1.00	1.00
Sample Weight	g	0.99954	1.00458	1.00422	1.00296	1.00428
U-Th Separated Date	M-D-Y	10/13/92	10/13/92	10/13/92	10/13/92	10/13/92
Counted Data of U-fraction	M-D-Y	10/29/92	10/29/92	10/29/92	10/30/92	10/30/92
Counted Date of Th-fraction	M-D-Y	11/6/92	11/5/92	11/5/92	11/2/92	11/2/92
MCA NO & Efficiency of U-fraction	NO&%	32.81	30.16	32.12	32.28	32.81
MCA NO & Efficiency of Th-fraction	NO&%	32.28	32.28	32.81	32.12	32.81
Counting Time of U-fraction	Sec	87701	87703	87721	78102	78102
U-238 Peak INT Counts	Counts	6967	9800	13189	21319	33669
U-234 Peak INT Counts	Counts	7115	9809	14786	18989	33894
U-232 Peak INT Counts	Counts	94988	62914	57894	80220	77161
Background Counting Time	Sec	410980	410979	410987	410988	410980
B.G. INT Counts of U-238 Peak	Counts	34	59	50	161	44
B.G. INT Counts of U-234 Peak	Counts	101	163	81	156	105
B.G. INT Counts of U-232 Peak	Counts	887	884	533	990	870
Counting Time of Th-fraction	Sec	84748	84407	82256	239252	239241
Th-232 INT Peak Counts	Counts	749	974	1427	3029	571
Th-230 INT Peak Counts	Counts	6175	3645	10192	83617	961
Th-228 INT Peak Counts	Counts	109762	34949	51560	278234	154287
Ra-224 INT Peak Counts	Counts	99120	29593	44838	241441.3	134250
Background Counting Time	Sec	410988	410988	410980	410987	410980
B.G. INT Counts of Th-232 Peak	Counts	115	101	34	40	19
B.G. INT Counts of Th-230 Peak	Counts	175	189	131	82	30
B.G. INT Counts of Th-228 Peak	Counts	1962	1976	1925	1023	1834
B.G. INT Counts of Ra-224 Peak	Counts	1453	1433	1359	716	1332
U-232 Activity on Counted Date	Bq/ml	3.87	3.87	3.87	3.87	3.87
Th-228 Activity on Separated Date	Bq/ml	3.97	3.97	3.97	3.97	3.97
Th-228 Activity on Counted	Bq/ml	3.88	3.88	3.88	3.89	3.89
U-238 Count Rate	cps	0.0794	0.1116	0.1502	0.2726	0.4310
U-234 Count Rate	cps	0.0809	0.1114	0.1684	0.2428	0.4337
U-232 Count Rate	cps	1.0809	0.7152	0.6587	1.0247	0.9858
Th-232 Count Rate	cps	0.0086	0.0113	0.0173	0.0126	0.0023
Th-230 Count Rate	cps	0.0724	0.0427	0.1236	0.3493	0.0039
Th-228 Count Rate	cps	1.2135	0.3773	0.5731	1.0890	0.6054
Error of Th-228 Count Rate	cps	0.0040	0.0023	0.0029	0.0023	0.0017
U-238 Activity in Sample	Bq/g	0.2839	0.6004	0.8779	1.0252	1.6827
Error of U-238 Activity in Sample	Bq/g	0.0148	0.0311	0.0453	0.0525	0.0859
U-234 Activity in Sample	Bq/g	0.2894	0.5996	0.9839	0.9130	1.6933
Error of U-234 Activity in Sample	Bq/g	0.0151	0.0311	0.0506	0.0468	0.0864
Th-230 Activity in Sample	Bq/g	0.2316	0.4376	0.8337	1.2451	0.0253
Error of Th-230 Activity in Sample	Bg/g	0.0121	0.0235	0.0432	0.0632	0.0015
U-234/U-238 Activity Ratio		1.0192	0.9987	1.1207	0.8906	1.0063
Error of U-234/U-238 Activity Ratio		0.0172	0.0143	0.0134	0.0089	0.0077
Th-230/U-234 Activity Ratio		0.8004	0.7298	0.8473	1.3637	0.0149
Error of Th-230/U-234 Activity Ratio		0.0591	0.0544	0.0619	0.0984	0.0012
Chemical Yield of U	%	85.23	61.35	53.05	82.12	77.73
Chemical Yield of Th	%	96.93	30.11	44.99	87.08	47.39
Concentration of U	ppm	23.00	48.63	71.11	83.04	136.30
Concentration of Th	ppm	6.76	28.57	28.77	11.06	3.70
Reference Result of U(China)	ppm	17.6	37.1	66.4	86.2	137.5
Reference Result of Th (China)	ppm	#44.4	29.8	29.4	11.9	1.7

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Table 2.2.6-2 Calculated Alpha Data (Continued)

Sample Name		11	12	13	14	15
		GBW04110	GBW04116	GBW04112	GBW04111	GBW04115
Certified Activity of Spike Tracer	Bq/ml	3.95	3.95	3.95	3.95	3.95
Error of Certified Activity	Bq/ml	0.20	0.20	0.20	0.20	0.20
Certified Date	M-D-Y	8/3/90	8/3/90	8/3/90	8/3/90	8/3/90
Added Volume of Spike Tracer	ml	1.00	1.00	1.00	1.00	1.00
Sample Weight	g	0.50130	0.20328	0.20092	0.19980	0.20041
U-Th Separated Date	M-D-Y	10/13/92	10/13/92	10/13/92	10/13/92	10/13/92
Counted Data of U-fraction	M-D-Y	10/30/92	10/30/92	10/30/92	10/30/92	10/30/92
Counted Date of Th-fraction	M-D-Y	11/5/92	11/6/92	11/2/92	11/5/92	11/6/92
MCA NO & Efficiency of U-fraction	NO&%	30.16	32.12	32.28	32.81	30.16
MCA NO & Efficiency of Th-fraction	NO&%	30.16	32.81	30.16	32.12	30.16
Counting Time of U-fraction	Sec	78104	78105	22302	22301	22307
U-238 Peak INT Counts	Counts	30361	15520	6044	8590	10551
U-234 Peak INT Counts	Counts	30653	15406	5591	8643	10501
U-232 Peak INT Counts	Counts	69628	47602	15302	18231	17380
Background Counting Time	Sec	410979	410987	410988	410980	410979
B.G. INT Counts of U-238 Peak	Counts	57	44	106	38	59
B.G. INT Counts of U-234 Peak	Counts	175	75	151	97	170
B.G. INT Counts of U-232 Peak	Counts	853	505	1120	863	862
Counting Time of Th-fraction	Sec	82458	84749	239243	167337	84722
Th-232 INT Peak Counts	Counts	957.3	37748	345	686	3882
Th-230 INT Peak Counts	Counts	32449.7	36026	124872.3	43657	38101
Th-228 INT Peak Counts	Counts	87045	162784	267812	99621	63592
Ra-224 INT Peak Counts	Counts	75549	87277	221237	88519	60202
Background Counting Time	Sec	410979	410980	410979	410987	410979
B.G. INT Counts of Th-232 Peak	Counts	1	69	0	18	37
B.G. INT Counts of Th-230 Peak	Counts	109.3	114	0	65	158
B.G. INT Counts of Th-228 Peak	Counts	1065	1935	1160	1013	1501
B.G. INT Counts of Ra-224 Peak	Counts	805	1361	722.3	712	1030
U-232 Activity on Counted Date	Bq/ml	3.87	3.87	3.87	3.87	3.87
Th-228 Activity on Separated Date	Bq/ml	3.97	3.97	3.97	3.97	3.97
Th-228 Activity on Counted	Bq/ml	3.88	3.88	3.89	3.88	3.88
U-238 Count Rate	cps	0.3886	0.1986	0.2707	0.3851	0.4728
U-234 Count Rate	cps	0.3920	0.1971	0.2503	0.3873	0.4703
U-232 Count Rate	cps	0.8894	0.6082	0.6834	0.8154	0.7770
Th-232 Count Rate	cps	0.0116	0.4452	0.0014	0.0041	0.0457
Th-230 Count Rate	cps	0.3933	0.4248	0.5219	0.2607	0.4493
Th-228 Count Rate	cps	0.9881	1.4107	1.0613	0.5580	0.6598
Error of Th-228 Count Rate	cps	0.0037	0.0054	0.0022	0.0019	0.0031
U-238 Activity in Sample	Bq/g	3.3689	6.2088	7.6219	9.1368	11.7370
Error of U-238 Activity in Sample	Bq/g	0.1721	0.3196	0.4030	0.4779	0.6117
U-234 Activity in Sample	Bq/g	3.3988	6.1608	7.0470	9.1898	11.6747
Error of U-234 Activity in Sample	Bq/g	0.1737	0.3171	0.3735	0.4806	0.6085
Th-230 Activity in Sample	Bq/g	3.0820	5.7449	9.5301	9.0790	13.1789
Error of Th-230 Activity in Sample	Bg/g	0.1574	0.2933	0.4837	0.4628	0.6736
U-234/U-238 Activity Ratio		1.0089	0.9923	0.9246	1.0058	0.9947
Error of U-234/U-238 Activity Ratio		0.0082	0.0113	0.0172	0.0153	0.0137
Th-230/U-234 Activity Ratio		0.9068	0.9325	1.3524	0.9879	1.1288
Error of Th-230/U-234 Activity Ratio		0.0655	0.0676	0.0992	0.0721	0.0824
Chemical Yield of U	%	76.29	48.99	54.77	64.29	66.65
Chemical Yield of Th	%	84.40	110.87	90.38	44.75	56.41
Concentration of U	ppm	272.88	502.91	617.37	740.08	950.70
Concentration of Th	ppm	22.47	1487.22	6.50	34.88	331.29
Reference Result of U (China)	ppm	285	535	682	788	986
Reference Result of Th (China)	ppm	25	#202	11	26	313

2.3 Gamma spectrometry

2.3.1 Apparatus

The high resolution 4096- channel gamma spectrometer used at PNC-Chubu Works was made in NAIG ,Japan. But the high pure Ge detector was made in Princeton Gamma-Tech U.S.A. The block diagram was given in Fig 2.1-7 , in which the outward view of main processor was shown in Fig 2.3.1-1, and the detector was shown in Fig2.3.1-2 , the personal computer connected to the main processor is the same as that of alpha spectrometer but employed gamma special software. For high resolution gamma spetrometry, the solid -state semiconductor detector is a key part of the instrument. With its extremely high resolution of gamma ray energies, the possibility of detecting gamma radiation from other daughters in the natural radioactive decay series has been opened up. The use of high resolution detector makes it possible to select a number of different energies of gamma rays for counting and a great deal of more information can be extracted from the gamma ray spectrum. However, the detector(Ge) must be cooling in liquid nitrogen when it is being operated, this is the main disadvantage. Of course , another disadvantage is its low detecting efficiency. Anyway, compared with Ge(Li)-detector,which must be not only operated but also kept in liquid nitrogen, the Ge-detector is more conventient.

2.3.2 Sample sealing

Most of the gamma radiations emitted by nuclides in the uranium series are not acturally from U-238 but from it daughts in the series . In order to determine the concentration of uranium and measure the activities of uranium series nuclides correctly, the radioactive decay series must reach equilibrium. So , it is necessary to seal a sample for a period time , generally, more than 2 weeks , about 6 times of the half life(3.85 days) of Rn-222. In this work, 10 rocks and minerals samples from China were sealed for more than 1 month in the standard plastic bottles for gamma spectrometry. The procedure was as follows:

1). Prepare 10 clean plastic bottles and number them;

2). Weigh 20g dried powdered sample and pour it into a bottle and make plain;

3). Cover a piece of filter paper disc on the sample;
4). Cover the caps of the bottle ;
5). Seal the joint of the bottle with adhesive tape.
6). Repeat procedure 2-5 for each sample;

7). Keep them in a safety place.

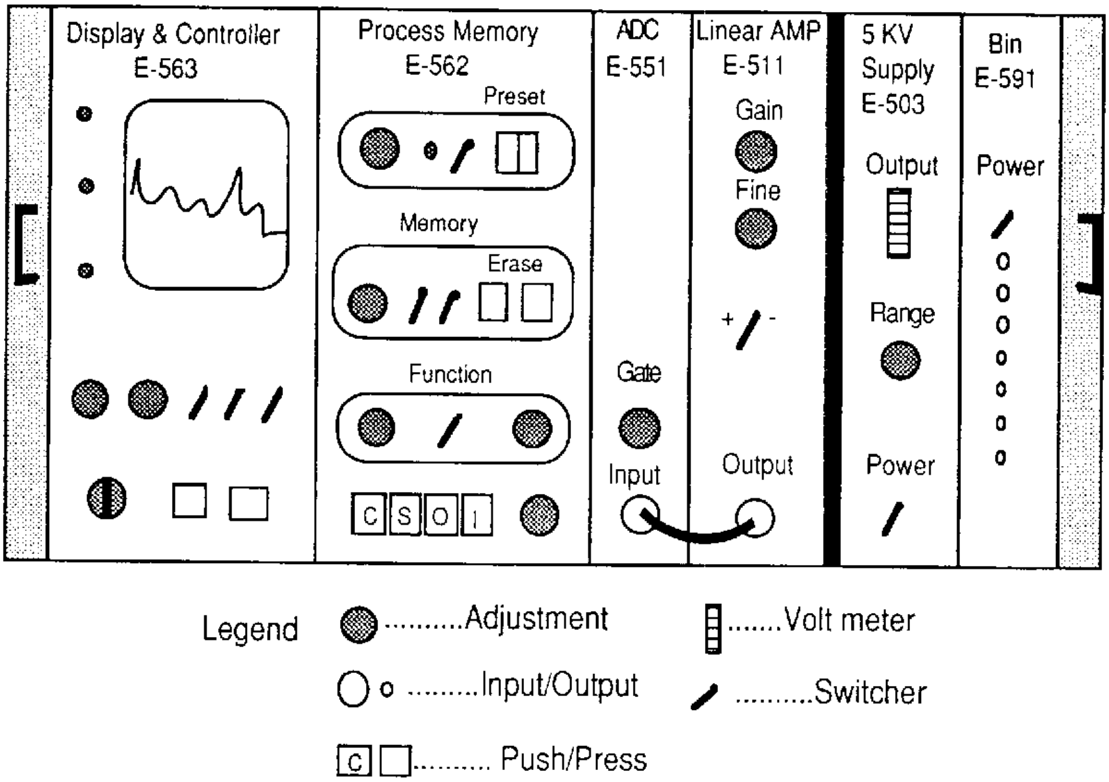


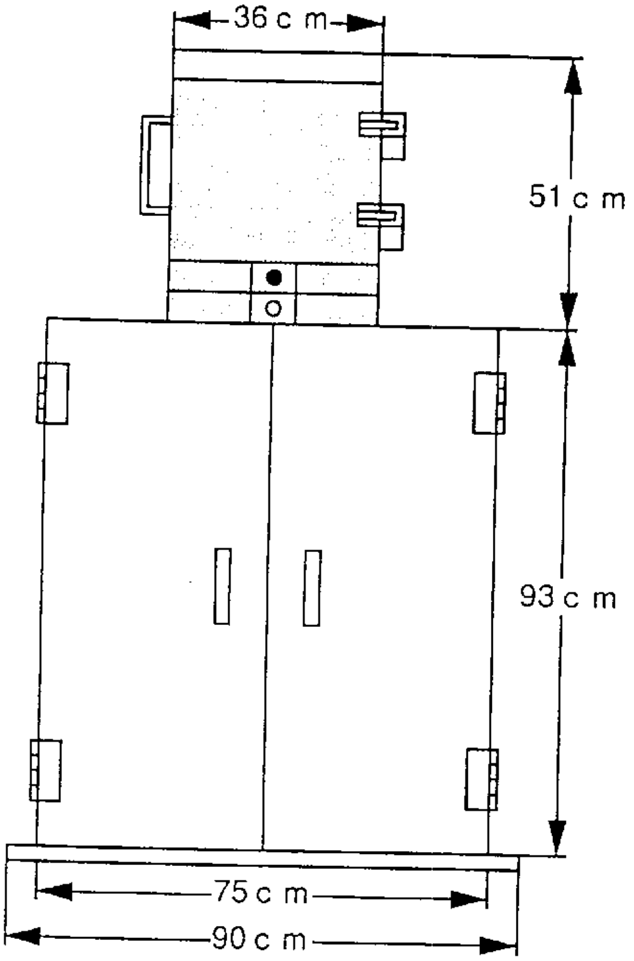
Fig 2.3.1-1 Main Processor of Gamma Spectrometer Show (Outward view from the front of)

2.3.3 Measurement

Similiar to alpha spectrometry, the measurement of gamma spectrometry included energy and FWHM as well as efficiency calibrations using IAEA uranium standrad sample(see APPENDIX C) ; background measurement ; sample measurement and the automatic analysis of gamma spectrum by the personal computer system connected to the main processor . The detailed procedure was shown in Fig 2.3.3-1, in which the " CRT-n" (n=1,2...) information can be seen in APPENDIX D. In this procedure , the detector refrigeration and the counting time should be paid more attention to. For the cooling system, if the weight of licuid nitrogen were less than the required amount, the more should be added into it,otherwise, the detector will be destroyed. For the counting time, many experiments should be done so as to select a proper time. However, this work has been done by PNC-Chu Works, who gave that the proper time for natural samples (such as rocks and minerals samples) was 50000 sec.

2.3.4 Calculation

Outward View from side



Outward View from Top

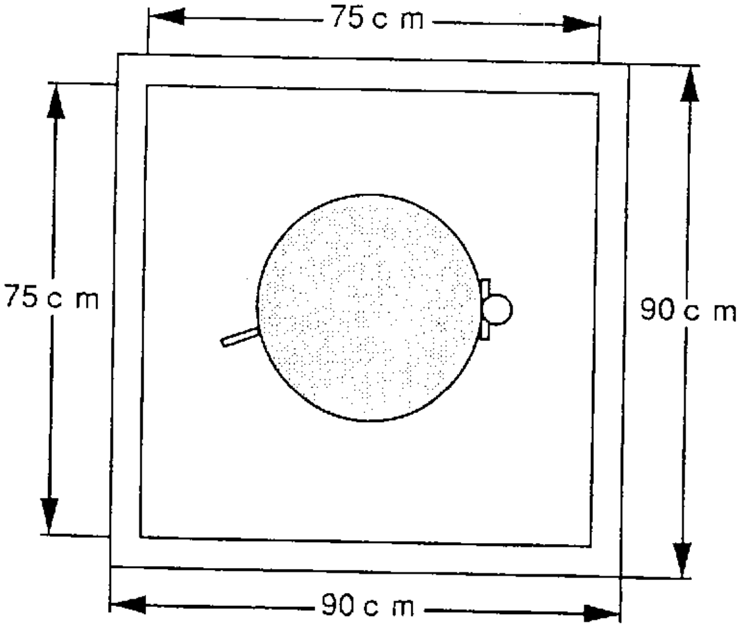


Fig 2.3.1-2 Gamma Detector used at PNC- Chubu Works(A)

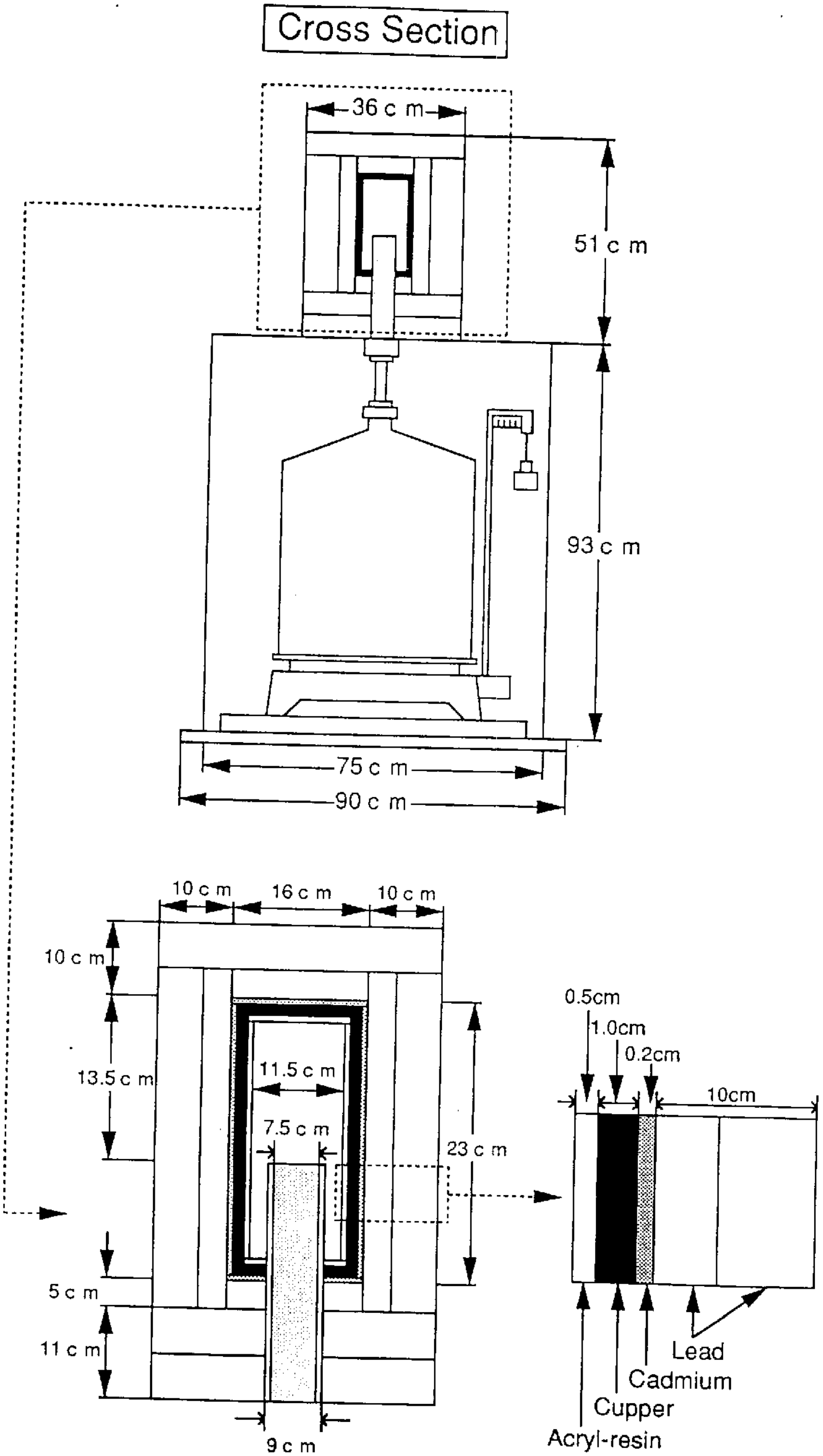


Fig 2.3.1-2 Gamma Detector used at PNC- Chubu Works(B)

Fig 2.3.3-1 Procedure of Measurement for Gamma Spectrometry

Sample preparation

1.crash sample
2.weigh 20g of sample into container
3.leave for more than 2 weeks

Detector refrigeration

1.pour liquid nitrgen into vacuum insulated container
2.pay attention to the weight of liquid nitrogen during measurement
(Full--47Kg , Empty--24Kg, Decreasing rate--1.2Kg/day)

Power on

1.power supply on(E-591)
2.high voltage on(E-503)
3.set heigh voltage dial to 50.0(2.5KV)

Energy and FWHM calibration

1.erase MCA data (E-562)
2.collect spectral data for 5x10ˆ4sec using IAEA uranium standard
3.PC-9801 personal computer & printer power on
4.connect GP-IB cable on the backside of E-562
5.set program & data disk of gamma spectrometry
6.push return key two times → (CRT-1)
7.select "MCA Moniter" by ↓key and push return → (CRT-2)
8.push f-1 key and push return (READ MCA) → (CRT-3)
9.wait for 1 min (spectrum is transfered to computer and displayed)
10.select "WRITE DISK" by ↓ key and push return, then input data name for example B:IAEAUSTD.D4K and push return → (CRT-4)
11.push f-1 and stop key
12.select "End" by ↓ key and push return → (CRT-2)
13.type system and push return, then type ecal and push return
(energy calibration proram runs) → (CRT-5)
14.select "Registration of Peak Energy" by ↓ key and input energy of major peaks and push stop → (CRT-6)
15.select "Automatic Calibration" by ↓ key and push return
→ (CRT-5)
16.input the name of data file used in energy calibration and push return
(peak search is carried out and energy & FWHM is calibrated with energy. the result of calibration is displayed → (CRT-6, 7)
17.Input file name of the calibration factors
18.select "End" by ↓ key → (CRT-5)
19.push stop and out at same time ,then push stop (E-562)

20.remove GP-IB cable

Efficiency calibration

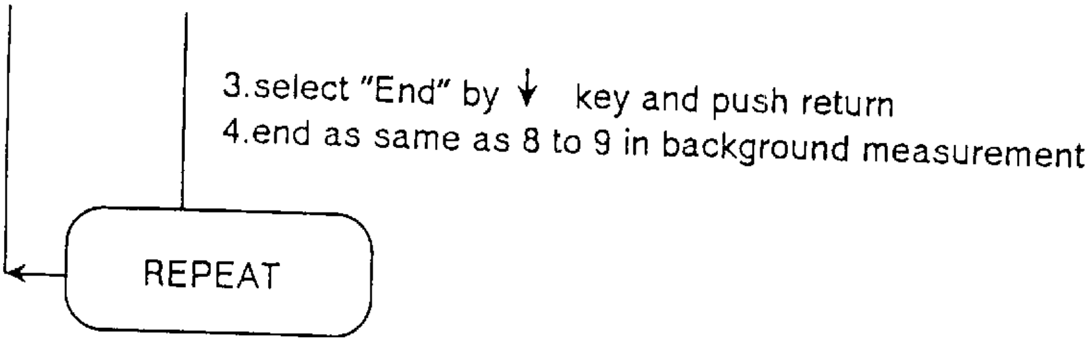
1.type "FCAL" and push return
2.select "Registraion of source" by ↓ key and push return
→ (CRT-8)
3.input all item requested
4.select "Automatic Calibration" by ↓ key and push return
5.input data file name of standard source measurement
(result of peak efficiency calcurated are displayed)
6.input "y" and input file name of calibration factors calcurated
(calibration factors for efficiency are printed out → (PRINT-1))
7.select "End" and push return
8.remove floppy disks, then computer and printer power off

Background measurement

1. do same as 1 to 11 in energy and FWHM calibration with no sample
2.select "Input of Measured Condition" by ↓ key and push return
→ (CRT-2)
3.input all requested items (CRT-10)
4.select "Imput of Analytical Condition" by ↓ key and push return
5.input all requested items → (CRT-811)
6.select "BG Data Analysis" by ↓ key and push return → (CRT-2)
(measured condition and analytical condition are printed out
→ (CRT-12,13))
(result of peak search and qualitative analysis are printed out
→ (CRT-14,15))
(calculated BG data ia automatically saved in data disk)
7.remove floppy disks ,then computer & printer power off
8.push stop and out at same time on E-562, then push stop
9.remove GP-IB cable

Sample measurement

1.do as same as 1 to 5 in background measurement with sample to be measured
2.select "Analysis for Fixed Nucildes" by ↓ key and push return
→ (CRT-2)
(measured conditions and analytical conditions are printed out continiously → (CRT-12,13))
(determination of uranium series nuclides is carried out automatically and the result is printed out → (PRINT-2,3))



3.select "End" by ↓ key and push return
4.end as same as 8 to 9 in background measurement

CAUTION

1.Don't remove Ge detector's cap and don't touch the head.
2.Clean up the surface of detector's cap by alchol ,when sample is changed.
3.Pay attention to the weight of liquid nitrogen.The weight should be more than 30kg whenever high voltage is supplied,or Ge detector will be broken.
4.Very gently and softly shut the door of radiation shielding made by heavy lead

<<<Specification of high pure germanium detector>>>

1.Type ; Intrinsic Germmanium Coaxial Detector
2.Size ; 48.8 mm Diameter x 38.5mm Height
3.Effective Volume ; 64 cm^3
4.Relative Efficiency ; 18%
5.Peak Resolution ; <2.0 keV at 1.33MeV
<0.98 keV at 122keV
6.Manufacturer ; Princeton Gamma-Tech U.S.A.

The calculation is divided into two stages. The frist stage is made by gamma spectrometer data processing station(PC),which can offer directly and automatically the calibrated data of energy , FWHM and efficiency of detector for each interested nuclide , the activities and errors of Pb-210,Pb-214, Bi-214,Th-234 and U-234 from the measured gamma spectrum .The final stage is performed in the Macintosh Plus personal computer system employed Microsoft Excel application software based on those data , which can give the activity of Ra-226, the ratios between interested nuclides and uranium content in sample.

1). Uranium standard sample for calibration

The main figures of uranium standard sample used are as follows:

U concent= 400 ppm , therefore,the activity of U-238 is:

$$A_{u-238}=0.4 \times 12.34=4.93\ Bq/g=0.0001335\ uCi/g\ .$$

In the case of 20 g sample(gamma sapectrometry standard weight), the total activity is 0.002229 uCi . Since the radioactive equilibrium between the parent and its daughts has been certified, the activities of both Ra-226 and Pb-210 are 0.002669 uCi. According to formula 2.3.4-1, the efficiency can be known. And from the standard spectrum, the FWHM and the relation between energy and channel can also be calibrated automatically.

$$E = \frac{R_{***}}{20 \times A_{***} \times Y} \qquad \cdots\cdots\cdots\cdots 2.3.4-1$$

where, A_{***} is the known activity of nuclide " ***" in uranium standard sample , E is the efficiency of detector for interested peak of the nuclide"***",Y is the branching ratio or yield of interested peak of the nuclide"***" , "20" is sample used weight(g), R_{***} counting rate of the nuclide"***" .

2). The activities of nuclides and uranium content in sample

The activities of nuclides in the sample can be expressed as follows:

$$A_{***} = \frac{R_{***}}{20 \times E \times Y} \qquad \cdots\cdots\cdots\cdots 2.3.4-2$$

where the symbols are the same as formula 2.3.4-1 but A_{***} meaning the activities of nuclides "###" except for Ra-226 , whose activity is expressed as formula 2.3.4-3.

$$A_{Ra-226} = [\, A_{Pb-214(241.9\ kev)} + A_{Pb-214(295.2\ kev)} + \cdots + A_{Bi-214(609\ kev)} + A_{Bi-214(768.7\ kev)} + \ldots] / N \quad \ldots\ldots\ldots\ldots 2.3.4\text{-}3$$

where, N is the number of nuclides of Pb-214 and Bi-214 which have different energies. And its error is:

$$EA_{Ra-226} = SD(\text{ Error of } A_{Pb-214} , \text{ Error of } A_{Bi-214}) \ldots\ldots 2.3.4\text{-}4$$

where SD(.....) is a calculating function of standard deviation. Finally the uranium content in sample is:

$$U_{ppm} = 81 \times A_{Th-234} \quad \ldots\ldots\ldots\ldots 2.3.4\text{-}5$$

2.3.5 Results

The calibrations were given in Fig2.3.5-1,Fig2.3.5-2, Fig2.3.5-3, Table 2.3.5-1 and Table 2.3.5-2. The analytical results of nuclides in 10 samples were given in Table 2.3.5-3.

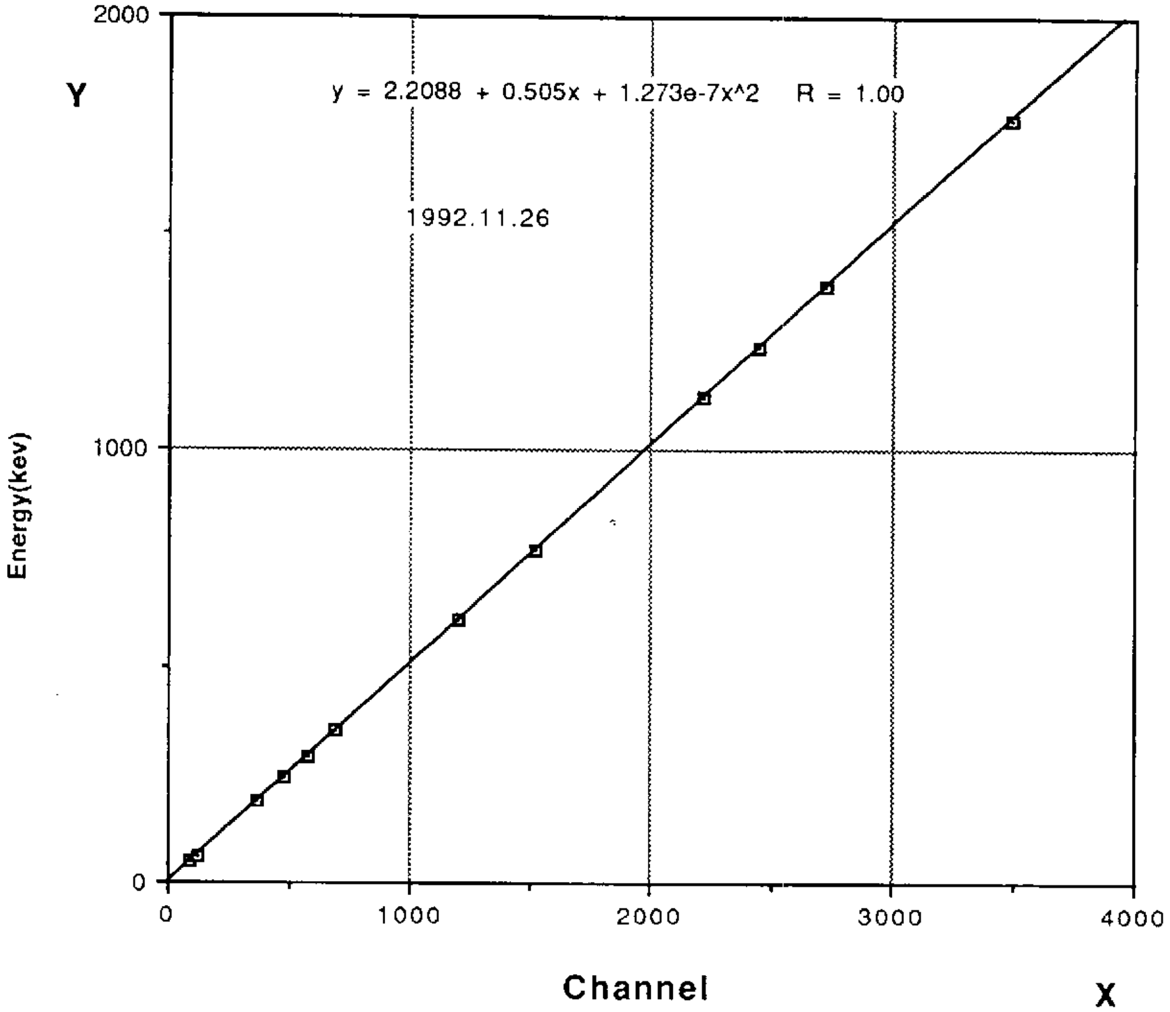


Fig 2.3.5-1 Correlation between Gamma Energy and Channel

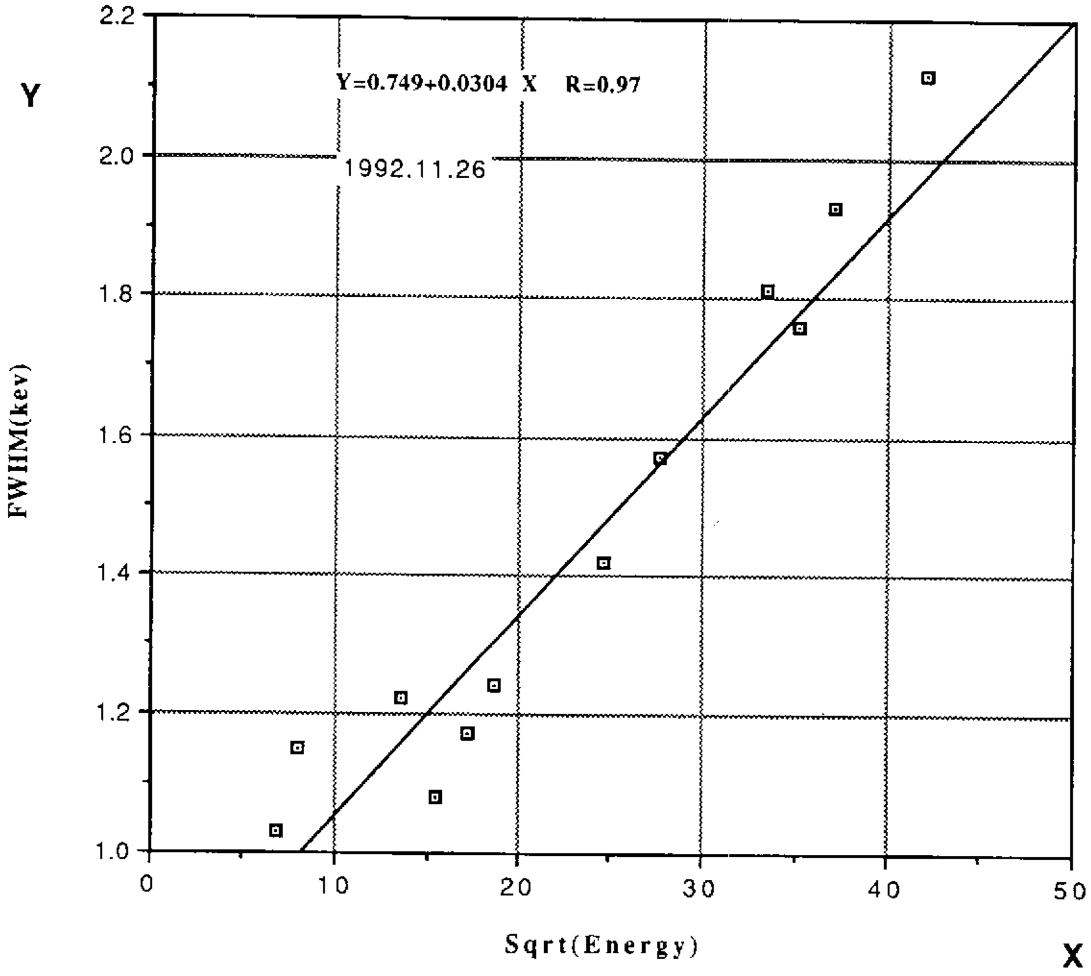


Fig2.3.5-2 Correlation between FWHM and SQRT(Energy)

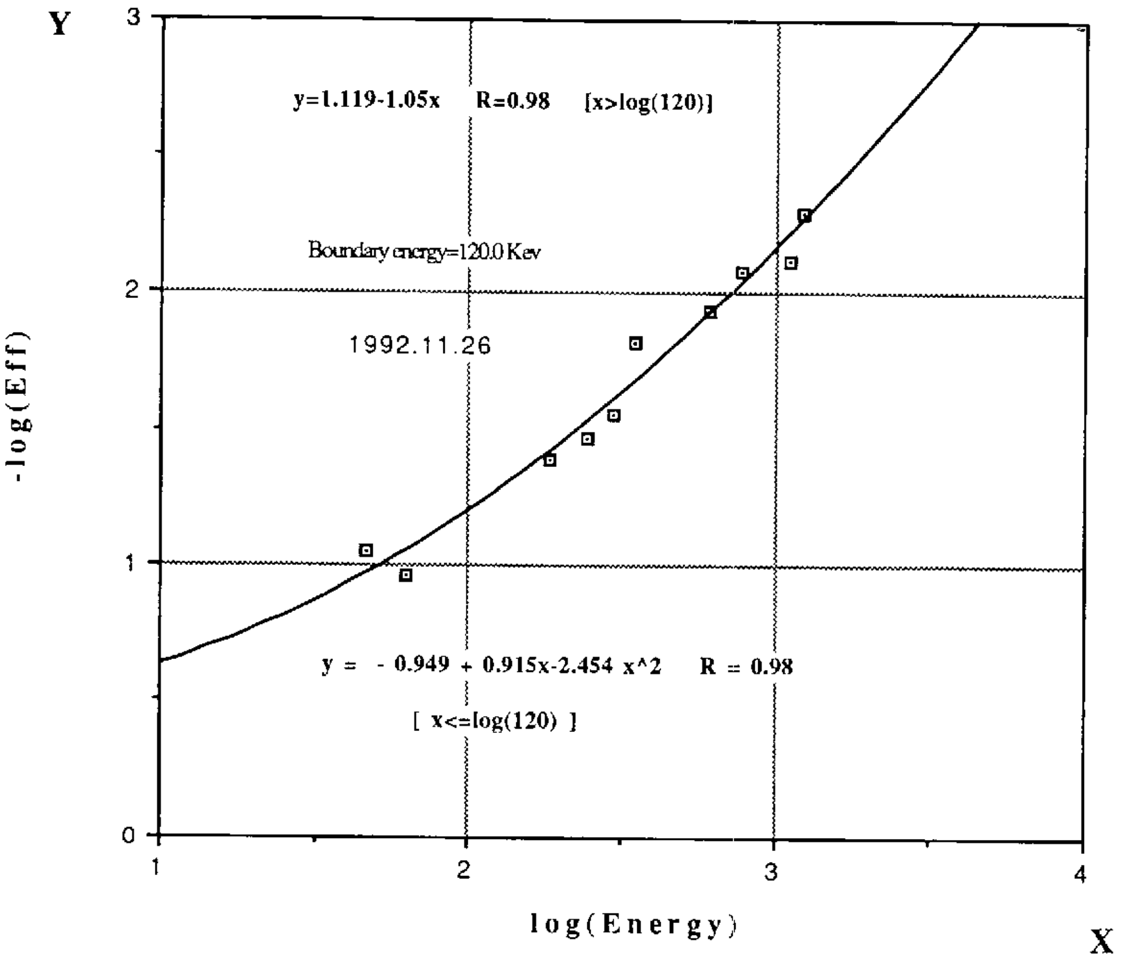


Fig2.3.5-3 Correlation between Energy and Efficiency

Table 2.3.5-1 Energy.FWHM Calibration Results

エネルギー・半値幅校正結果

	チャネル	エネルギー（keV）			半値幅（keV）		
		測定値	計算値	偏差	測定値	計算値	偏差
1	88.23	46.50	46.77	-0.27	1.03	0.96	0.07
2	121.20	63.30	63.42	-0.12	1.15	0.99	0.16
3	363.55	186.02	185.83	0.19	1.22	1.16	0.06
4	474.34	241.95	241.79	0.16	1.08	1.22	-0.14
5	579.68	295.17	295.01	0.16	1.17	1.27	-0.10
6	692.01	351.90	351.75	0.15	1.24	1.32	-0.08
7	1202.18	609.30	609.52	-0.22	1.42	1.50	-0.08
8	1517.13	768.70	768.69	0.01	1.57	1.59	-0.02
9	2213.12	1120.40	1120.51	-0.11	1.81	1.77	0.04
10	2445.97	1238.00	1238.25	-0.25	1.76	1.82	-0.05
11	2721.70	1378.00	1377.68	0.32	1.93	1.88	0.05
12	3485.49	1764.00	1764.02	-0.02	2.12	2.03	0.10

エネルギー・半値幅 校正式：

```
(ｴﾈﾙｷﾞｰ[keV])  = C0 + C1*(ﾁｬﾈﾙ[ch]) + C2*(ﾁｬﾈﾙ[ch])^2
(FWHM[keV])    = C3 + C4*SQRT(ｴﾈﾙｷﾞｰ[keV])

         C0 =      2.2079453E0
         C1 =     5.0502747E-1
         C2 =     1.2667119E-7

         C3 =     7.4929678E-1
         C4 =     3.0386460E-2
```

エネルギー校正ファイル名：　[B:ECAF.ECL]

Table 2.3.5-2 Efficiency Calibration Results

```
                       検    出    効    率    校    正    結    果

       エ ネ ル ギ ー                 検       出       効        率
        (keV)                測 定 値           計 算 値             偏 差
-----------------------------------------------------------------------------------
  1        46.50         0.08899210        0.08934872      -0.00035661( -0.40%)
  2        63.30         0.10986343        0.10890177       0.00096166(  0.88%)
  3       241.90         0.04070808        0.04119221      -0.00048413( -1.18%)
  4       295.17         0.03395968        0.03342133       0.00053835(  1.61%)
  5       351.90         0.02827709        0.02778626       0.00049083(  1.77%)
  6       609.30         0.01523350        0.01561011      -0.00037661( -2.41%)
  7       768.70         0.01170790        0.01222912      -0.00052122( -4.26%)
  8      1120.40         0.00836382        0.00823257       0.00013125(  1.59%)
  9      1238.00         0.00756061        0.00741317       0.00014744(  1.99%)
 10      1764.00         0.00514158        0.00511067       0.00003091(  0.60%)


  検 出 効 率  校 正 式 :

   log(EFF[-]) = C0 + C1*log(ｴﾈﾙｷﾞｰ[keV]) + C2*log(ｴﾈﾙｷﾞｰ[keV])^2
                                              ( (ｴﾈﾙｷﾞｰ[keV]) ≦ KNEE )

   log(EFF[-]) = C3 + C4*log(ｴﾈﾙｷﾞｰ[keV])
                                              ( (ｴﾈﾙｷﾞｰ[keV]) > KNEE )

          C0  =     -9.489863E0
          C1  =      9.154028E0
          C2  =     -2.453949E0

          C3  =      1.118548E0
          C4  =     -1.050384E0

          KNEE  =  120.00


  検 出 効 率 校 正 フ ァ イ ル 名 :   [ B:EFFCAF.FCL ]
```

Table 2.3.5-3 Calculated Gamma Data

Sample Name		EJB21-85		GBW04324		EJB18-85		EJB22-85	
Sample NO		1		2		3		4	
File Name of Saved Spectrum		EJB21-85.D4K		GBW04324.D4K		EJB18-85.D4K		EJB22-85.D4K	
Volume	g	20		20		20		20	
Sealed Date	M-D-Y	10/9/92		10/9/92		10/9/92		10/9/92	
Counted Date	M-D-Y	11/27/92		12/1/92		12/2/92		12/3/92	
		Determined	Error	Determined	Error	Determined	Error	Determined	Error
Pb-210Activity(46.5KeV)	Bq/g	0.119	0.018	0.285	0.0191	0.443	0.0268	0.956	0.0349
Pb-214Activity(241.9KeV)	Bq/g	0.0921	0.0131	0.225	0.0147	0.515	0.0201	0.993	0.0259
Pb-214Activity(295.2KeV)	Bq/g	0.0663	0.00661	0.237	0.00818	0.447	0.011	0.928	0.0157
Pb-214Activity(351.9KeV)	Bq/g	0.0645	0.00449	0.237	0.00649	0.448	0.00789	0.952	0.0113
Bi-214Activity(609.0KeV)	Bq/g	0.0708	0.0045	0.222	0.00715	0.427	0.00963	0.937	0.0129
Bi-214Activity(768.7KeV)	Bq/g	0.0581	0.0229	0.211	0.0299	0.343	0.0423	0.734	0.0652
Bi-214Activity(1120KeV)	Bq/g	0.0911	0.0143	0.25	0.0214	0.402	0.025	1.01	0.0357
Bi-214Activity(1238KeV)	Bq/g	0.0994	0.0408	0.168	0.0382	0.405	0.0484	0.956	0.0637
Bi-214Activity(1764KeV)	Bq/g	0.099	0.0136	0.231	0.021	0.49	0.0272	0.992	0.0396
Th-234Activity(63.3KeV)	Bq/g	0.191	0.0174	0.317	0.0203	0.498	0.0268	0.772	0.0331
Th-230Activity(by Alpha)	Bq/g	0.0742	0.0049	0.2316	0.0121	0.4376	0.0235	0.8337	0.0432
Ra-226Activity	Bq/g	0.08	0.02	0.22	0.02	0.43	0.05	0.94	0.08
Pb-210Activity	Bq/g	0.12	0.02	0.29	0.02	0.44	0.03	0.96	0.03
Ra-226/Th-230 Ratio		1.080	0.225	0.961	0.113	0.993	0.127	1.125	0.114
Pb-210/Ra-226 Ratio		1.484	0.369	1.280	0.159	1.019	0.133	1.019	0.096
U Content(from Th-234)	ppm	15	1	26	2	40	2	63	3
U Content(by Wet Chem.)	ppm	no data		no data		no data		65	
U Content(by Alpha)	ppm	19.5		23		48.6		71.1	

go on to the next page

Table 2.3.5-3 Calculated Gamma Data (continued)

Sample Name		Y1-04		GBW04110		GBW04116		GBW04112	
Sample NO		5		6		7		8	
File Name of Saved Spectrum		Y1-04.D4K		GBW04110.D4K		GBW04116.D4K		GBW04112.D4K	
Volume	g	20		20		20		20	
Sealed Date	M-D-Y	10/9/92		10/9/92		10/9/92		10/9/92	
Counted Date	M-D-Y	12/4/92		12/5/92		12/8/92		12/9/92	
		Determined	Error	Determined	Error	Determined	Error	Determined	Error
Pb-210Activity(46.5KeV)	Bq/g	0	0.00249	2.56	0.0709	0.716	0.064	0	0.00471
Pb-214Activity(241.9KeV)	Bq/g	1.74	0.0339	2.98	0.0428	7.97	0.0738	7.7	0.0694
Pb-214Activity(295.2KeV)	Bq/g	1.79	0.0209	2.91	0.0252	4.02	0.0374	7.76	0.042
Pb-214Activity(351.9KeV)	Bq/g	1.85	0.0148	2.9	0.0197	4.21	0.025	7.76	0.0305
Bi-214Activity(609.0KeV)	Bq/g	1.75	0.0177	2.84	0.0227	4.04	0.0307	7.51	0.036
Bi-214Activity(768.7KeV)	Bq/g	1.58	0.0775	2.46	0.0987	3.48	0.174	6.56	0.162
Bi-214Activity(1120KeV)	Bq/g	1.81	0.0473	2.88	0.059	4.09	0.0733	7.65	0.0947
Bi-214Activity(1238KeV)	Bq/g	1.86	0.0892	2.91	0.114	4.01	0.155	7.43	0.173
Bi-214Activity(1764KeV)	Bq/g	1.78	0.0532	2.86	0.0631	4	0.0854	7.66	0.102
Th-234Activity(63.3KeV)	Bq/g	1.54	0.0464	2.95	0.0609	2.13	0.0845	6.81	0.0937
Th-230Activity(by Alpha)	Bq/g	0.0253	0.0015	3.082	0.1574	5.7449	0.2933	9.5301	0.4837
Ra-226Activity	Bq/g	1.77	0.08	2.84	0.15	4.48	1.34	7.50	0.37
Pb-210Activity	Bq/g	0.00	0.00	2.56	0.07	0.72	0.06	0.00	0.00
Ra-226/Th-230 Ratio		69.960	5.268	0.922	0.068	0.779	0.236	0.787	0.056
Pb-210/Ra-226 Ratio		0.000	#DIV/0!	0.901	0.054	0.160	0.050	0.000	#DIV/0!
U Content(from Th-234)	ppm	125	4	239	5	173##	7	552	8
U Content(by Wet Chem.)	ppm	127		244		477		688	
U Content(by Alpha)	ppm	136.3		272.9		503		617	

go on to the next page

Table 2.3.5-3 Calculated Gamma Data (continued)

Sample Name		GBW04111		GBW04115					
Sample NO		9		10					
File Name of Saved Spectrum		GBW04111.D4K		GBW04115.D4K					
Volume	g	20		20					
Sealed Date	M-D-Y	10/9/92		10/9/92					
Counted Date	M-D-Y	12/10/92		12/11/92					
		Determined	Error	Determined	Error				
Pb-210Activity(46.5KeV)	Bq/g	8.45	0.0917	0	0.00609				
Pb-214Activity(241.9KeV)	Bq/g	8.68	0.0687	13.7	0.086				
Pb-214Activity(295.2KeV)	Bq/g	8.83	0.0447	13.2	0.0552				
Pb-214Activity(351.9KeV)	Bq/g	8.98	0.033	13.4	0.0409				
Bi-214Activity(609.0KeV)	Bq/g	8.59	0.039	12.9	0.0477				
Bi-214Activity(768.7KeV)	Bq/g	7.94	0.183	11.6	0.223				
Bi-214Activity(1120KeV)	Bq/g	8.78	0.101	13	0.125				
Bi-214Activity(1238KeV)	Bq/g	8.71	0.191	13.3	0.237				
Bi-214Activity(1764KeV)	Bq/g	8.67	0.111	13.1	0.135				
Th-234Activity(63.3KeV)	Bq/g	8.01	0.109	9.11	0.108				
Th-230Activity(by Alpha)	Bq/g	9.079	0.4628	13.18	0.6736				
Ra-226Activity	Bq/g	8.65	0.29	13.03	0.59				
Pb-210Activity	Bq/g	8.45	0.09	0.00	0.01				
Ra-226/Th-230 Ratio		0.952	0.058	0.988	0.067				
Pb-210/Ra-226 Ratio		0.977	0.034	0.000	#DIV/0!				
U Content(from Th-234)	ppm	649	9	738	9				
U Content(by Wet Chem.)	ppm	771		1028					
U Content(by Alpha)	ppm	741		951					

Chapter 3 Chemical Analysis of Uranium and Thorium in Rocks and Minerals Samples

3.1 Brief outline

By now, many chemical analysis methods for U anf Th in rocks and minerals samples have been developed. depending on the contents of U and Th ,the established methods mainly include volumetric methods for high content,spectrophotometry for micro content and fluorimetry for trace content . For example,ferrous-ammonium vanadate titrimetric method for U(>300ppm) ;TOPO-extraction separation, Br-PADAP spectrophotometry for U((10-300 ppm) and laser fluorimetry for U(<10ppm); N-263 extraction chromatographic separation, ArsenazoIII for Th(10-300ppm) and Morin fluorimetry for Th(<1ppm for water sample,for rocks and minerals, being studied).

As rocks and minerals samples complicated, the decompositions and separations of samples are very important. Alkaline fusion, mixed ammonium salts flux and acids digestion are usually employed for decomposition of samples. Since uranium is easier to disolve than thorium,it is possible to use only acids digestion method. But for thorium, especially when samples are complicated, the acids digestion may not decompose the samples completely , resulting in bigger error. Relatively, the mixed ammonium salts flux method would be better.

Separation and preconcentration for micro and trace analyses are necessary. The common methods are solvent extraction ,ion exchange , extraction chromatographic and coprecipitation methods. Since the chemical properities of U and Th are quite different, generally, it is easy to separate U-fraction from Th-fraction. But it is more complicated to separate U from its matrix and Th from its co-existed elements such as Fe, Zr ,REEs and so on. Therefore ,both solvent extraction and ion exchange methods or extraction chromatographic method are usually performed.

In the experiment here, the mixed acids (HF-HNO_3-$HClO_4$) digestion method was used for U and Th decompositons, while TBP-kerosene extraction and stong alkaline anion exchange techniques were independently used to separate U from its matrix and Th from its matrix,respectively. And the measurement was based on that oxine reacts uranium in chloroform media to form colour complex which maximum absorption at 330 nm ; Arsenazo III reacts thorium in HCl(8M) media to form colour complex which maxmium absportion at 665 nm. Finally , the absorbance was measured in the spectrophotometer, meanwhile , the calibration was also made.

3.2 Determination of Uranium

3.2.1 Reagents and apparatus

1). HNO_3 ,(1+10)

2). HF

3). $HClO_4$

4). $NaNO_3$, KIO_3

5). $(NH_4)_2SO_4$(25%)

6). $HN_3.H_2O$ (1+1)

7). EDTA(2Na) (5%)

8). TBP- Kerosene (3+7)

All reagents used in the experiment were analytical grade.

9). PH-meter

10). Clinical spectrophotometer(UVIDEC-77)

11). Other general analytical apparatus

3.2.2 Procedure

The procedure included open mixed acids digestion decompostion, TBP-Kerosene extraction separation, oxine-colour and measurement. The detailed procedure was shown in Fig 3.2.2-1, in which the calibration was as follows:

Take 0,100,150,200 and 300 ug uranium standard solution into 100ml-beakers and add 10 ml HNO_3 , then evaporate in the sand-bath till dryness. The next procedure was the same as those of sample (after sample decompositon). Finally, the calibration curve was able to be given as follows:

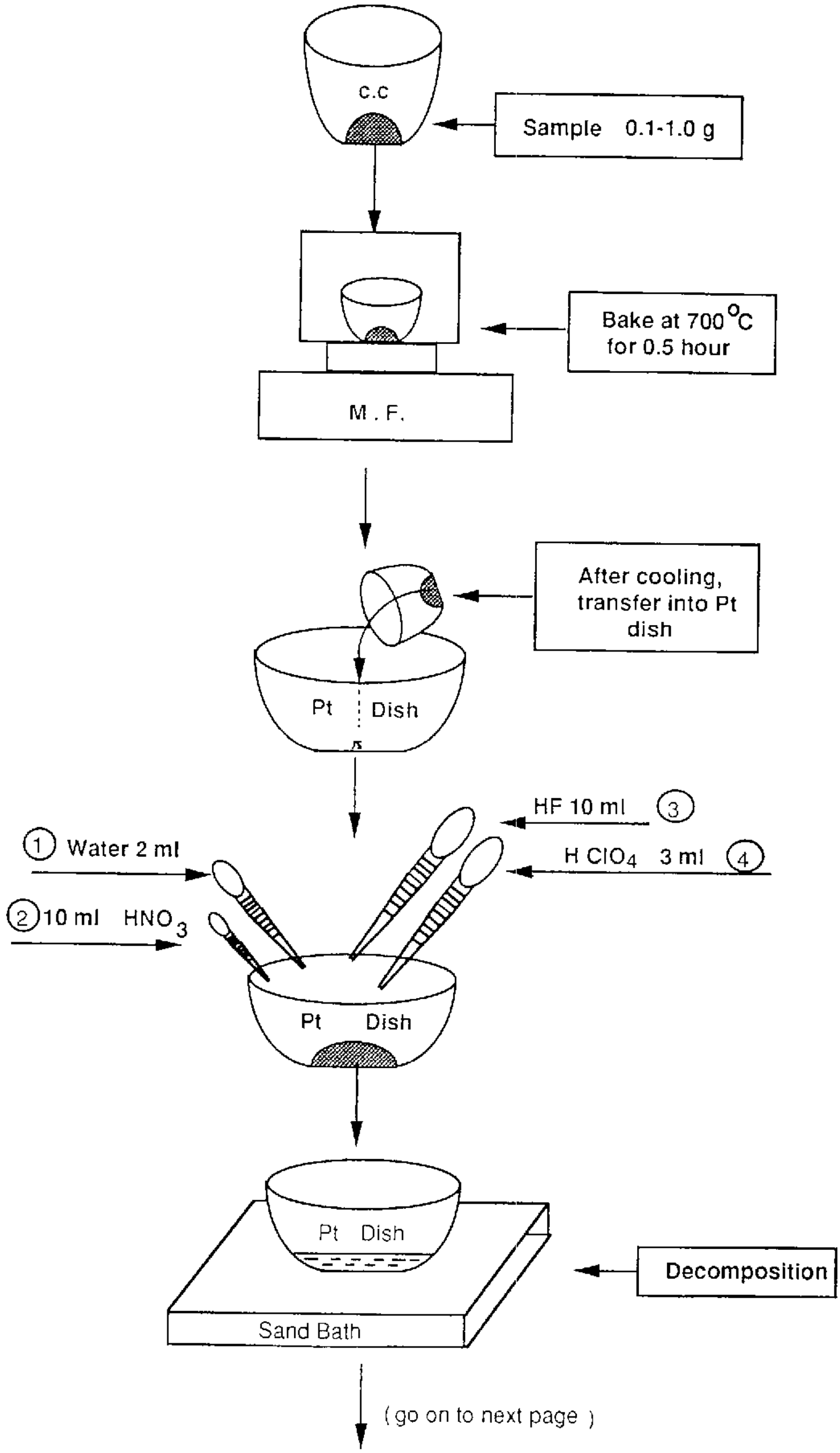
$$A= a+b\ C \qquad \text{.......................................}3.2.2-1$$

where , A is the absorbance; C is the amount of U in solution ; a and b are the coefficients.

3.2.3 Result

The results of 8 rocks and minerals samples from China were given in Table 3.2.3-1 .

Fig3.2.2-1 **Chemical Analysis Procedure for Uranium**



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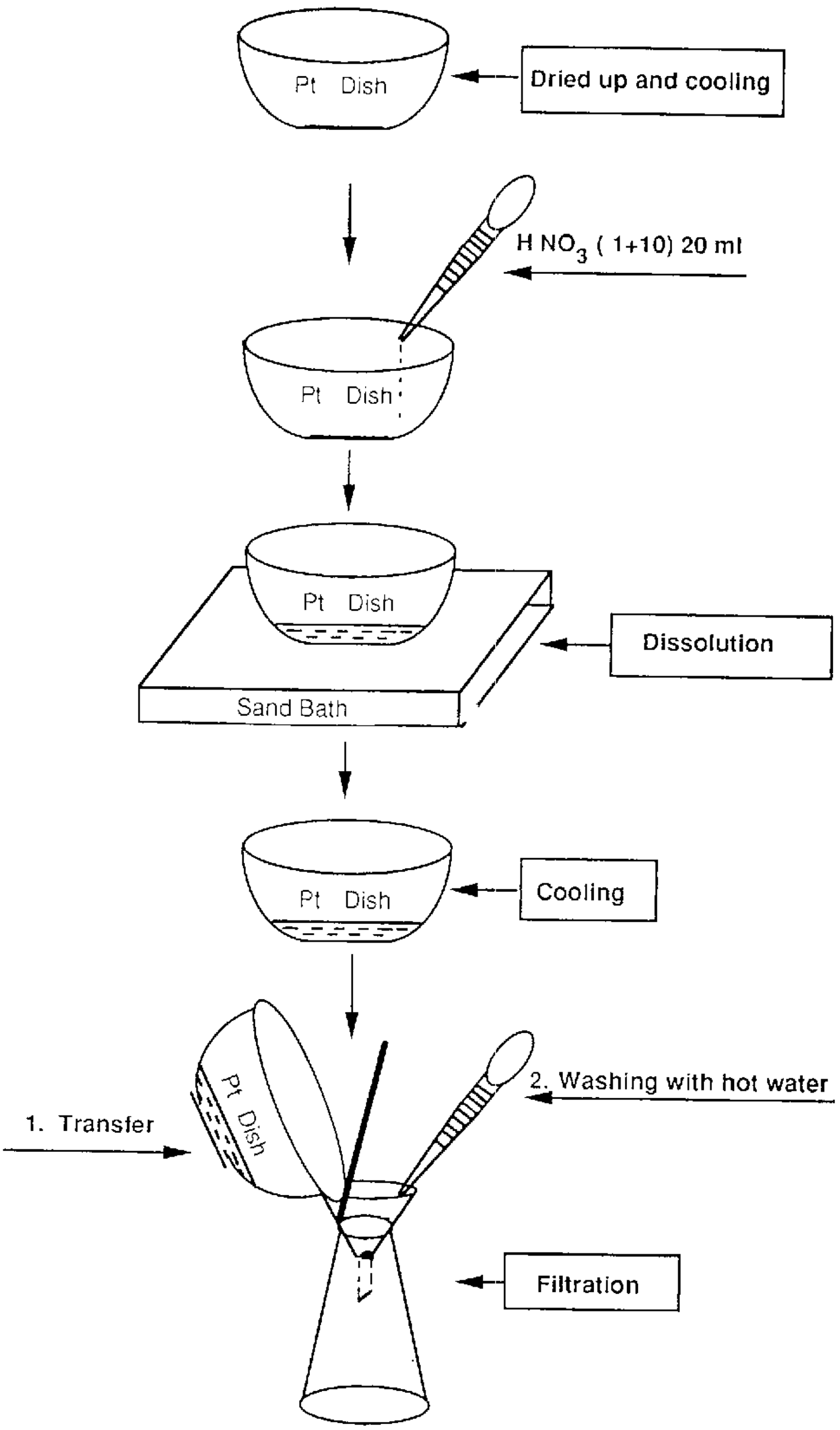

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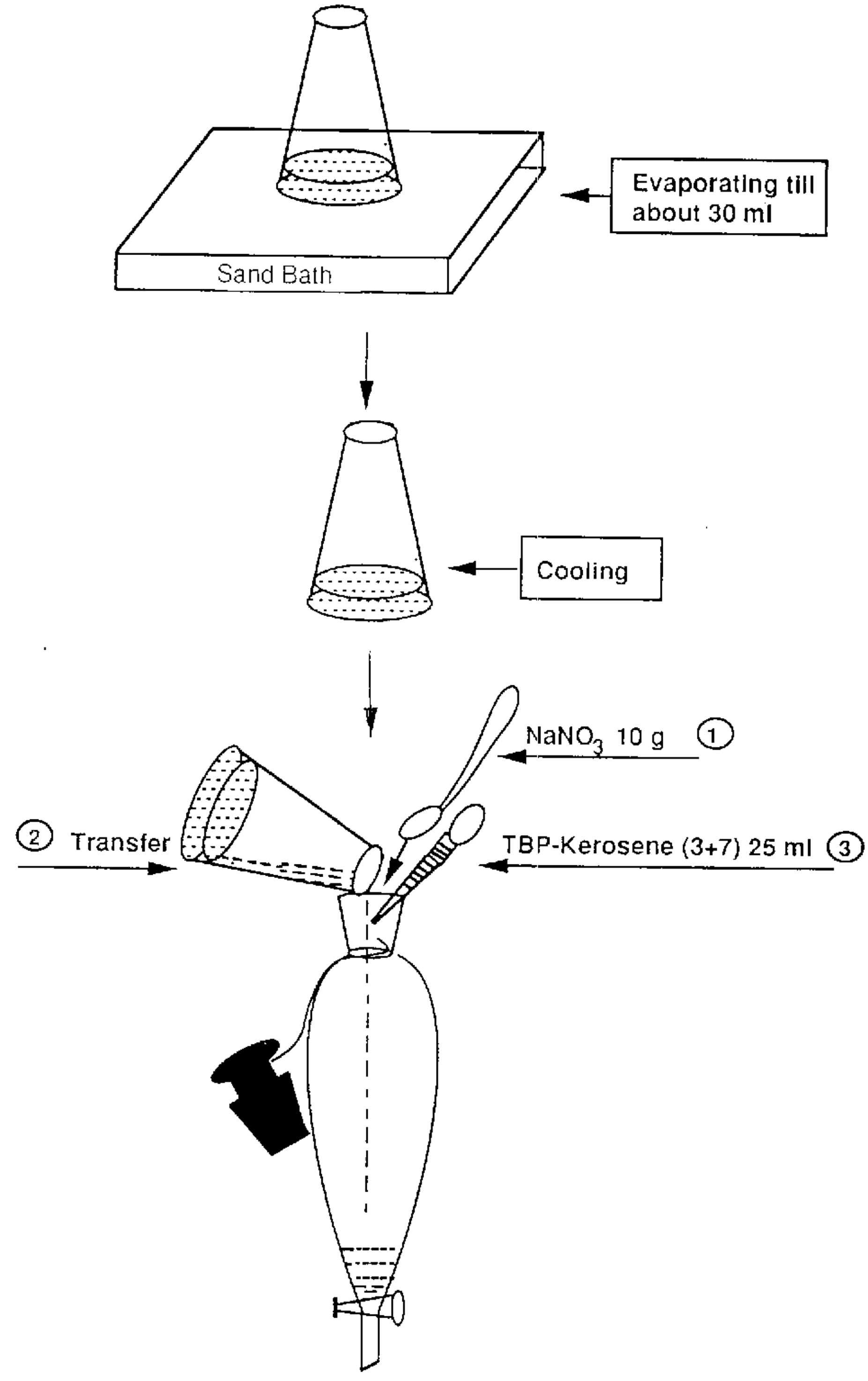

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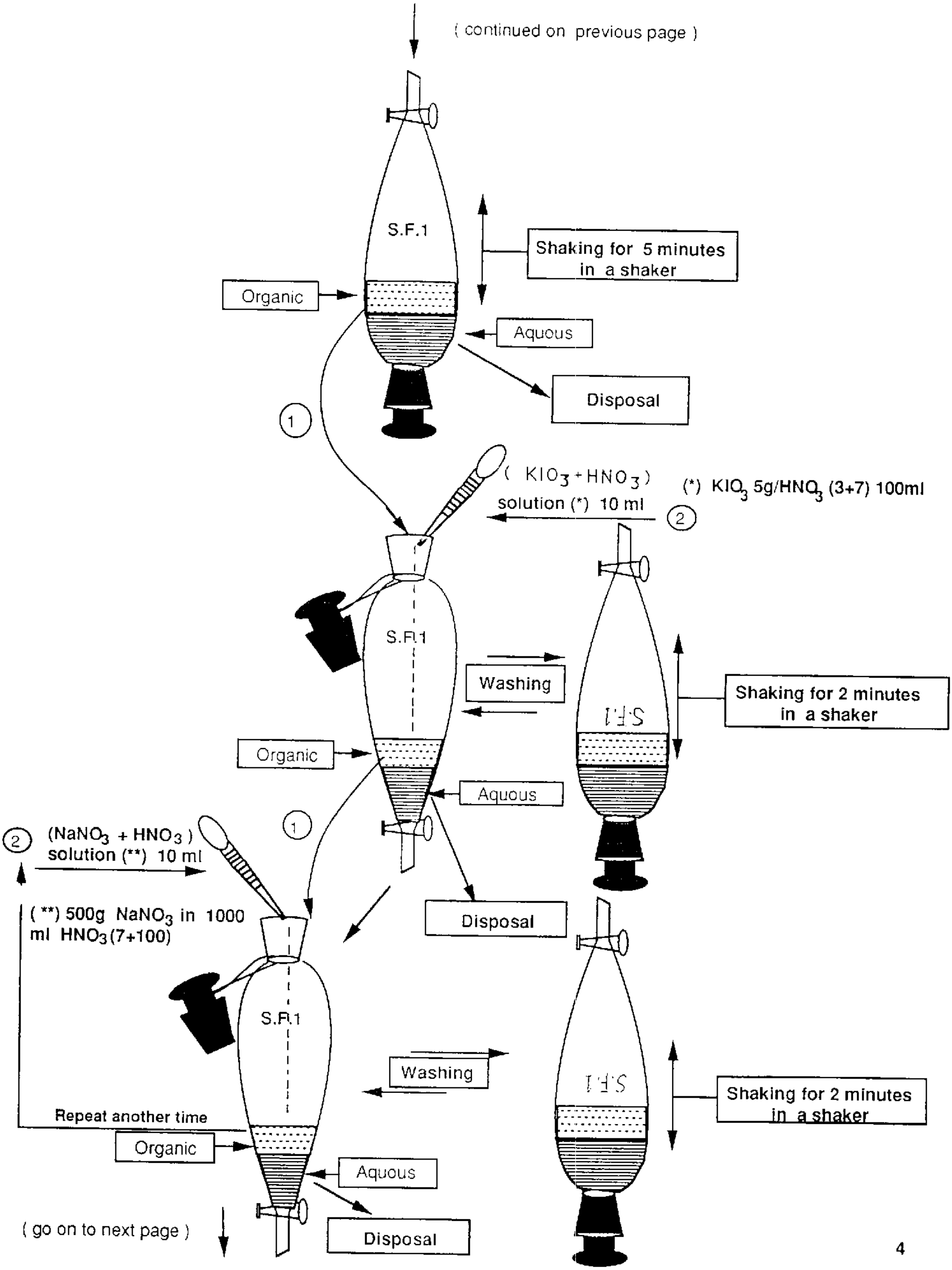

(*) KIO_3 5g/HNO_3 (3+7) 100ml

(**) 500g $NaNO_3$ in 1000 ml HNO_3(7+100)

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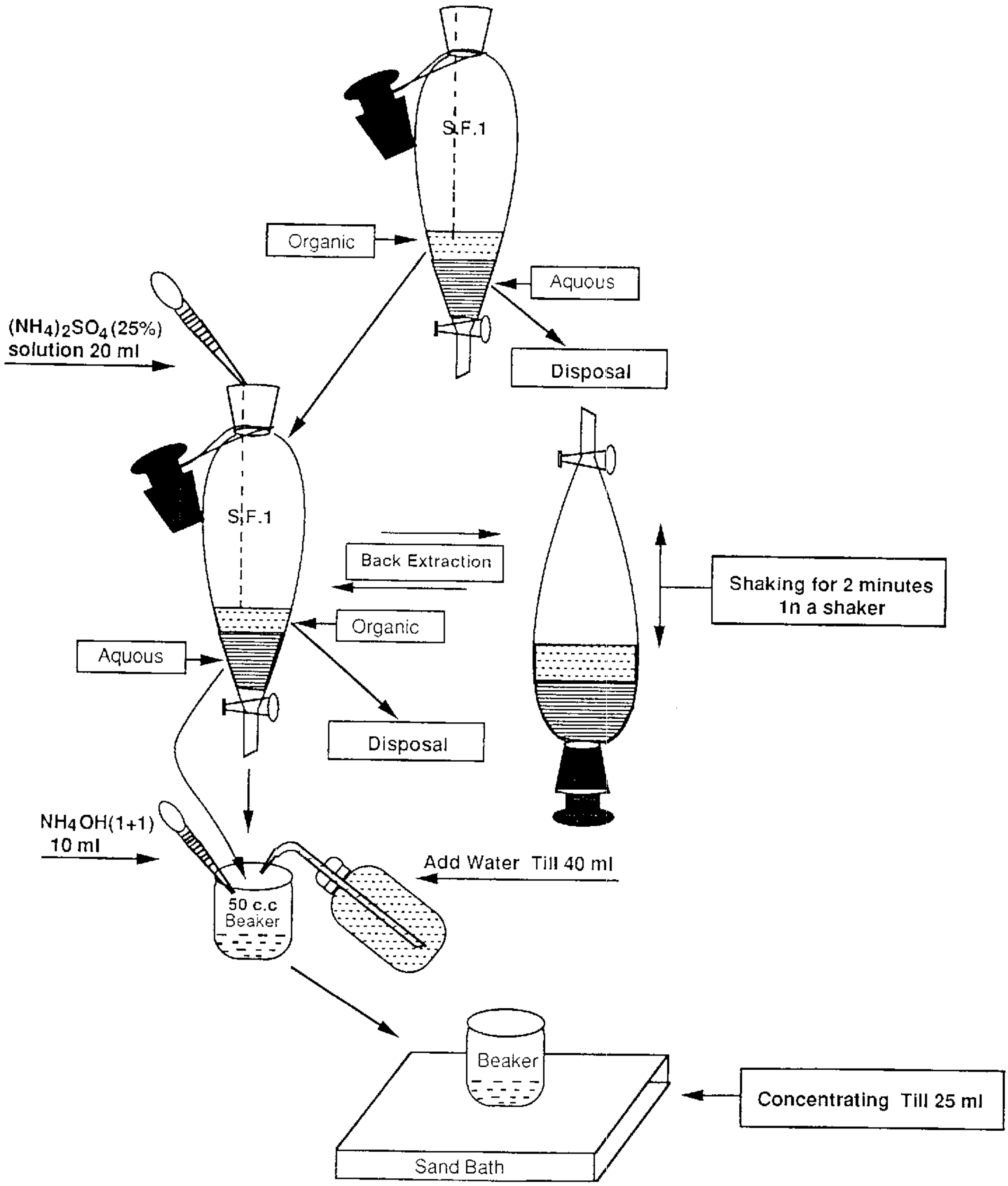

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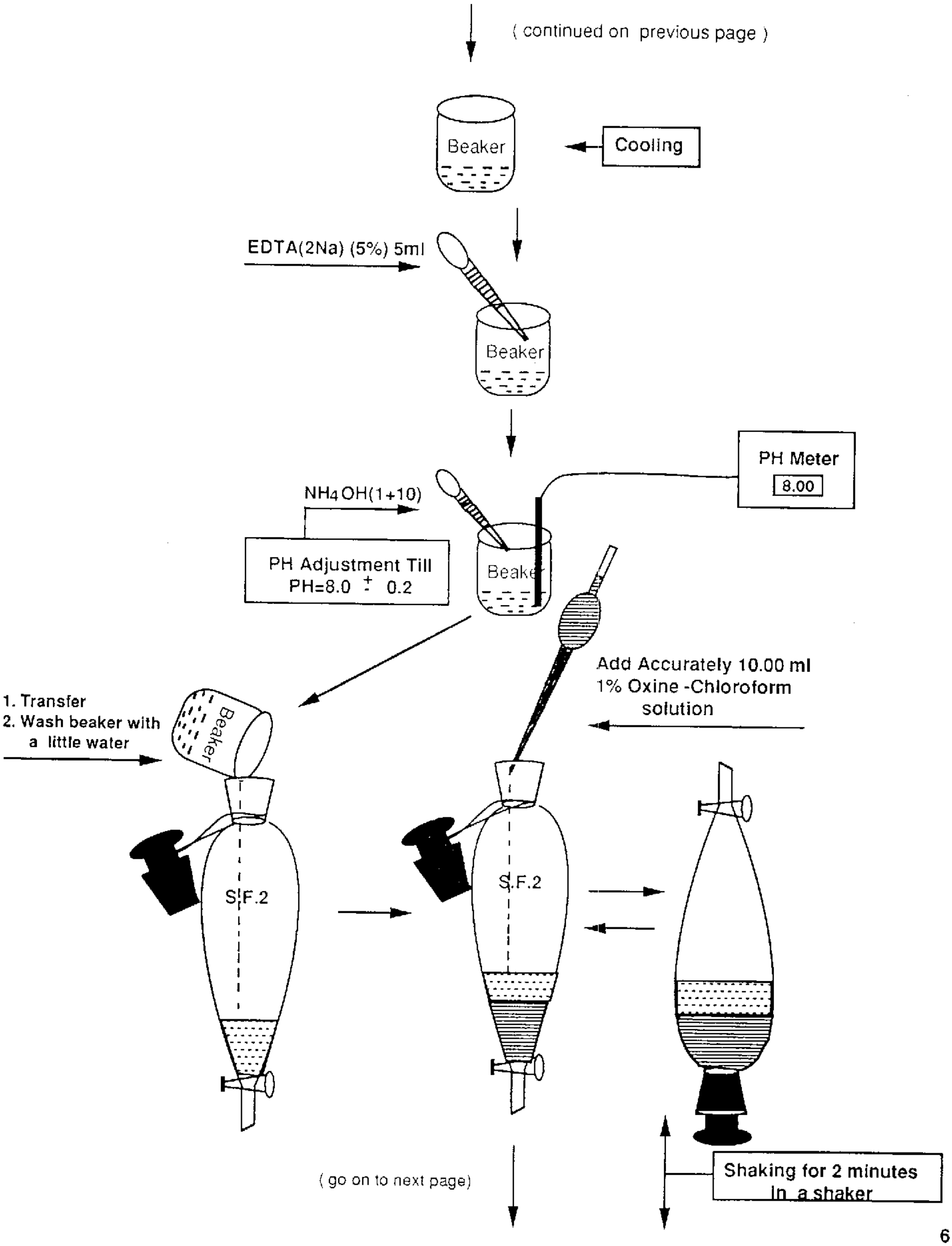

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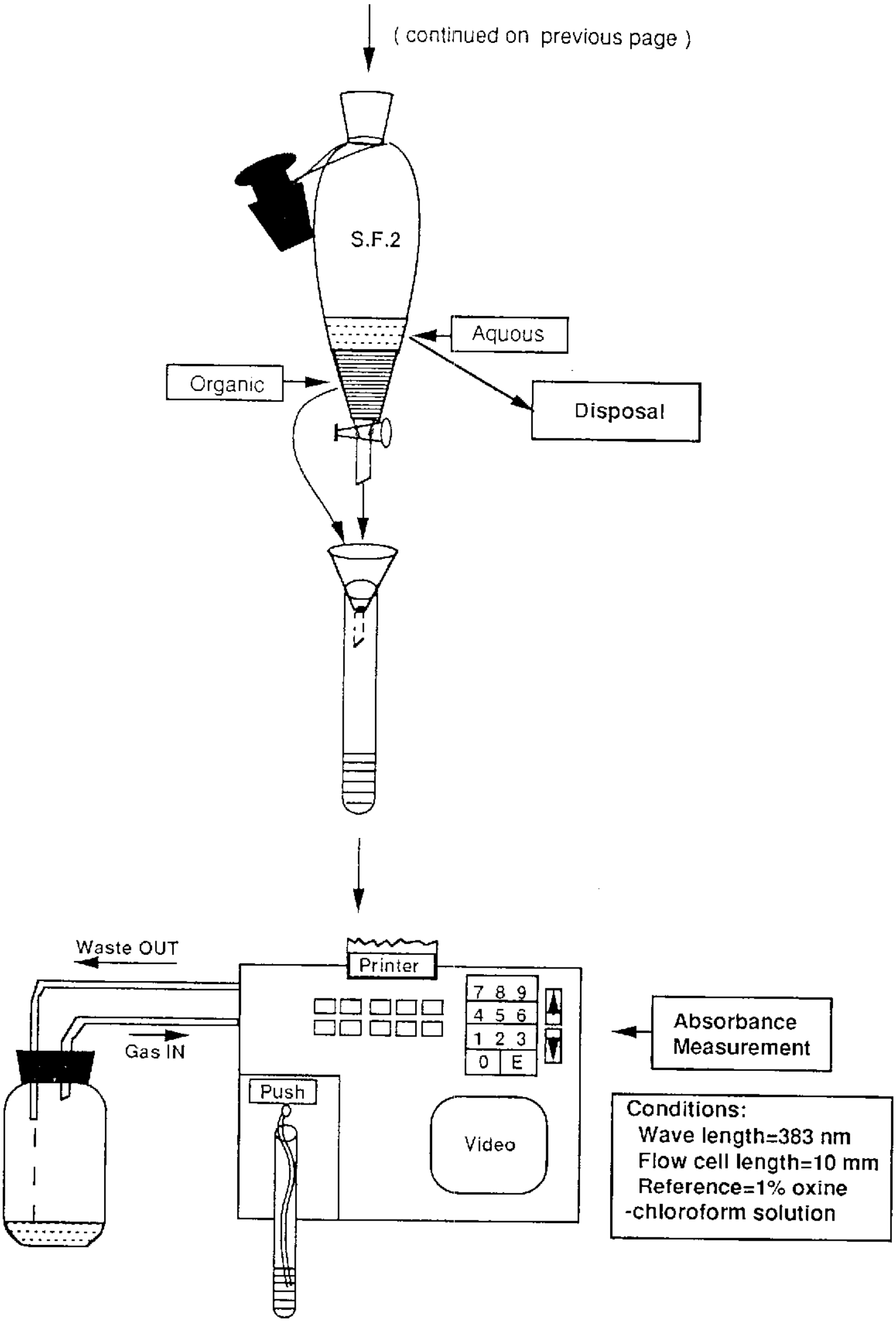


Conditions:
Wave length=383 nm
Flow cell length=10 mm
Reference=1% oxine -chloroform solution

UVIDEC-77 Clinical Spectrophotometer
(View from the front of it .)

TABLE 3.2.3-1 Chemical Analytical Results of Uranium

No.	Sample Name	Weight Used(g)	Determined(ppm)	Average(ppm)	*Reference(ppm	Error(%)	Note
1	EJB22-85	1.00232	64.8	65.0	66.4	-1.5	
		1.00506	65.2				
2	EJB19-85	1.00656	85.3	85.4	86.2	- 3	
		1.00446	85.5				
3	Y1-04	0.50743	132	127	137.5	- 7	Undisolved material existed
		0.50109	121				
4	GBW04110	0.51223	243	244	285	-7.5	"
		0.50825	245				
5	GBW04116	0.20082	456	477	536	-11	"
		0.20717	498				
6	GBW04112	0.20212	686	688	682	0.9	
		0.20767	689				
7	GBW04111	0.20169	791	771	788	-2.1	
		0.20253	751				
8	GBW04115	0.2006	1006	1028	986	4.3	
		0.20573	1050				

* Determined in CNNC-BRIUG

3.3 Determination of Thorium

3.3.1 Reagents and apparatus

1). HNO_3 ,8M

2). HF

3). HCl, 10M, 6M

4). $H_2C_2O_4$(5%)

5). ArsenazoIII (0.2%)

6). Anion exchange resin AG1x8(the same as chemicla procedure for alpha)

All reagents used in the experiment were analytical grade.

7). Clinical spectrophotometer(UVIDEC-77)

8). Other general analytical apparatus

3.3.2 Procedure

The procedure included open mixed acids digestion decompostion, AG1x8 anion exchange separation, ArsenazoIII -colour and measurement. The detailed procedure was shown in Fig 3.3.2-1, in which the calibration was as follows:

Take 0,10 ,15 ,20 ug thorium standard solution into 50 ml- beakers and add 10 ml HCl , then evaporate in the sand-bath till dryness. The next procedure was the same as those of sample (after sample decompositon). Finally, the calibration curve was able to be given as follows:

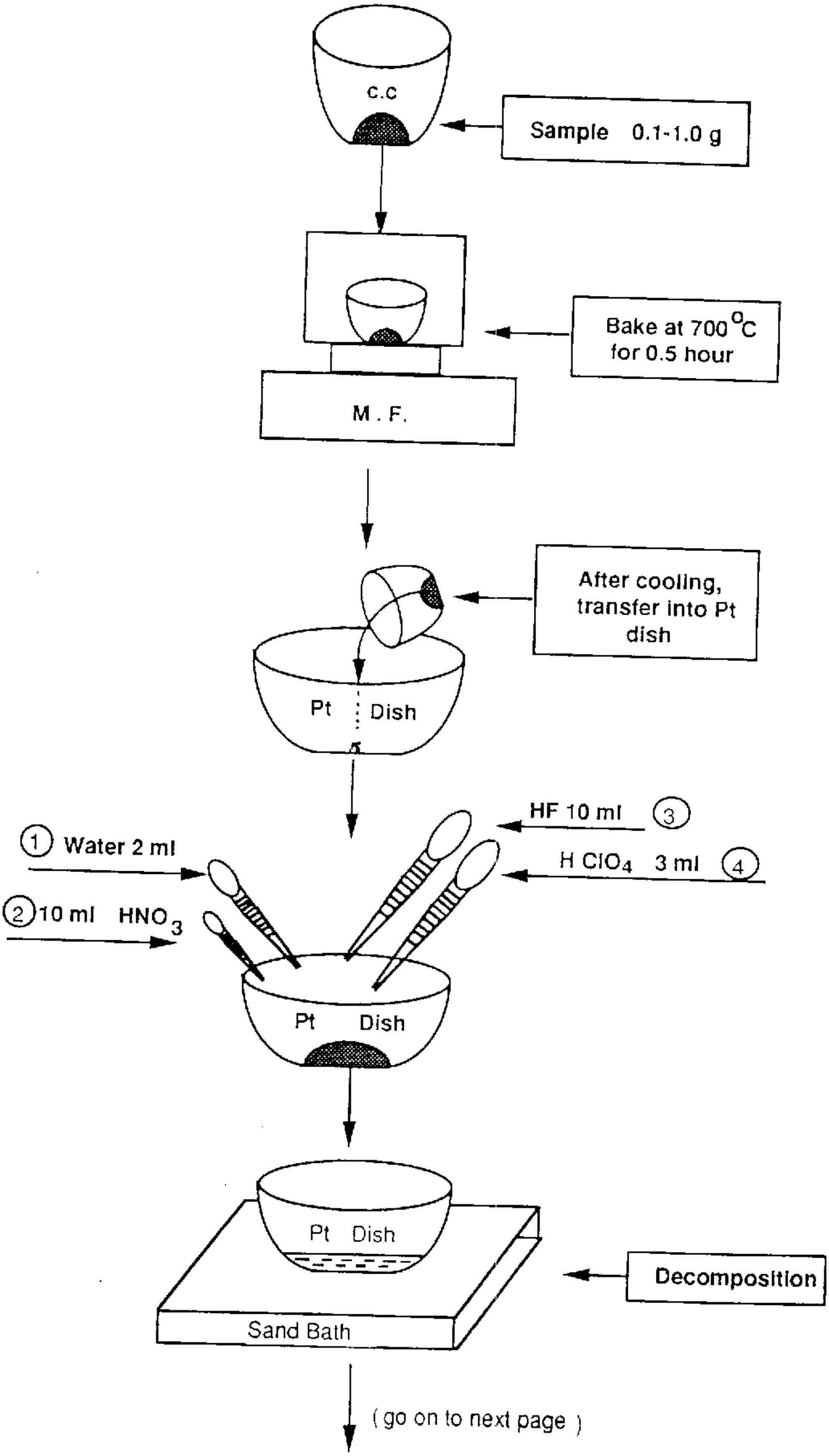
$$A= a+b\ C \qquad \text{..3.3.2-1}$$

where , A is the absorbance; C is the amount of Th in solution ; a and b are the coefficients.

3.3.3 Result

The results of 8 rocks and minerals samples from China were given in Table 3.3.3-1 .

Fig 3.3.2-1 **Chemical Analysis Procedure for Thorium**



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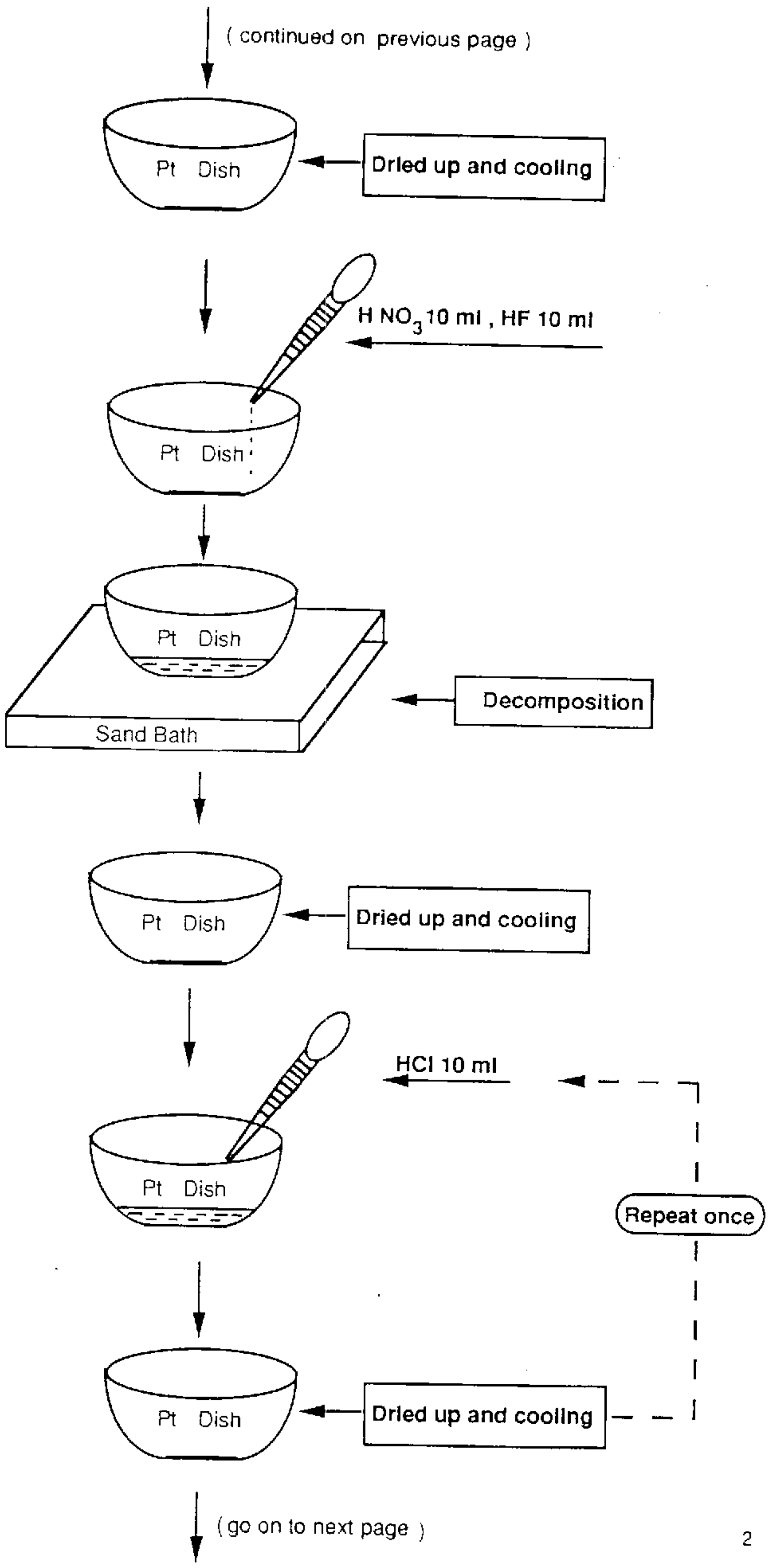
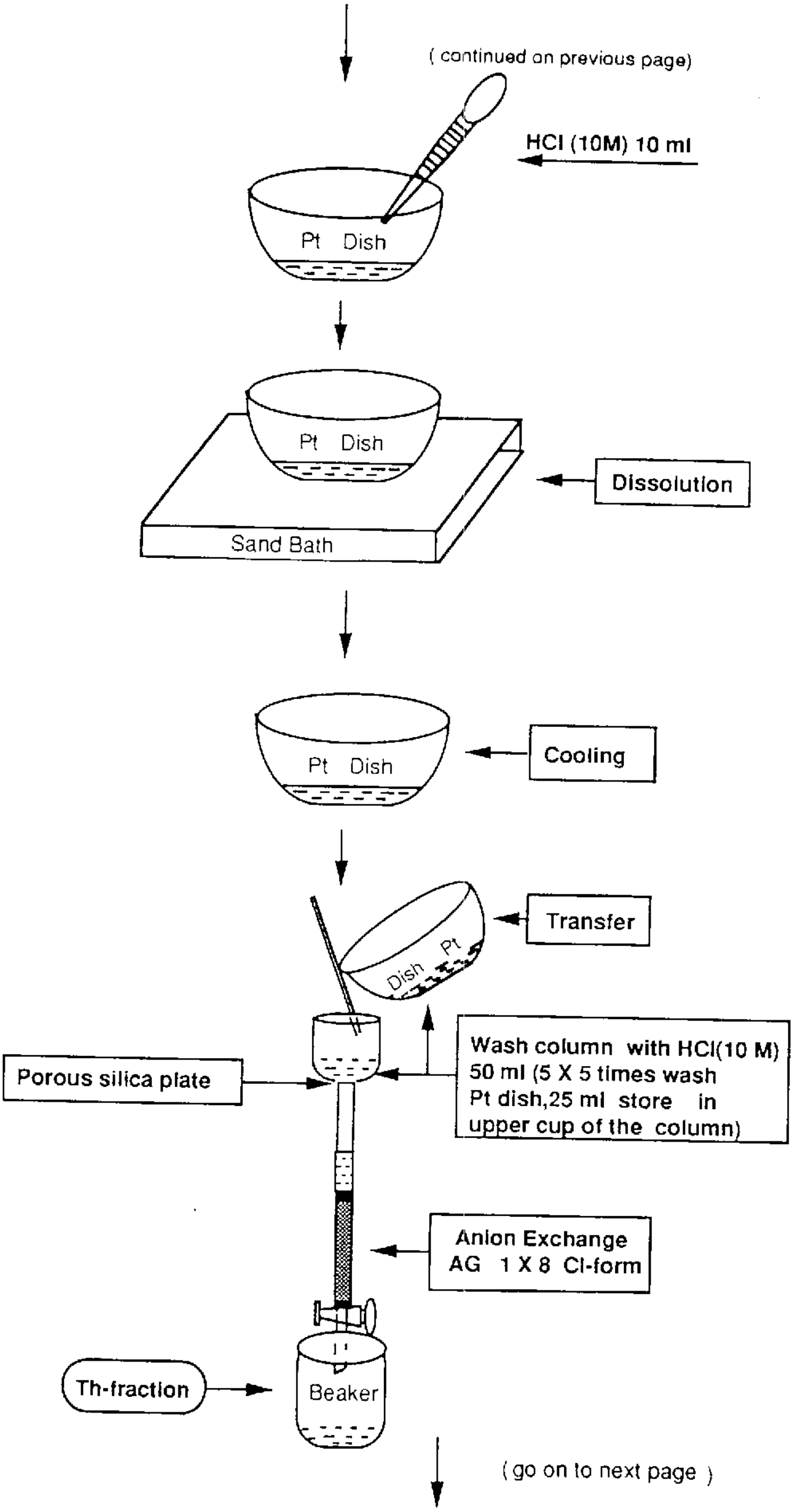

(continued on previous page)
Pt Dish
Dried up and cooling
H NO_3 10 ml , HF 10 ml
Pt Dish
Pt Dish
Sand Bath
Decomposition
Pt Dish
Dried up and cooling
HCl 10 ml
Pt Dish
Repeat once
Pt Dish
Dried up and cooling
(go on to next page)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HCl (10M) 10 ml
Pt Dish
Pt Dish
Sand Bath
Dissolution
Pt Dish
Cooling
Transfer
Pt Dish
Porous silica plate
Wash column with HCl(10 M) 50 ml (5 X 5 times wash Pt dish,25 ml store in upper cup of the column)
Anion Exchange AG 1 X 8 Cl-form
Th-fraction
Beaker
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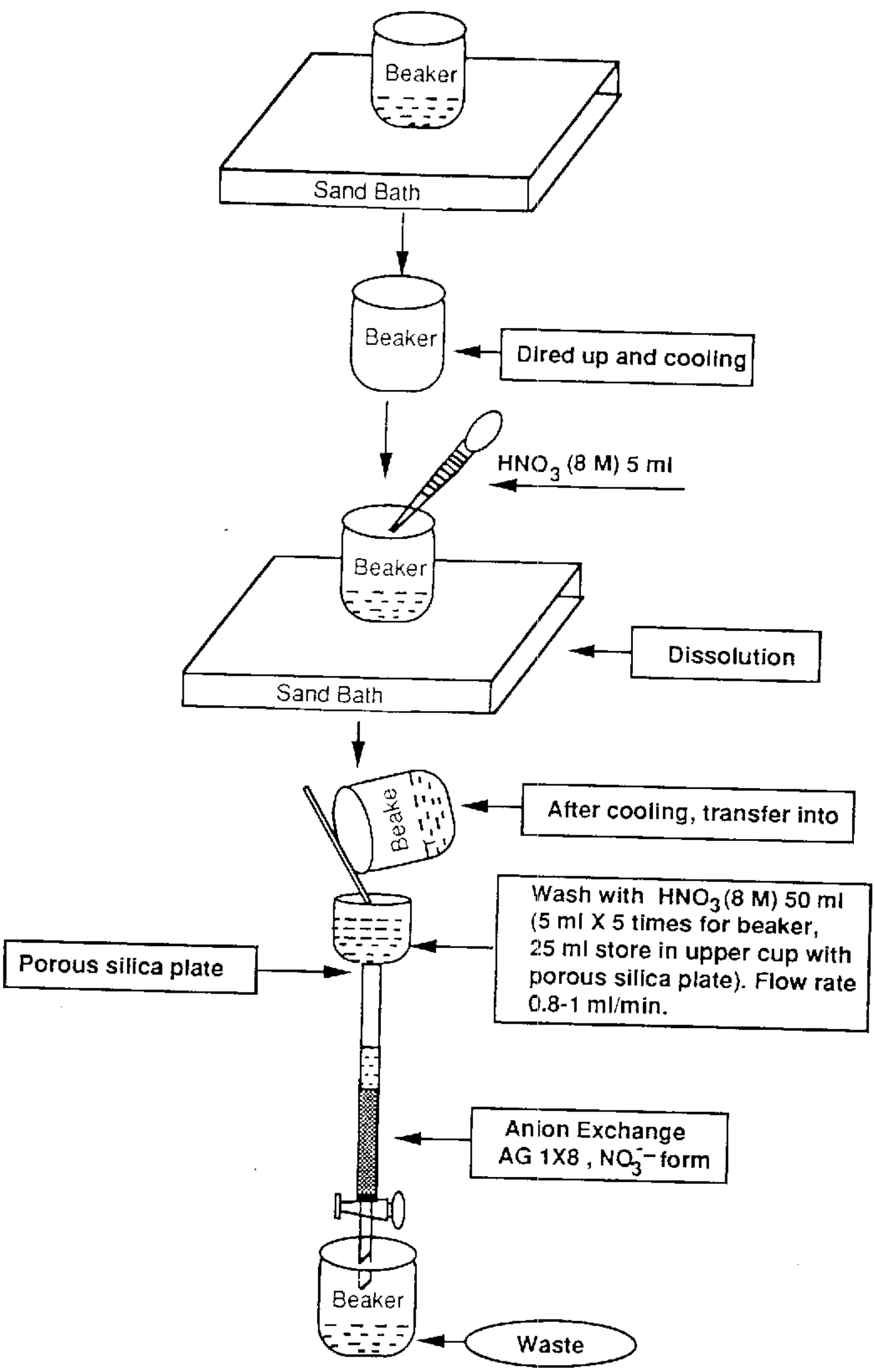

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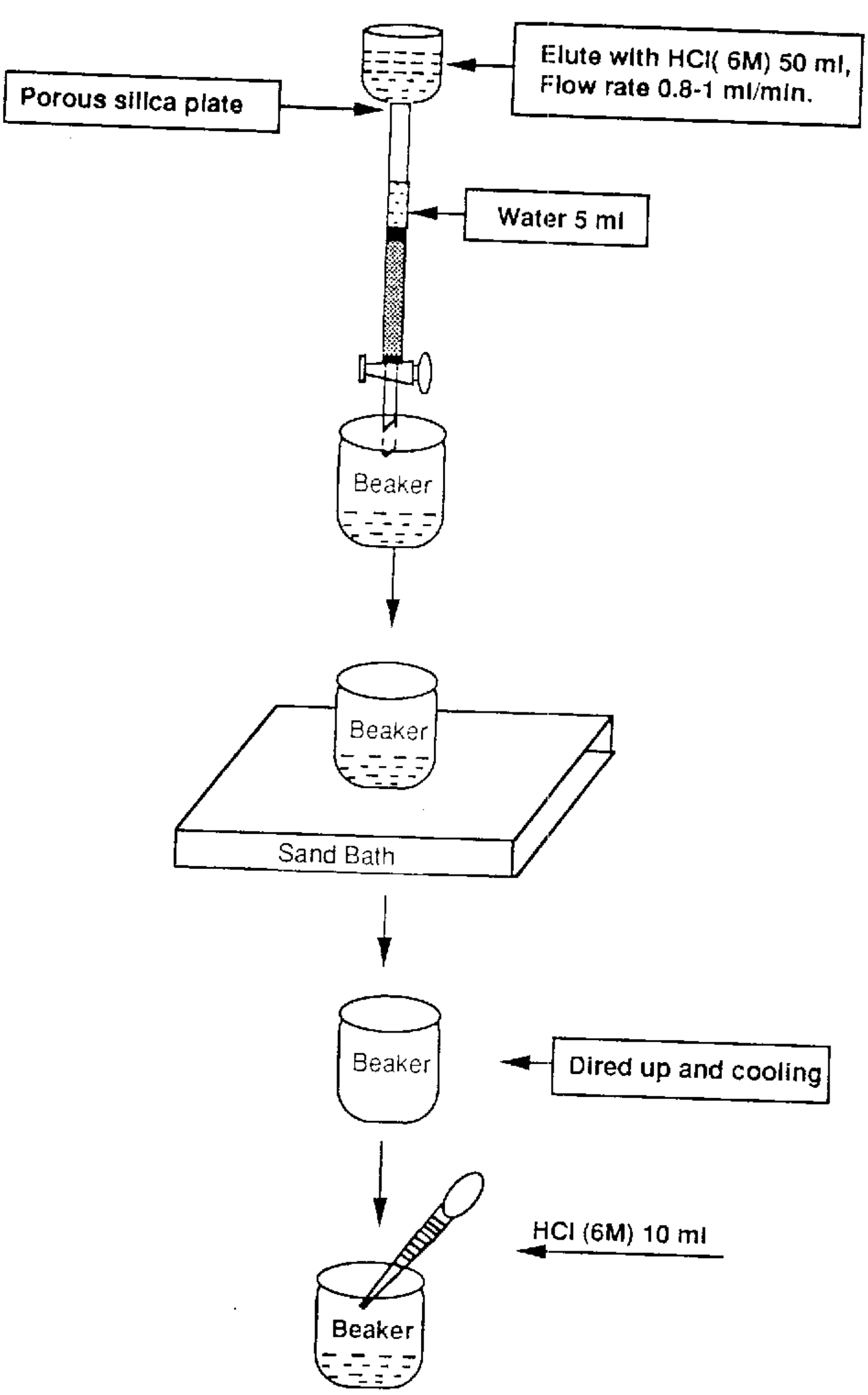

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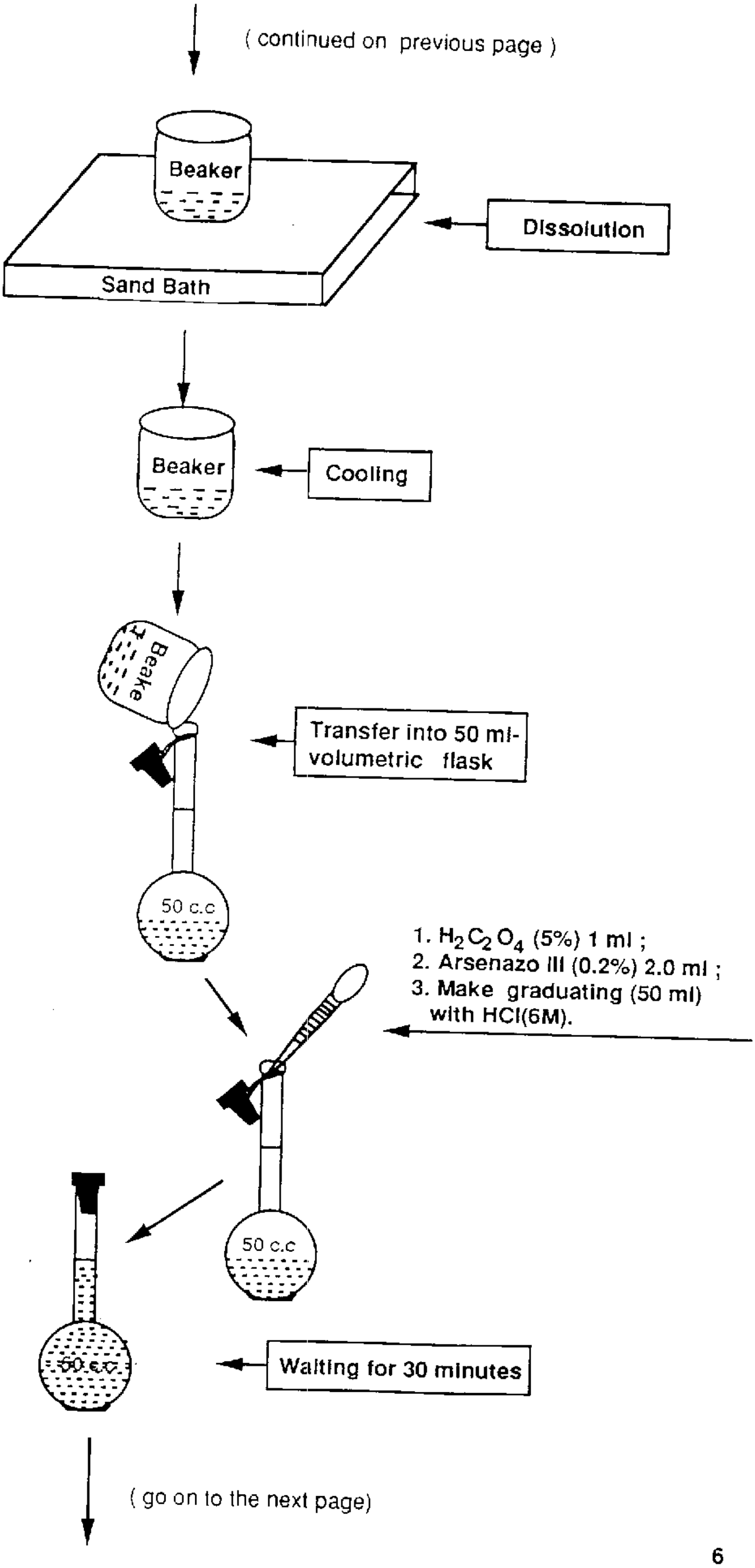

1. $H_2C_2O_4$ (5%) 1 ml ;
2. Arsenazo III (0.2%) 2.0 ml ;
3. Make graduating (50 ml) with HCl(6M).

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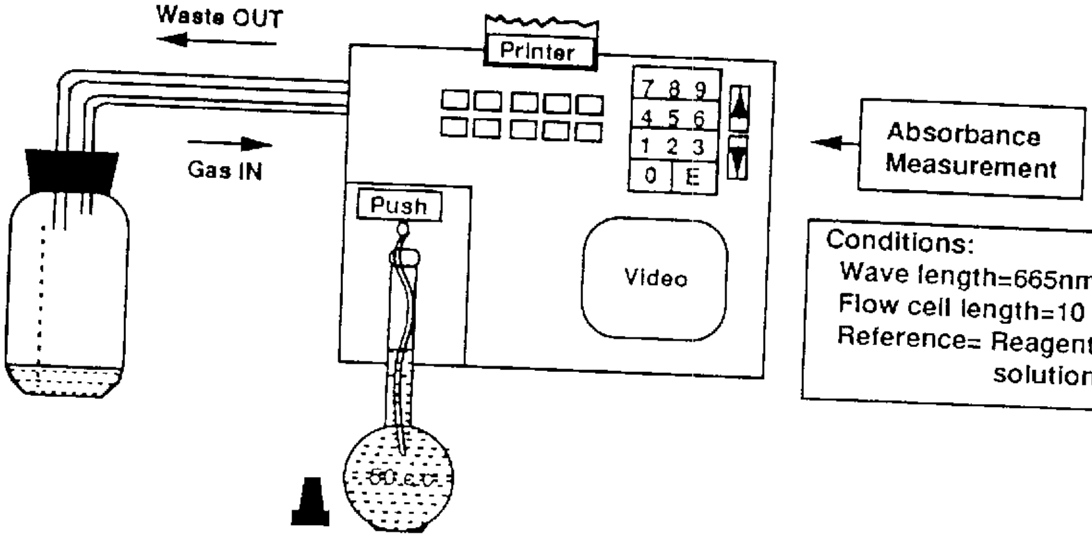


Conditions:
Wave length=665nm
Flow cell length=10 mm
Reference= Reagents solution

UVIDEC-77 Clinical Spectrophotometer
(View from the front of it .)

TABLE 3.3.3-1 Chemical Analytical Results of Thorium

No.	Sample Name	Weight Used(g)	Determined(ppm)	Average(ppm)	*Reference(ppm	Error(%)	Note
1	GSS-4	0.51777	21.8	22.0	28.0	-21	
	"	0.50026	22.1				
2	GSD-11	0.50959	23.6	22.7	23.1	-1.7	
	"	0.50427	21.7				
3	GBW04324	0.30764	4.6	4.1	5.0	-18	
	"	0.30735	3.6				
4	EJB18-85	0.50067	18.1	20.9	21.9	-4.7	
	"	0.50464	23.6				
5	EJB22-85	0.50402	29.4	27.1	28.8	-5.9	
	"	0.51702	24.8				
6	GBW04110	0.49574	25.1	24.3	25.0	-2.8	
	"	0.50163	23.4				
7	GBW04116	0.51463	676	595.0	202	###!!!	
	"	0.50149	513				
8	GBW04112	1.00016	10.9	9.7	11.0	-12	
	"	1.00172	8.5				
9	GBW04111	0.49812	27	26.9	26.0	3.5	
	"	0.50147	26.7				
10	GBW04115	0.51335	264	300	313	-4.3	
	"	0.49958	336				
				* Determined in CNNC-BRIUG			

Chapter 4 Comparison of Analytical Techniques for Uranium and Thorium in Rocks and Minerals Samples between PNC-Chubu Works and CNNC-BRIUG

4.1 Analytical results comparison

From the data* in Chapter 2,3, the comparison of analytical results was able to be made and shown in Fig4.1-1,4.1-2 and 4.1-3. From these figures, it can be seen that most of the results have no big deviation or error. However, the results of Th for a few samples were not satisfied, maybe resulting from sample decomposition and separation uncompletely. (* The data marked by"**" were cancelled in the figures.)

4.2 Analytical methods comparison

In order to compare with the analytical techniques for U and Th as well as the U-series nuclides in rocks and minerals, it is necessary to introduce briefly the established analytical methods at CNNC-BRIUG. Since it was born in 1950s, CNNC-BRIUG has established and developed a lot of analytical techniques for them. Table 4.2-1 and Table 4.2-2 show the analytical methods for uranium(U-series nuclides) and thorium ,respectively. Considering trace analysis of U, the standard addition laser fluorimetry is excellent one, which does not need chemical separation and has very high sensitivity without interference. Nowdays, this method is being used widely in most labs in China. Anyway, the Th and U-series analytical methods are similar to these of PNC-Chubu Works except for their decomposition and separation techniques. Table 4.2-3, 4.2-4 and 4.2-5 demonstrate the comparison about the methods attached at PNC-Chubu Works.

4.3 Advantages and disadvantages

Through 3-month work at PNC-Chubu Works' Labs, in author's opinion , the advantages and disadvantages for the techniques attached here can be concluded as Table 4.3-1.

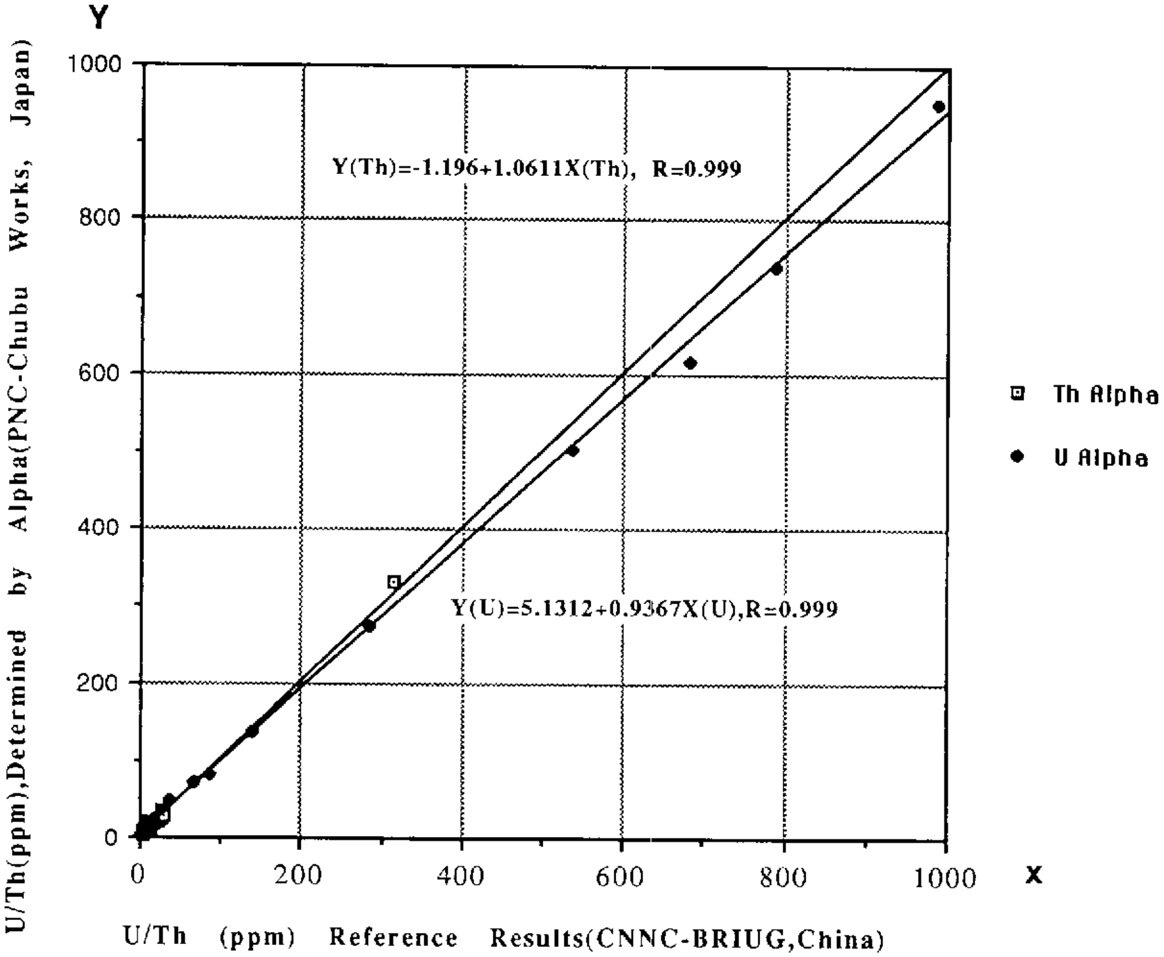


Fig4.1-1 Correlation between Alpha and Reference

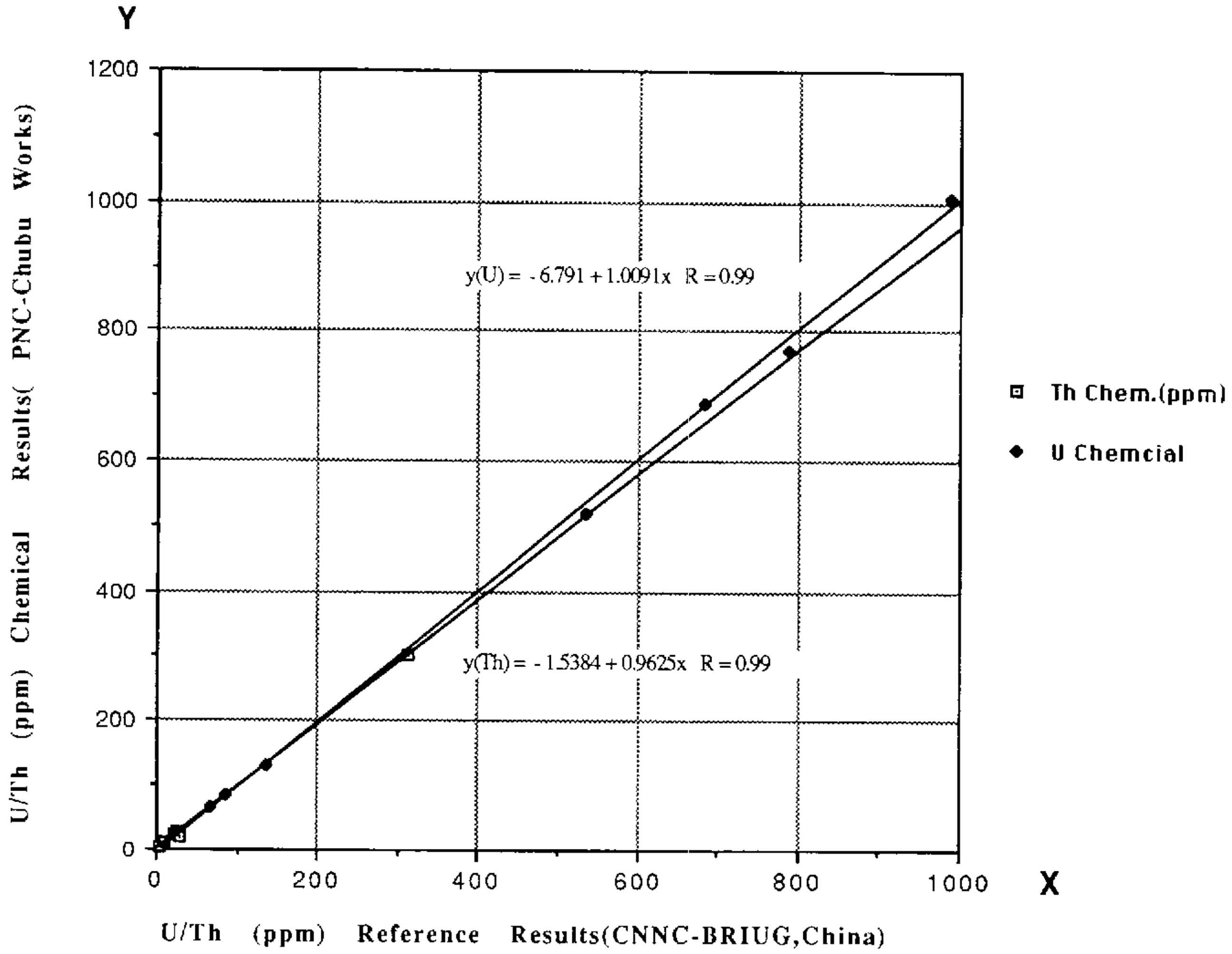


Fig4.1-2 Correlation between Chemical and Reference Results

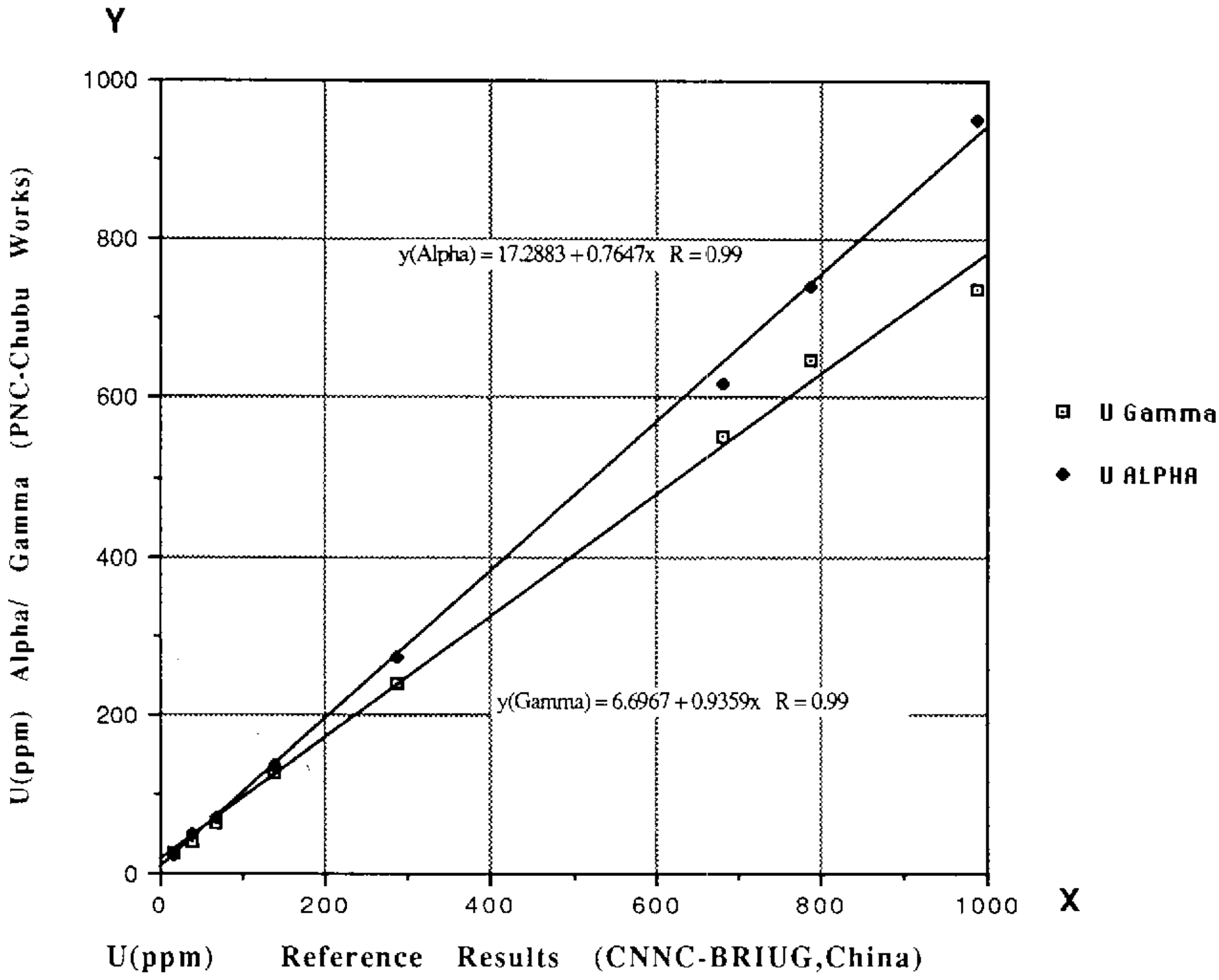


Fig4.1-3 Correlation between Alpha/Gamma and Referecnce Results

Table 4.2-1 Analytical methods for uranium at CNNC-BRIUG

No.	Method	Key words
1.	Ferrous/stannous/ titanous/method	Ferrous/ stannous/ titanous reductant, ammonium vanadate, tityimetry , 30% H_3PO_4 $K_2Cr_2O_7$, indicator
2.	Br-PADAP spectrophotometry I	TOPO, extraction separation, 80% alcohol media, Br-PADAP, absorbance, calibration
	Br-PADAP spectrophotometry II	TPB, extraction chromatographic separation, impuries washed by HCl(6M), U eluted by water , 40 % ethanol or acetone media, Br-PADAP,absorbance, calibration
3.	ArsenazoIII spectrophotometry	Strong alkaline anion exchange resin, impuries washed mixed solution , U eluted by water, ArsenazoIII ,absorbance, calibration
4.	Standard addition laser fluorimetry	Mixed ammonium salts decomposition, PH 7, special fluorescence reagent, standard addition technique, very high sensitivity
5.	Beta-gamma counting	Made in China
6.	Gamma spectrometry	U-series nuclides, Made in USA
7.	Alpha spectrometry	U-series nuclides , Made in USA
8.	Neutron activation analysis	Made in USA

Table 4.2-2 Analytical methods for thorium at CNNC-BRIUG

No.	Method	Key words
1.	ArsenazoIII spectrophotometry I	PMBP extraction in PH2, back-extraction and colouring in HCl(4N), ArsenazoIII ,absorbance, calibration
	ArsenazoIII spectrophotometry II	N_{263} extraction chromatographic separation, impuries washed by mixed solution,Th eluted by HCl(4 N) ArsenazoIII ,absorbance, calibration
	ArsenazoIII spectrophotometry II	Cation exchange resin, impuries washd HCl(5-6M),Th eluted by ammonium oxalate, Arsenazo III, absorbance calibration
2.	Morin fluorometry	Water sample, N_{263} -on line preconcentration, fluorescence spectrophotometry , special fluorescence reagent, high sensitivity, calibration
3.	Gamma spectrometry	Made in USA
4.	Alpha spectrometry	Made in USA
5.	Neutron activation analysis	Made in USA

Table 4.2-3 Comparison of Chemical Procedure for Alpha Spectrometry

	PNC Chubu Works(Japan)	CNNC BRIUG(China) [see APPENDIX E]
Sample Weight(g)	0.1-1	0.1-1
Decomposition method	mixed acids	mixed ammonium salts
Decomposition time	more than 3 hrs	less than 2 hrs
Dissolution	HCl(10M)	reverse aqua regia
Separation method	anion exchange and solvent extraction	extraction chromatography
Mixture of U and Th loading (1)	Cl-form anion exchange column(10 M HCl)	extraction chromatographic column
Loading (1)	HCl(10M),10 ml	aluminium nitrate(10%)+tartaric acid(2%)+nitric acid(15%),15ml
Washing (1)	HCl(10M),50 ml	tartaric acid(2%)+nitric acid(15%),15 ml
Effect	separation for U-fraction and Th-fraction	separation for U-Th fraction and other elements
On column(1)	U and other elements	U and Th
In solution(1)	Th and other elements	other elements which are not interesting
Elutate 1 for column(1)	HCl(0.1 M) ,100 ml	HCl(5 M) ,20 ml
Interesting element	U	Th
Elutate 1-2 for column(1)	not needed	sodium fluoride (0.2%), 10 ml
Interesting element	no	U
Further use of column(1)	no	yes(after regeneration)
Treatment of solution(1)	drying up for next anion exchange separation	useless
Process of eluate1	drying up for next solvent extraction separation	drying up for Th source preparation
Process of eluate1-2	no	drying up for U source preparation

Page 1 of the table

Table 4.2-3 Comparison of Chemical Procedure for Alpha Spectrometry

Column(2)	nitrate-form anion exchange column(8 M nitric acid)	
Loading(2)	nitric acid(8M),5ml	
Washing(2)	nitric acid(8M),50 ml	
Eluate2	HCl(6M),50ml	
Process of eluate 2	drying up for Th source preparation	
Solvent extraction	TBP-CCl4 method (twice extraction)	
Organic phase	TBP-CCl4 (10%), 20ml(1st),10ml(2nd)	
Aquous phase	sodium nitrate(50%)20ml+nitric acid(3+11) 30ml	
Back extraction solution	HCl(1+11),30ml	
Process of back extraction solution	drying up for U source preparation	
Full procedure time	4 days	1day
Source preparation	electrodepositon	electrodepositon
Chemical conditions for U	ammonia,sulfuric acid,PH=2,Volume=12-15 ml	ammonium chloride(2%)+ammonium oxalate(5%),PH=6,Vol=12-15ml
Chemical conditions for Th	ammonia,sulfuric acid,PH=2,Volume=12-15 ml	ammonium chloride(2%)+ammonium oxalate(5%),PH=2,Vol=12-15ml

Page 2 of the table

Table 4.2-4 Comparison of Chemical Analysis of Uranium

	PNC Chubu Works(Japan)	CNNC BRIUG(China) [See APPENDIX F]
Sample Weight(g)	0.1-1	0.1
Decomposition method	open mixed acids	closed mixed acids
Decomposition time	more than 3 hrs	less than 3 hrs
Dissolution	nitric acid(1+20)	nitric acid(1+2)
Separation method	TBP-Kerosene extraction	non
	Conditions: sodium nitrate+nitric acid(1+10)	
	1st washing: potassium iodate(5%)+nitric acid (30%)	
	2nd washing:sodium nitrate(50%)+nitric acid(6.5%)	
	Back-exttraction: ammonium sulfate(25%)	
Measurement method	oxine-chloroform spectrophotometry	standard addition laser fluorimetry
	Conditions: EDTA-2Na(5%),PH=8.0,oxine-chloroform	Conditions: special fluorescence reagent
Sensitivity(detection limit)	low(ppm level)	high(ppb level)
Full flow time	4 days for 10 samples	2 days for 25 samples

Table 4.2-5 Comparison of Chemical Analysis of Thorium

	PNC Chubu Works(Japan)	CNNC BRIUG(China) [see APPENDIX G]
Sample Weight(g)	0.1-1	0.1-1
Decomposition method	mixed acids	mixed ammonium salts
Decomposition time	more than 3 hrs	less than 2 hrs
Dissolution	HCl(10M)	nitric acid (15%)
Separation method	anion exchange (twice)	N-263 extraction chromatography
Mixture of U and Th loading (1)	Cl-form anion exchange column(10 M HCl)	extraction chromatographic column
Loading (1)	HCl(10M),10 ml	aluminium nitrate(10%)+tartaric acid(2%)+nitric acid(15%),15ml
Washing (1)	HCl(10M),50 ml	tartaric acid(2%)+nitric acid(15%),15 ml
Effect	separation for U-fraction and Th-fraction	separation for U-Th fraction and other elements
On column(1)	U and other elements	U and Th
In solution(1)	Th and other elements	other elements which are not interesting
Elutate 1 for column(1)	non	HCl(4 M) ,20 ml
Interesting element	non	Th
Further use of column(1)	non	yes(after regeneration)
Treatment of solution(1)	drying up for next anion exchange separation	useless
Process of eluate1	disposal	
Column(2)	nitrate-form anion exchange column(8 M nitric acid)	
Loading(2)	nitric acid(8M),5ml	
Washing(2)	nitric acid(8M),50 ml	
Eluate2	HCl(6M),50ml	
Process of eluate 2	dried up then dissolved in HCl(6M) for measurement	
Measurement(spectrophotometry)	ArsenazoIII, 6M HCl	ArsenazoIII, 4 M HCl
Full flow time	4 days for 10 samples	1 days for 25 samples

Table 4.3-1 Advantages and disadvantages of the techniques

No.	Techniques	Advantages	Disadvantages
1.	Decompsiton	. Low blank . Simple reagents	. Uncompletely for complicated samples . long time
2.	Separation	. Simple reagents	. High acidity and organic solvent used bad for both health and environment . Long procedure
3.	Measurement of U (by chemical method)	Not special reagents	. Low sensitivity . Linear range not wide
4.	Measurement of Th (by chemical method)	Not special reagents	. High acidity
5.	Alpha spectrometry	. High quality instrument , . 8 detectors, low background, . Automatic analysis of spectrum	. costly
6.	Gamma spectrometry	. High quality ,high resolution instrument, low background, .High pure Ge detector cooling only in operation, automatically.	. costly
7.	Data processing system	. Convenient,easy operation . Multi-functional . Excellent softwares	

Chapter 5 Computer System for Data processing

5.1 About Apple Macintosh Plus system and the softwares used for data processing

The Apple Macintosh Plus system , a powerful personal computer system, is widely being used at PNC-Chubu Works, including data processing, database managing system , OA management and so on. The basic parameters are as follows:

CPU: 68020
RAM: 2 MB
Harddisk: 40 MB
Floppy disks: 700 KB X 2 ; 3.5 inch
Monitor: Mono. 11 inch
Keyboard: Apple
Mouse:M0100
Operating/File system: MAC OS (V6.05)

The softwares used for data processing are mainly Mircrosoft Excel 2.2 and Cricket GRAPH 1.05 . For more information, following references can be looked up.

1). Microsoft Excel Reference (Microsoft Excel Quick Reference Guide): Complete Spreadsheet with Business Graphics and Database Version 2.2 (For Apple Macintosh)

2). Getting Started with Microsoft Excel :Complete Spreadsheet with Business Graphics and Database Version 2.2 (For Apple Macintosh)

3). Microsoft Excel Functions and Macros (For Apple Macintosh)

4). Cricket GRAPH Presentation Graphics for Science and Business.

5.2 About application system for this report

This report was prepared in the computer system, including words , procedures, diagrams, figures and tables. The employed softwares were Microsoft Word, Claris MacDrawII, Cricket GRAPH and Microsoft Excel. For more information , the references metioned above and followings can be found.

1). Macintosh System Software User's Guide Version 6.0 (For Apple Macintosh)

2). CLARIS MacDraw II (For Apple Macintosh)

3). Microsoft Word ((For Apple Macintosh)

References

1. PNC , Atomic Power (1991,Japanese)
2. C. KURONUMA, Uranium Resource Lecture (No.5), PNC-Chubu Works(1992)
3. DENG ZHENGHAN, Report on Research and Training Program , PNC-Chubu Works(1991)
4. M.IVANOVICH AND R.S.HARMON, Uranium Series Disequilibrium: Applications to Environmental Problems, CLARENDON PRESS.OXFORD(1982)
5. ZHENG CHENFA et.al., Ratiation Measurement, ATOMIC ENERGY PRESS(1983,Chinese)

APPENDIX

A: Am-241 Standard Source for Alpha Spectrometry

B : An Example of Alpha Spectrum ---I: U-fraction II: Th-fraction

C: IAEA Uranium Standard Source for Gamma Spectrometry

D: CRT-n Show for Gamma Spectrometry

E: Alpha Spectrometry at CNNC-BRIUG

F: Chemical Analysis of Uranium at CNNC-BRIUG

G: Chemical Analysis of Thorium at CNNC-BRIUG

Amersham International plc
Amersham UK

APPENDIX A: Am-241 Standard for Alpha Spectrometry

Certificate of measurement of alpha emitting radioactive reference source

A 2797

Description

Principal radionuclide: Americium-241

Product code: AMR.22

Source number: 6431RA

Measurement

Reference time: 1200 GMT on 7 February 1983

Rate of emergence of alpha particles from the front surface: 1.94×10^4 alpha particles per minute

Estimated disintegration rate of the active material: 3.81×10^4 disintegrations per minute

Method of measurement: 38100 dpm/60 sec/min = 635 dps ⇒ ~~[illegible]~~

The rate of emergence of alpha particles was measured in a proportional counter under conditions of 2-pi geometry.

0.01716 μCi

Accuracy

The overall uncertainty in the rate of emergence of alpha particles quoted above was: ± 2.0 %

The limits of uncertainty were taken as the arithmetic sum of the uncertainty due to random variations, calculated at the 99.7% confidence level, and the estimated systematic uncertainties in the measurement.

Physical Data

Radionuclide	Recommended half life	Important alpha particle energies MeV
Americium-241	433 years	5.442(12.5%), 5.484(85.2%)
Curium-244	17.8 years	5.763(23.6%), 5.806(76.4%)
Plutonium-239	24,100 years	5.103(11%), 5.142(15%), 5.155(73%)

Rema

The ratio of the disintegration rate to the rate of emergence of alpha particles was estimated to be 1.96. This ratio includes the conversion from 2-pi to 4-pi geometry and the backscatter in the source. It assumes that there is no self-absorption in the active material.

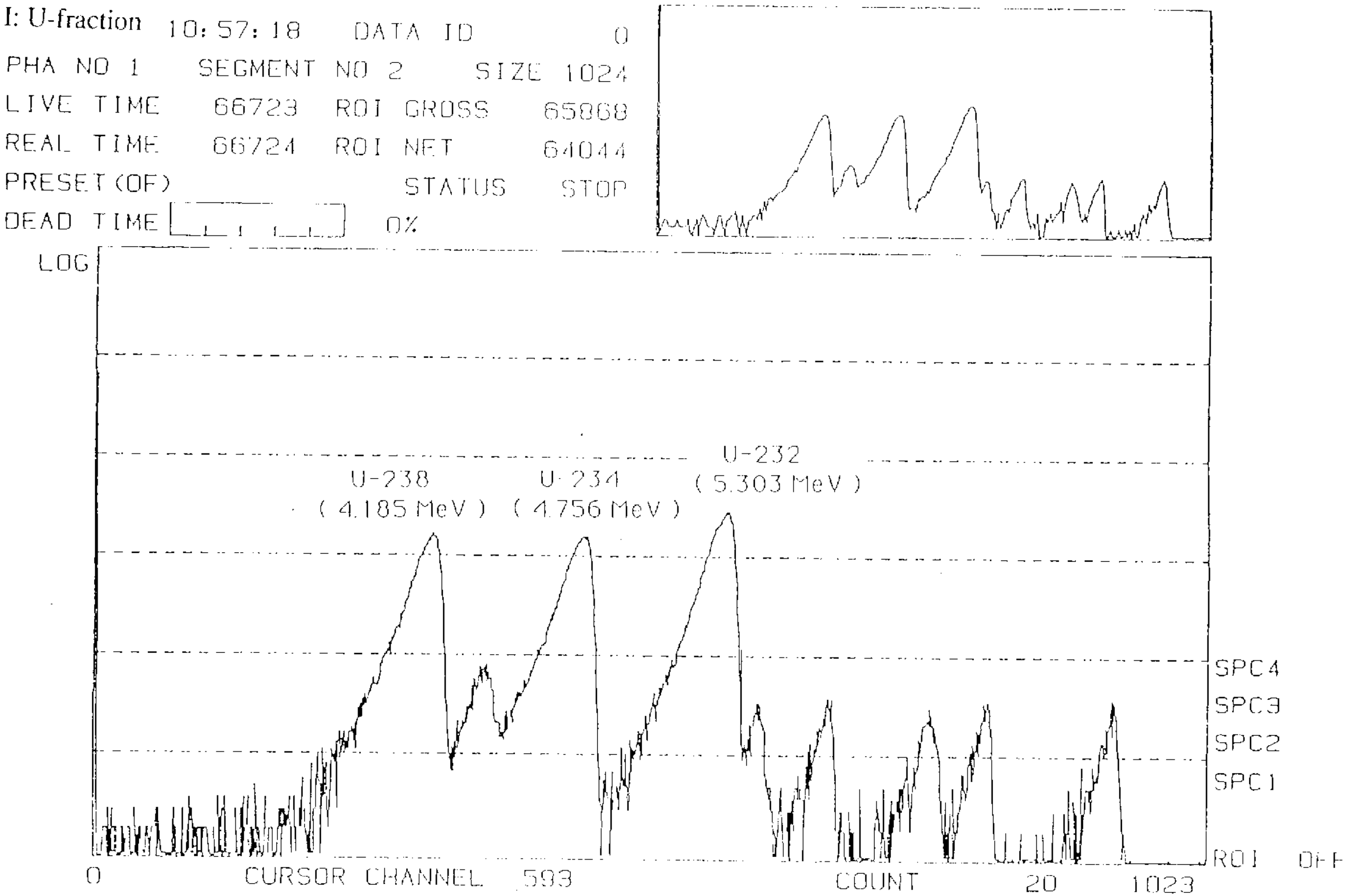
The disintegration rate so derived does not include the disintegration rate of any traces of radioactive material that may be present in the source other than that on the front face. (Such activity is normally less than 5% of the total activity.)

A gold surface barrier alpha spectrometer was used to show that the measured alpha resolution (full width at half maximum height) was less than 20 keV.

proved

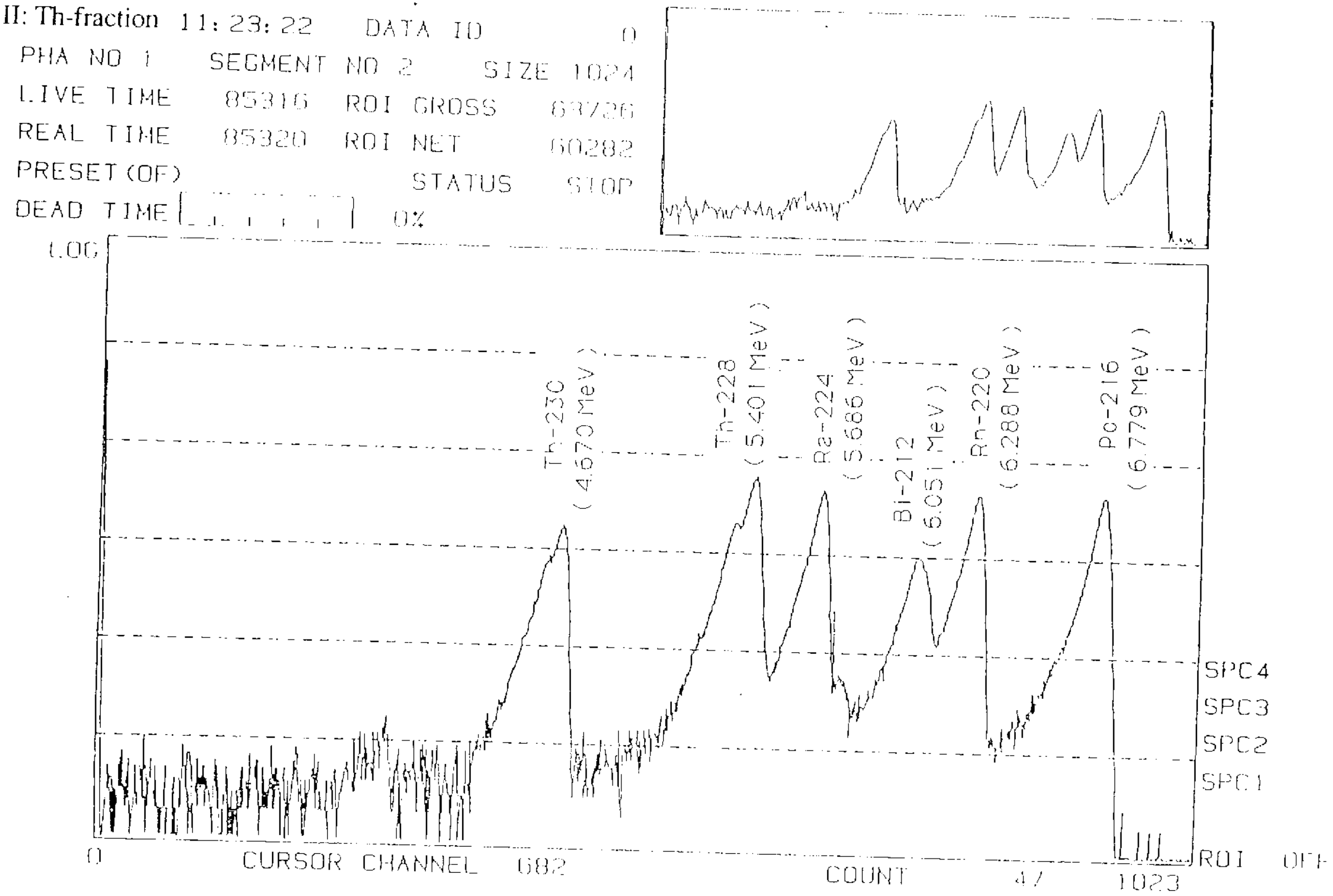
Amersham

APPENDIX B : An Example of Alpha Spectrum



```
I: U-fraction   10: 57: 18    DATA ID          0
PHA NO 1    SEGMENT NO 2     SIZE 1024
LIVE TIME     66723   ROI GROSS     65868
REAL TIME     66724   ROI NET       64044
PRESET (OF)                 STATUS    STOP
DEAD TIME                  0%
```

II: Th-fraction



```
11: 23: 22      DATA ID              0
PHA NO 1        SEGMENT NO 2     SIZE 1024
LIVE TIME       85316   ROI GROSS    63726
REAL TIME       85320   ROI NET      60282
PRESET(OF)                  STATUS    STOP
DEAD TIME                             0%
```

APPENDIX C: IAEA Uranium Standard Source for Gamma

INTERNATIONAL ATOMIC ENERGY AGENCY

REFERENCE MATERIAL
FOR
GAMMA-RAY SPECTROMETRIC ANALYSIS
OF
GEOLOGICAL MATERIALS

IAEA/RGU-1

CERTIFICATE OF ANALYSIS

COMPONENT	CONCENTRATION*	CONFIDENCE INTERVAL**
Uranium	400 µg/g	± 2 µg/g
Thorium	less than 1 µg/g	---
Potassium	less than 20 µg/g	---

*Expressed on dry weight basis (constant weight at 130°C)
**At a significance level of 0.05

DESCRIPTION OF MATERIAL

RGU-1, RGTh-1 and RGK-1 are intended for use in calibrating laboratory gamma-ray spectrometers for the determination of U, Th and K in geological materials. RGU-1 was prepared by the Canada Centre for Mineral and Energy Technology (CANMET) under a contract with the International Atomic Energy Agency. The material was prepared by dilution of Canada Certified Reference Material Project (CCRMP) uranium ore BL-5 (7.09% U) with a floated silica powder of similar grain size distribution. BL-5 has been certified for uranium, ^{226}Ra and ^{210}Pb confirming that it is in radioactive equilibrium. The complete description of the preparation and certification of RGU-1 may be found in the reference.

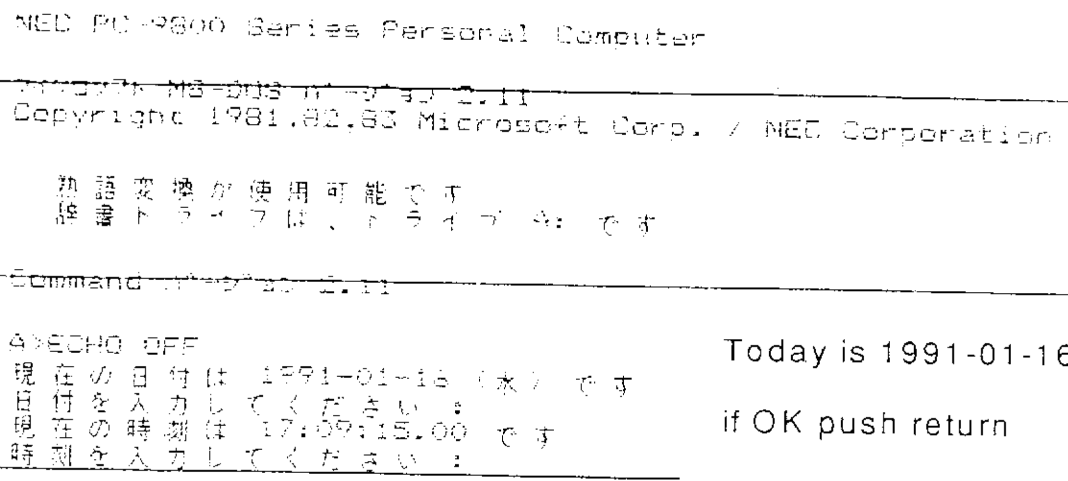
REFERENCE

Preparation of Gamma-ray Spectrometry Reference Materials
RGU-1, RGTh-1 and RGK-1 Report - IAEA/RL/148, Vienna, 1987

This report may be obtained from:
INTERNATIONAL ATOMIC ENERGY AGENCY
Agency's Laboratories
Analytical Quality Control Services
P.O.Box 100
A-1400 Vienna, AUSTRIA

APPENDIX D: CRT-n Show for Gamma Spectrometry

<<< CRT-1 >>>



```
NEC PC-9800 Series Personal Computer
マイクロソフト MS-DOS バージョン 2.11
Copyright 1981,82,83 Microsoft Corp. / NEC Corporation

   熟語変換が使用可能です
   辞書ドライブは、ドライブ A: です

Command バージョン 2.11

A>ECHO OFF
現在の日付は 1991-01-16 (水) です
日付を入力してください :
現在の時刻は 17:09:15.00 です
時刻を入力してください :
```

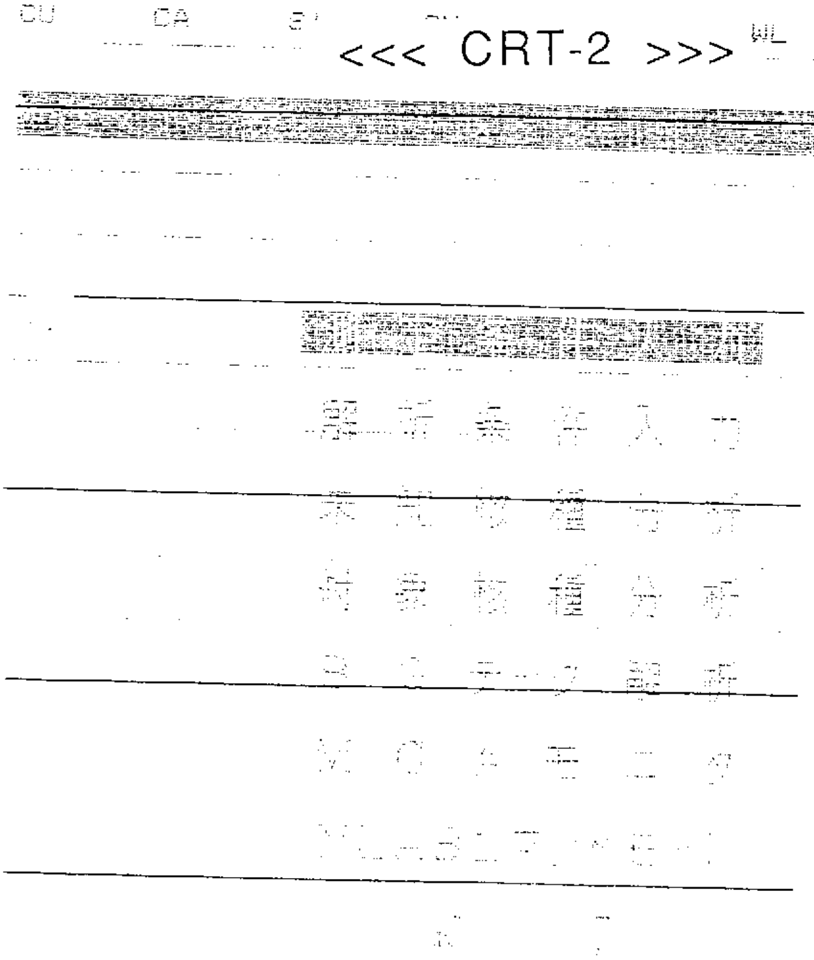
Today is 1991-01-16 (水)

if OK push return

Time is 17:09:15.00

if OK push return

<<< CRT-2 >>>



```
CU    CA                                WL    INS    REP

      [illegible]
      解析条件入力
      未知核種分析
      特定核種分析
      BGデータ解析
      MCAモニタ
      NLABコマンド
      終了
```

Input of Measured Condition

Input of Analytical Condition

Analysis of Unknown Nuclides

Analysis of Fixed Nuclide

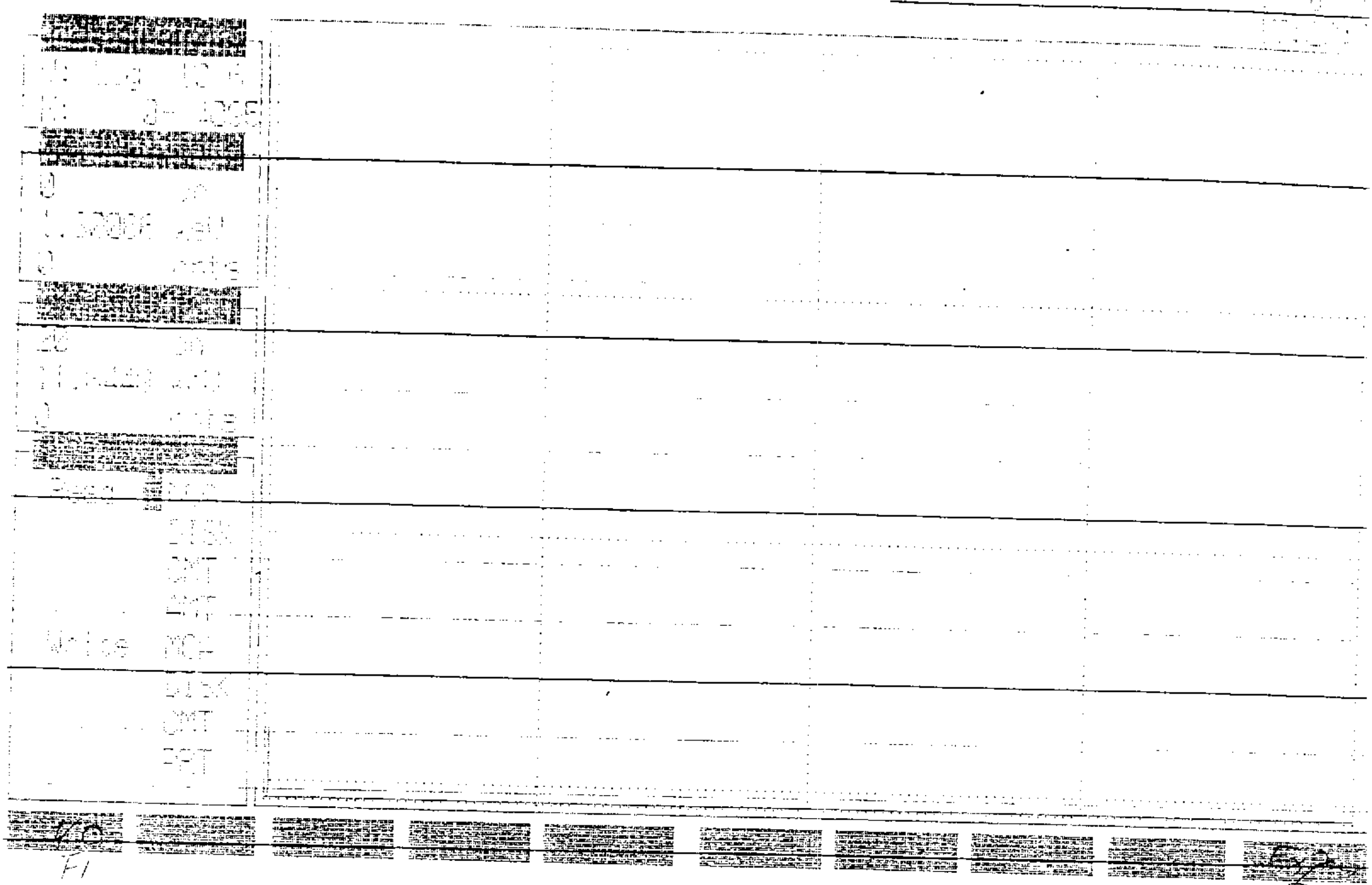
Analysis of BG Data Analysis

MCA Moniter

NLAB Command

END

<<< CRT-3 >>>

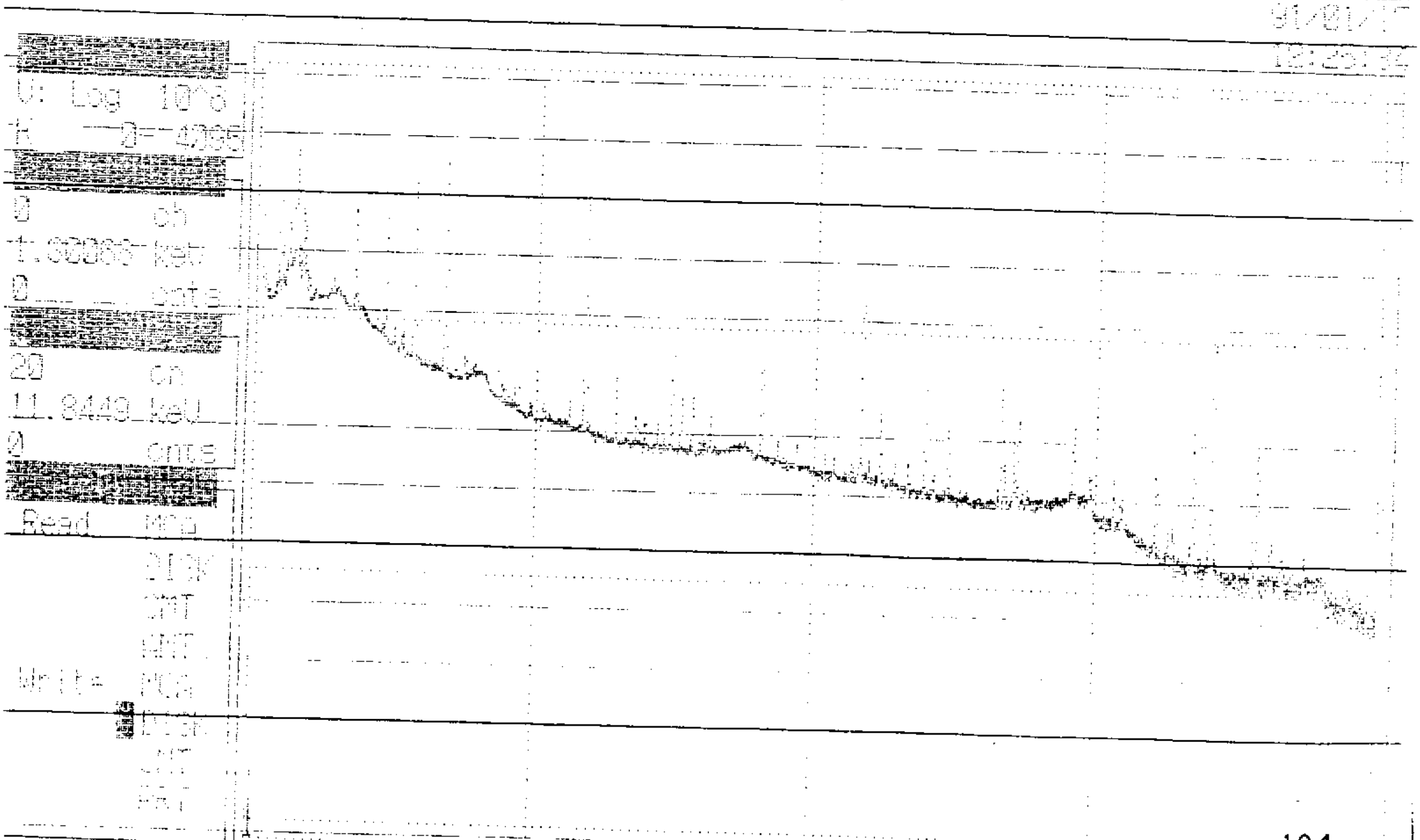


F1

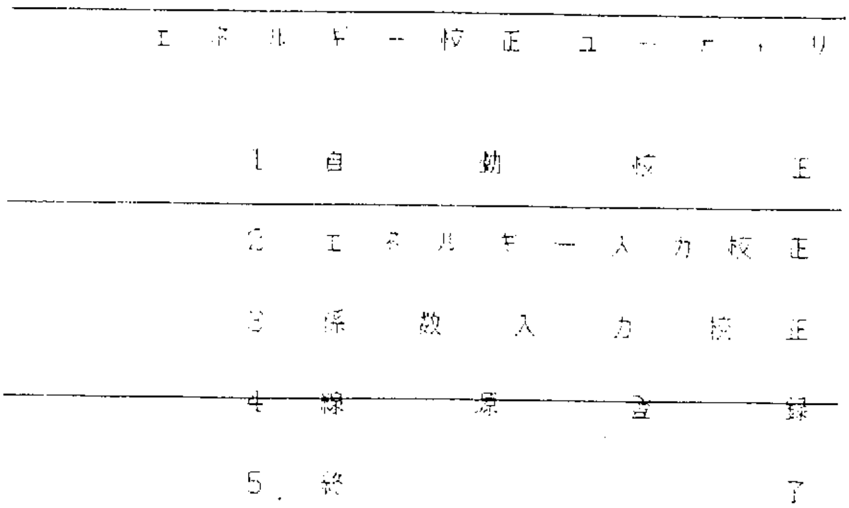
Exit

F10

<<< CRT-4 >>>



<<< CRT-5 >>>



```
エネルギー校正ユーティリ

1 自動校正

2 エネルギー入力校正

3 係数入力校正

4 線源登録

5. 終了
```

Energy Calibration Program

1.Automatic Calibration

2.Energy Input

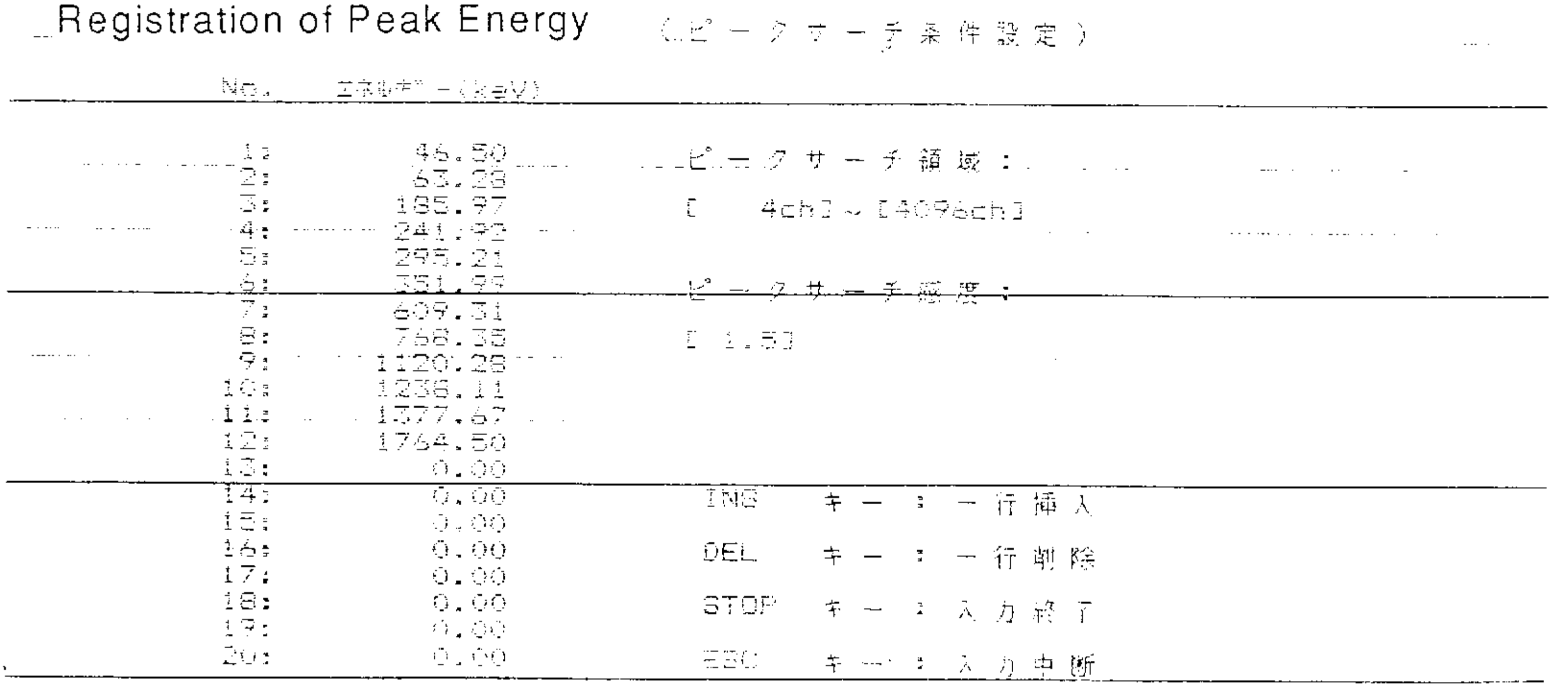
3.Factor Input

4.Registration of Peak Energy

5.End

<<< CRT-6 >>>

Registration of Peak Energy



```
(ピークサーチ条件設定)

  No.    ｴﾈﾙｷﾞｰ(keV)

   1:       46.50      ピークサーチ領域：
   2:       63.28
   3:      185.97      [   4ch]～[4096ch]
   4:      241.92
   5:      295.21
   6:      351.99      ピークサーチ感度：
   7:      609.31
   8:      768.35      [ 1.5]
   9:     1120.28
  10:     1238.11
  11:     1377.67
  12:     1764.50
  13:        0.00
  14:        0.00      INS   キー ： 一行挿入
  15:        0.00
  16:        0.00      DEL   キー ： 一行削除
  17:        0.00
  18:        0.00      STOP  キー ： 入力終了
  19:        0.00
  20:        0.00      ESC   キー ： 入力中断
```

<<< CRT-7 >>>

Result of Energy & FWHM Calibration

	Channel	Energy (keV)			FWHM (keV)		
		measured	calcurated	deviation	measured	calcurated	deviation
1	88.61	46.50	46.85	-0.35	1.31	1.23	0.08
2	121.64	63.28	63.50	-0.22	1.29	1.27	0.02
3	364.00	185.77	185.65	0.12	1.56	1.46	0.10
4	475.21	241.92	241.75	0.17	1.49	1.52	-0.03
5	580.68	295.21	294.97	0.25	1.51	1.58	-0.07
6	693.13	351.99	351.67	0.32	1.58	1.63	-0.05
7	1203.98	609.31	609.36	-0.05	1.74	1.83	-0.09
8	1519.32	768.33	768.51	-0.18	2.01	1.93	0.08
9	2216.19	1120.28	1120.41	-0.13	2.10	2.13	-0.03
10	2449.38	1238.11	1238.22	-0.11	1.99	2.18	-0.20
11	2725.36	1377.67	1377.69	-0.02	2.17	2.25	-0.08
12	3490.04	1764.50	1764.37	0.13	2.68	2.41	0.27

Calibrated Equation

Energy(keV)=C0+C1x (channel)+C2x(channel)^2

FWHM(keV)=C3+C4xSQRT(energy(keV))

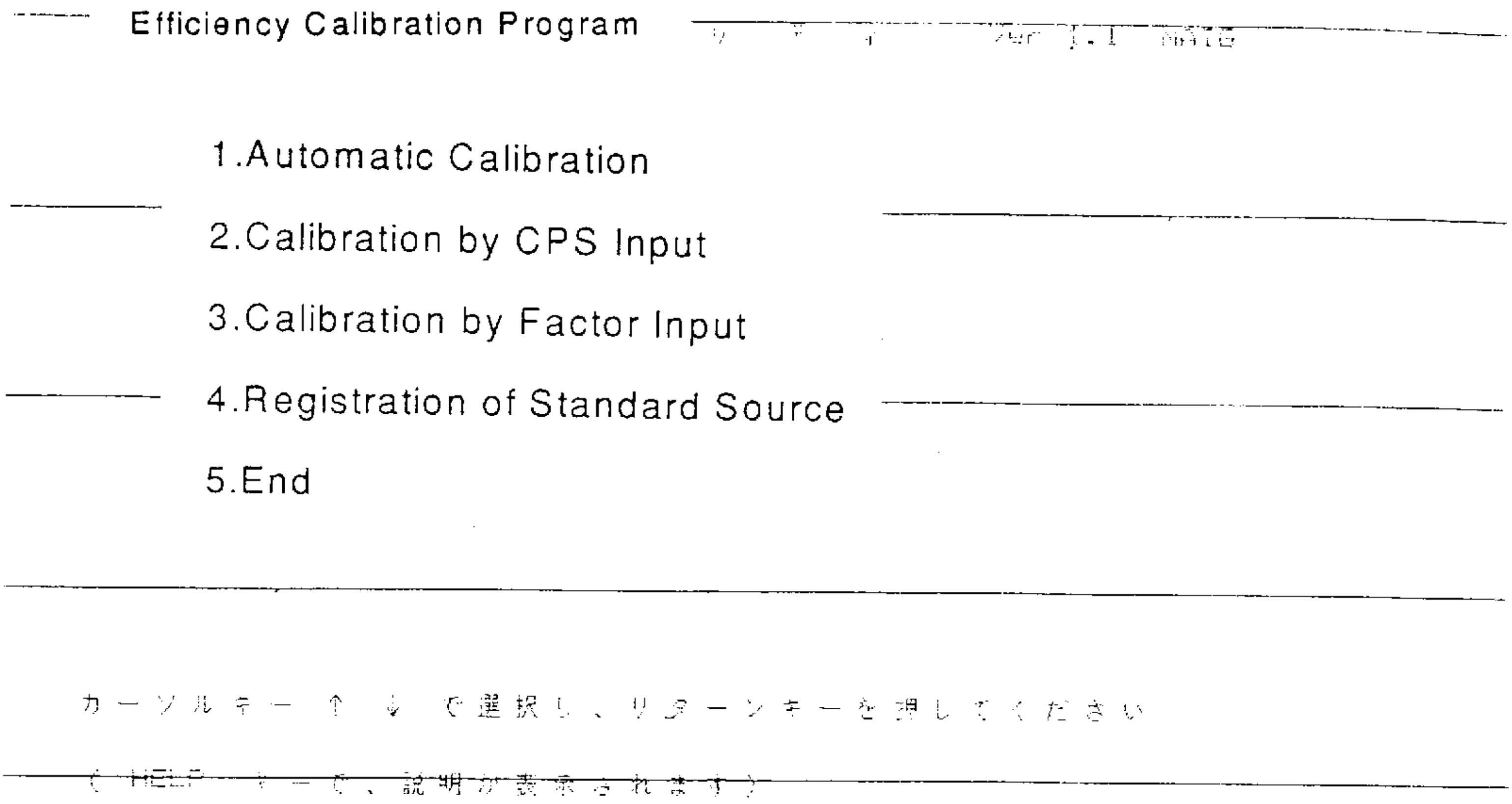
+C5x(cn1)^2

C0 = 2.1949129E0
C1 = 5.0397026E-1
C2 = 2.6875156E-7

C3 = 1.0004705E0
C4 = 3.3656511E-2

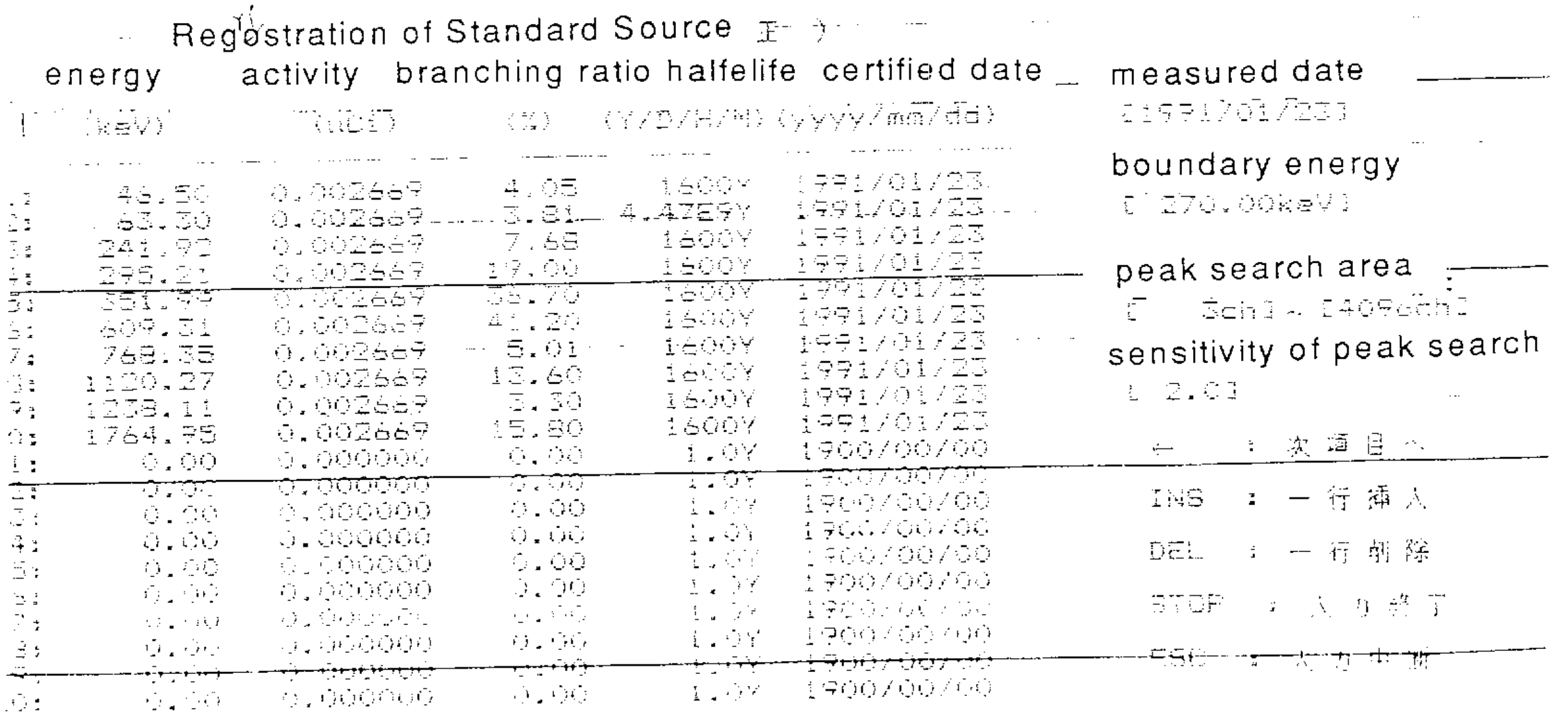
File name of enegy calibrated data : [B:ECAL9101.ECL]

<<< CRT-8 >>>



```
Efficiency Calibration Program                     Ver 1.1

        1.Automatic Calibration

        2.Calibration by CPS Input

        3.Calibration by Factor Input

        4.Registration of Standard Source

        5.End

カーソルキー ↑ ↓ で選択し、リターンキーを押してください
（ HELP キーで、説明が表示されます ）
```

<<< CRT-9 >>>



```
     Regostration of Standard Source
 energy      activity   branching ratio halfelife  certified date   measured date
  (keV)        (uCi)          (%)     (Y/D/H/M) (yyyy/mm/dd)       [1991/01/23]
                                                                   boundary energy
 1:    46.50    0.002669      4.05       1600Y   1991/01/23        [ 270.00keV]
 2:    53.30    0.002669      3.81    4.47E9Y    1991/01/23
 3:   241.92    0.002669      7.68       1600Y   1991/01/23        peak search area
 4:   295.21    0.002669     19.00       1600Y   1991/01/23        [    3ch] ~ [4096ch]
 5:   351.99    0.002669     35.70       1600Y   1991/01/23
 6:   609.31    0.002669     41.20       1600Y   1991/01/23        sensitivity of peak search
 7:   768.35    0.002669      5.01       1600Y   1991/01/23        [ 2.0]
 8:  1120.27    0.002669     13.60       1600Y   1991/01/23
 9:  1238.11    0.002669      5.30       1600Y   1991/01/23
 0:  1764.75    0.002669     15.80       1600Y   1991/01/23          ←    : 次項目へ
 1:     0.00    0.000000      0.00        1.0Y   1900/00/00
 2:     0.00    0.000000      0.00        1.0Y   1900/00/00          INS  : 一行挿入
 3:     0.00    0.000000      0.00        1.0Y   1900/00/00
 4:     0.00    0.000000      0.00        1.0Y   1900/00/00          DEL  : 一行削除
 5:     0.00    0.000000      0.00        1.0Y   1900/00/00
 6:     0.00    0.000000      0.00        1.0Y   1900/00/00          STOP : 入力終了
 7:     0.00    0.000000      0.00        1.0Y   1900/00/00
 8:     0.00    0.000000      0.00        1.0Y   1900/00/00          ESC  : 入力中断
 9:     0.00    0.000000      0.00        1.0Y   1900/00/00
 0:     0.00    0.000000      0.00        1.0Y   1900/00/00
```

<<< CRT-10 >>>

Input of Measured Condition

data size MCA [1]

sample ID [4] kch

sampled date [B.G.] sample name [BG-DATA

weight on sampling [90/11/28 10:00:00 measured date [91/01/21 15:00:00

efficiency of sampling [20.00000][g] weight on measuring [20.00000](g)

flow rate [100.00] (%) height of sample [0.0] (mm)

comment [0.000000](g/sec) time for samlping [0] (sec)

[5*10^4 SEC]

更新 ? [Y/N] :

<<< CRT-11 >>>

Input of Analytical Condition

name of data file [B:BG9101.D4K name of BG data file [ ]

area of peak search : [2] - [4093] sensitivity of peak search [2.00]

library mark : [U] priority [3]

factor of peak width : [1.00] × FWHM factor of scatered area [1.10] × FWHM

name of library file : [A:U-SERIES.NLB decay compensation factor [9999]

filename of energy calibration 1.ECL file name of efficiency [B:NBL001%.EFL]

dimension of activity, 2: nCi, 3: uCi, 4: mCi, 5: Bq) : [5]

activity/weight or total activity(1:/weight 2:total) : [1]

out put (1:CRT 2:printer 3:CRT+printer) : [3]

content of output (1:result of anaysis 2:all information) : [1]

更新 ? [Y/N] :

<<< CRT-12 >>>

Measured Condition

```
sample ID                  :   B.G.
sample name                :   BG-DATA
name of data file          :   B:BG9101.D4K
data size                  :   4096(ch)
MCA                        :   1
sampled date               :   1990/11/20 10:00:00
measured date              :   1991/01/21 10:00:00
weight on sampling         :          20 (g)
weight on measuring        :          20 (g)
efficiency of sampling     :   100.0 (%)
height of sample           :     0.0 (mm)
flow rate                  :           0 (g/sec)
time for samlping          :           0 (sec)
comment                    :   5*10^4 SEC
```

<<< CRT-13 >>>

Analytical Condition

```
area of peak search                :   2-4093(ch)
sensitivity of peak search         :   2.0
factor of peak width               :   1.0  (× FWHM)
factor of scalered area            :   1.1  (× FWHM)
name of library file               :   A:O-SERIES.NLB
library mark                       :   0
filename of energy calibration     :   B:E9101.ECL
priority                           :   9999.0
name of BG data file               :   3
file name of efficiency            :
dimension of activity              :   B:NBL001%.FCL
                                       [Bq]
```

energy calibration formula

Energy(keV)=C0+C1x (channel)+C2x(channel)^2

(チャネル[ch])^2

FWHM(keV)=C3+C4xSQRT(energy(keV))

)

```
C0 = 2.105072E0          C1 = 5.041558E-1          C2 = 2.664525E-7
C3 = 1.533792E0          C4 = 2.457503E-2
```

efficiency calibration formula

energy(keV) <= KNEE

log(EFF(-))=C0+C1xlog(energy(kev))+C2xlog(energy(keV))^2

^-[keV])^2

energy(keV)>KNEE

log(EFF(-))=C3+C4xlog(energy(keV))

```
C0 = -4.602700E0         C1 = 3.937699E0           C2 = -1.098500E0
C3 = 1.101500E0          C4 = -1.066700E0
KNEE = 190.00 keV
```

<<< CRT-14 >>>

* * * * * * * * * * * * * Result of peak search * * * * * * * * * * * * * *

data name

comment : B:BG9101.D4K

region of analysis : 5*10^4 SEC

. 2 4093

counting time(sec) : 50000 (秒)

sensitivity of peak search : 3.0

No.	peak center (CH)	peak area (CH) – (CH)	peak area (カウント)	cps (カウント／秒)	scatter (カウント)	error (%)	FWHM (CH)	detection limi (カウント)
1	28.06	22 – 30	879	0.0176	581	6.26	2.10	144
2	88.40	85 – 91	283	0.0057	792	15.55	1.56	122
3	121.67	118 – 125	520	0.0104	1079	10.36	2.37	155
4	179.54	176 – 183	864	0.0173	1140	6.63	2.60	157
5	363.58	361 – 367	351	0.0070	675	11.40	2.07	110

<<< CRT-15 >>>

* * * * * * * * * * Result of qualitative analysis * * * * *

data name : B:BG9101.D4K

comment : 5*10^4 SEC

decay compensation factor : 9999.0

decay time : 4.6656E6 (秒)

No.	peak center (CH)	energy (keV)	FWHM (keV)	nuclide	factor of decay compensation 係 数
1	28.06	16.25	1.06		
2	88.40	46.67	1.29	Pb-210	1.00E0
3	121.67	63.45	1.19	Th-234	1.00E0
4	179.54	92.63	1.31		
5	363.58	185.44	1.02	U -235	1.00E0
				Ra-226	1.00E0

<<< PRINT-1 >>>

Result of Efficiency Calibration 正 結 果

```
  energy                      efficiency     効    率
   (keV)              measured        calcurated        deviation
------------------------------------------------------------------------
  1      46.50       0.09047338      0.09055103    -0.00007765( -0.09%)
  2    [illegible]   [illegible]     [illegible]     [illegible]
  3     241.97       0.04128566      0.04073678     0.00054887(  1.35%)
  4     295.21       0.03387932      0.03316710     0.00071222(  2.15%)
  5     351.99       0.02785801      0.02756850     0.00028951(  1.05%)
  6     609.31       0.01522726      0.01548658    -0.00025932( -1.67%)
  7     768.35       0.01079732      0.01217667    -0.00137936(-11.04%)
  8    [illegible]   [illegible]     [illegible]     [illegible]
  9    1238.11       0.00762719      0.00735082     0.00027637(  3.76%)
 10    1764.95       0.00510415      0.00506422     0.00003993(  0.79%)
```

Calibration curve for peak efficiency

```
  log(EFF[-]) = C0 + C1*log(ｴﾈﾙｷﾞｰ[keV]) + C2*log(ｴﾈﾙｷﾞｰ[keV])^2
                                          ( (ｴﾈﾙｷﾞｰ[keV]) ≦ KNEE )
  log(EFF[-]) = C3 + C4*log(ｴﾈﾙｷﾞｰ[keV])
                                          ( (ｴﾈﾙｷﾞｰ[keV]) > KNEE )

          C0 =    -3.01039060E0
          C1 =     2.34395388E0
          C2 =    -6.98154286E-1

          C3 =     1.11677733E0
          C4 =    -1.05098830E0

          KNEE = 270.00
```

File name of peak efficiency: [B:IAEA.FCL]

<< PRINT-2 >>

Measured Condition

sample ID : [illegible]
sample name : [illegible]
name of data file : [illegible]
MCA : [illegible]
: [illegible]
sampled date : 1990/11/22 [illegible]
measured date : 1991/01/24 [illegible]
weight on sampling : [illegible] (g)
weight on measuring : [illegible] (g)
efficiency of sampling : [illegible]
height of sample : [illegible] (mm)
flow rate : [illegible] (l/sec)
time for sampling : [illegible] (sec)
comment : [illegible]

Analytical Condition

area of peak search : 2 4095(ch)
sensitivity of peak search : 3.0
factor of peak width : 1.[illegible] (x FWHM)
factor of scatered area : 1.1 (x FWHM)
name of library file : A:U-SERIES.NLB
library mark : U
filename of energy calibration : B:EF101.ECL
priority : 9999.0
: I
name of BG data file : DBF101.DOD
file name of efficiency : B:IAEA.FCL
dimension of activity : [Bq]

energy calibration formula

```
(エネルギー[keV]) = C0 + C1*(チャネル[ch]) + C2*(チャネル[ch])^2
(FWHM[keV])      = C3 + C4*SQRT(エネルギー[keV])

C0 = 2.105072E0        C1 = 5.041558E-1        C2 = 2.6450[illegible]
C3 = 1.335792E0        C4 = 2.457503E-1
```

efficiency calibration formula

```
((エネルギー[keV]) ≦ KNEE)
    log(EFF[-]) = C0 + C1*log(エネルギー[keV]) + C2*log(エネルギー[keV])^2
((エネルギー[keV]) > KNEE)
    log(EFF[-]) = C3 + C4*log(エネルギー[keV])

C0 = -3.010390E0       C1 = 2.343954E0         C2 = -[illegible]E-1
C3 = 1.116773E0        C4 = -1.050983E0
KNEE = 270.00 keV
```

<< PRINT-2 >>>

* * * * * * * * * * * Calcuration of peak area , 検出限界値算出 * * * * * * * *

data name : B:H2-131.04K
comment : 5*10^-8E0
counting time (sec) : 50000 (秒)

No.	核種名	ピーク位置 (keV)	(CH)	ピーク領域 (CH) - (CH)	ピーク面積 (カウント)	散乱面積 (カウント)	検出限界 (カウント)
1	Pb-210	46.55	93.39	88 - 97	90641 ± 474	61058	1115
2	Pb-214	241.90	475.01	471 - 479	56185 ± 333	11150	439
3	Pb-214	295.17	580.47	574 - 587	136774 ± 442	21776	730
4	Pb-214	351.90	692.94	685 - 698	216550 ± 512	14701	580
5	Bi-214	609.00	1203.71	1197 - 1210	130276 ± 708	1237	396
6	Bi-214	768.70	1517.06	1510 - 1524	12407 ± 160	5074	344
7	Bi-214	1120.40	2215.72	2206 - 2224	24193 ± 188	3442	327
8	Bi-214	1238.20	2448.90	2443 - 2455	2179 ± 114	1203	217
9	Bi-214	1764.00	3489.64	3482 - 3497	17407 ± 137	614	124
10	Th-234	63.30	121.51	115 - 127	75962 ± 596	104914	1390

* * * * * * * * * * * * * * Result of quantitative analysis * * * * * * * * * * * *

data name : B:H2-131.04K
comment : 5*10^-8E0
sample weight : 20 (g)
date of sampling : 1990/11/28 10:00:00
date of counting : 1991/01/29 10:00:00
decay time : 5.3568E6 (秒)

nuclide	energy	decay cop.factor	efficiency	activity 濃度 (Bq/g)	detection limit (Bq/g)	ピーク No.
Pb-210	46.55	1.00E0	0.090560	2.25E1 ± 1.29E-1	3.10E-1	1
Pb-214	241.90	1.00E0	0.040740	2.14E1 ± 1.07E-1	2.06E-1	2
Pb-214	295.17	1.00E0	0.033172	2.17E1 ± 7.01E-2	1.15E-1	3
Pb-214	351.90	1.00E0	0.027576	2.18E1 ± 5.15E-2	6.54E-2	4
Bi-214	609.00	1.00E0	0.015495	2.07E1 ± 6.08E-2	7.70E-2	5
Bi-214	768.70	1.00E0	0.012131	2.20E1 ± 2.89E-1	6.46E-1	6
Bi-214	1120.40	1.00E0	0.008165	2.18E1 ± 1.65E-1	2.91E-1	7
Bi-214	1238.20	1.00E0	0.007050	2.10E1 ± 2.73E-1	5.56E-1	8
Bi-214	1764.00	1.00E0	0.005067	2.17E1 ± 1.71E-1	1.54E-1	9
Th-234	63.30	1.00E0	0.088403	1.26E1 ± 1.77E-1	4.73E-1	10

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```
                          Result of nuclides determination
  data name
  comment             : [illegible]
  sample weight(g)    : [illegible]
  sampled date        : [illegible] 10:00:00
  counted date        : [illegible]
  decay time(sec)     : 5.[illegible]E+ (秒)

 nuclides  energy decay comp.fac.  efficiency     activity              detection limit  ピーク
           (keV)       係数          (-)          (Bq/g)                (Bq/g)           No

 Pb-210     46.55      1.00E0      0.090560    2.13E1 ± 1.29E-1        [illegible]          1
 Pb-214    241.90      1.00E0      0.040740    2.14E1 ± 1.37E-1        [illegible]          2
 Pb-214    295.17      1.00E0      0.113172    2.17E1 ± 7.[illegible]E-2    [illegible]     3
 Pb-214    351.90      1.00E0      0.027376    2.13E1 ± 5.[illegible]E-2    [illegible]     4
 Bi-214    609.[illegible]  1.00E0  0.015195    2.07E1 ± [illegible]E-2   [illegible]E-2    5
 Bi-214    768.70      1.00E0      0.012101    2.[illegible]E1 ± 6.61E-1   [illegible].46E-1  6
 Bi-214   1120.40      1.00E0      0.006152    2.16E1 ± 1.69E-1        [illegible]          7
 Bi-214   1238.20      1.00E0      0.007350    2.10E1 ± 2.77E-1        [illegible]          8
 Bi-214   1764.[illegible]  1.00E0  0.005067    2.17E1 ± 1.[illegible]E-1   [illegible].54E-1  [illegible]
 Th-234     63.30      1.00E0      0.088403    2.36E1 ± 1.77E-1        4.72E-1             10
```

APPENDIX E: Alpha Spectrometry at CNNC-BRIUG

Determination of Radioactive Ratios of $^{234}U/^{238}U$ and $^{230}Th/^{232}Th$ in Geological Samples by P350 Extraction Chromatographic Separation Apha-Spectrometry

I. Introduction

A. Purpose and Applicability

This method is used for the assay of ratios of $^{234}U/^{238}U$ and $^{230}Th/^{232}Th$ in geological samples with separation and preconcentration and employed an apha-spectrometry. Geological samples including water,rocks and minerals forms. Isotopic activities should be grater than 1.23E-3 Bq/L for water samples and 6.15E-3 Bq/L for solid samples. In addition, $^{230}Th/^{232}Th$ ratio should not be greater than 15.

B. Summary of Method

Water samples were treated with nitric acid,ferric chloride(as carrier), ammonia and ammonium chloride to form coprecipitate,mean that the ferric hydroxide precipitate contained uranium and thorium,which was separated from the supernate and washed. These were discared and the precipitate was dissloved in concentrated nitric acid and loaded onto a P350 chromatographic column.

solid samples were decomposed with mixed ammonium salts and prepared in a mixed solution which contained aluminium nitrate (10%),tartaric acid(2%) and nitric acid(15%), and loaded onto a P350 chromatographic column.

After passing through the column and washed, U and Th were separated one another and from matrix and other elements. Source of U and Th were made by use of electrodeposition and determined by apha-spectrometry. The ratios were calculated from the apha spectra.

II. Reagents and Apparatus

A. Reagents

1. Mixed ammonium salts,proporation is as follows:
   $NH_4F:(NH_4)_2SO_4:NH_4Cl:NH_4NO_3=3:0.5:1:1$,dried(<70 °C),ground.
2. D201 or K-5 resin (polyphenylethyl matrix),60-80 mesh
3. Di-1-methylheptyl-1-methylheptylphosphonate(P350)
4. 200# kerosene
5. Equalizing and washing solution:tartaric acid(2%)+nitric acid(15%)
6. Loading solution:aluminium nitrate(10%)+tartaric acid(2%)+nitric acid(15%)
7. Eluate for thorium:hydrochloric acid (5 mol/L)
8. Eluate for uranium:sodium fluoride (0.2%)
9. Ferric chloride (15% m/m)
10. Ammonium chloride (2% m/m)
11. Ammonia
12. Hydrochloric acid
13. Nitric acid
14. Perchloric acid
15. Ammomium oxalate (5% m/m)
16. Electrolyte solution for U:
    2g ammonium chloride and 5g ammonium oxalate are dissloved in 100 ml deioned water and adjusted PH=6 with hydrochloric acid.
17. Electrolyte solution for Th:
    2g ammonium chloride and 5g ammonium oxalate are dissloved in 100 ml deioned water and adjusted PH=2 with hydrochloric acid.

B. Apparatus

1. Apha Spectrometer(made in Nuclear DTATA INC.) ,equiped with as follows
   (1). Au-Si surface barrier semiconductor detector

    (2). Electric charge sensitive head amplifier
    (3). Main amplifier and pulse shaper
    (4). Pulse discriminator
    (5). ADC
    (6). 1036 channels pulse height analyser
    (7). Computer system (PDP-11) and its exteral equipment(disc device, printer and video et.al.)
    (8). Apha vaccum chamber
    (9). Vaccum pump
2. Platinum electrode
3. Stainless steel disc
4. Direct current constant voltage power supply
5. Electrodepositing cylinder cell, volume 20 ml
6. Constant temperature water bath
7. Column: 7x70 mm
8. Other general apparatus used in laboratory.

III. Procedure

1. Preparation of P350 column

a. Purity of D201

60-80 mesh D201 (commerical name, a kind of resin) is taken in a beaker and non aquous alcohol is added and stirred and transferred into a direct tube. The alcohol is continually added to wash impurities till non yellow colour. After lique is out ,the resin is taken out and laid in an open vessel and dried at 70-80 C till non alcohol exists. Finally, the pure D201 is stored in a clean glass bottle and sealed.

b. 10g P350 is weighed in a clean beaker 15 ml 200# kerosene is added and stirred to dissolve P350 .3-4 drops 2-octanol are added to assist dissolve and stirred till uniform. P350 solution is obtained.

c. 10g pure D201 is weighed and poured quickly into P350 solution prepared in step b and stirred immediately till uniform. 10 minutes later, a solid P350-D201 resin will be gotten. Let it dry in natural condition untill non kerosene exists. The resin (called CL-P350) should be sealed in a glass container.

d. Pour CL-P350 into (II.A.5) to equalize for 4 hours.

e Pack column(7x70mm) with CL-P350 which has been prepared in step d above, make flow rate 1.0-1.2 ml/min, add 15 ml (II.A.5) to equalize it. Now, it has been ready to use.

2. Samples preparation

a. Water sample

Take 5 liter water sample which has been acdified with nitric acid in a 5-liter beaker to be heated to boil. Add FeCl (II.A.9) and NH Cl(II.A.10) and ammonia while stirring to adjust PH= 8-9, when Fe(OH) precipitate involving U and Th will be occuring. Allow the mixture stand for 2 hours. Then discard supernate and disslove precipitate with 20-30 ml concentrated nitric acid in a 400-ml beaker. Evaporate it till 5 ml in volume and add 5 ml nitric acid and 1 ml hydrofluoric acid then still evaporate till non while smoke. The mixture is dissloved in solution (II.A.6).

b. Solid Sample-Mixed ammonium salts decomposition

0.3g sample is weighed in a 150-ml beaker and 10g (II.A.1) mixed in uniform. Set it on an electric furance be heated untill non white smoke exists. Cool till 50-60 ^{0}C ,add 8-10 ml reverse aqua regia and heat untill non white smoke occurs. Another 4-6 ml reverse aqua regia is added and still heated untill non white smoke exists again. A few drops reverse aqua regia are added to disslove the residue and warm up, then 15 ml (II.A.6) are added and heated till slight boiling.

3. Separation with P350 column

The sample solution prepared in step (III.2) is poured into the column prepared in (III.1.e). After the solution passing, wash it with 15 ml (II.A.5) solution 2ml (II.A.7). 20 ml (II.A.7) is eluted (divided 3 times) and collected in a 50-ml beaker. The solution is used for thorium electrodeposition.

1.5 ml (II.A.8) is added in the column where thorium has been eluted, When it has passed, 10 ml NaF(II.A.8) is added (divided 3 times) to elute uranium and collected in a 50-ml beaker. The solution is used for uranium electrodeposition.

4. Source preparation- electrodeposition

a. Source for uranium

1 ml nitric acid and 0.5 ml perchloric acid are added in the pure containing uranium solution separated in (III.3) and evaporated till non white smoke . After cooling slight, 1 ml hydrochloric acid is added and evaporated to incipient dryness at a low temperature. Add 10 ml electrolyte solution(II.A.16) to dissolve salts after cooling slight. Then pour the solution into a electrodepositing cell (II.B.5) and set the cell in a constant temperature water bath (II.B.6) at 70°C. Switch on the power supply (II.B.4) and set its current be 1.2A when PH of the solution should be 6. 30 minutes later, the PH changed from 6 to 8 then to 2 ,at this time, 3 drops of ammonia is added and continue electrodeposition for 3-5 minutes. Turn off the power(II.B.4) and take the cathode disc out of the bath and wash it with deioned water and number it.

b. Source for thorium

1 ml nitric acid and 0.5 ml perchloric acid are added in the pure containing uranium solution separated in (III.3) and evaporated till non white smoke . After cooling slight, 1 ml hydrochloric acid is added and evaporated to incipient dryness at a low temperature. Add 10 ml electrolyte solution(II.A.17) to dissolve salts after cooling slight. Then pour the solution into a electrodepositing cell (II.B.5) and set the cell in a constant temperature water bath (II.B.6) at 70°C. Switch on the power supply (II.B.4) and set its current be 1.4A when PH of the solution should be 2. 40 minutes later, the PH changed from 2 to 8 then to 2 ,at this time, 3 drops of ammonia is added and continue electrodeposition for 3-5 minutes. Turn off the power(II.B.4) and take the cathode disc out of the bath and wash it with deioned water and number it.

5. Measurement

5.1. Selection of operating conditions

a. Energy resolution: Set Am or U or Th standard apha source into the chamber[II.B.1.(8)] ,pump till vaccum degree 10 Pa, measure its apha-spectrum in the system(II.B.1). The energy resolution can be obtained as follows:

$$R(\%) = 100 \times \Delta E/E ,$$

where E is the maximum of energy ; ΔE is energy width at half distribution of maximum. R should be less than 2%.

b. Select operating voltage of the detector : Change bias voltage and measrue the energy resolution at this voltage. The best energy resolution should be obtained . Therefore, the bias voltage at the best energy resolution is the choice.

c. Change ampiifing gain of linear amplifier to let the spectrum on the middle of video.

5.2. Calibration of instrument

Set a known apha-source with activity 1 Bq in the vaccum chamber and pump to make vaccum degree 13 Pa, measure apha spectrum and calibrate the channel number of the known energies shown in Table 1.

Table 1 U and Th isotopes apha spectra

Nuclides	Apha particles energies,kev	Intensities(%)
^{238}U	4195 4147	77 23
^{234}U	4773 4722	72 28
^{232}Th	4012 3953	77 23
^{230}Th	4684 4618	76 23

5.3. Counting efficiency

Set a known uranium apha source in the chamber and pump to make vaccum degree 13 Pa, measure apha spectrum of ^{238}U and ^{234}U to calculate counting efficiency shown as follows:

Counting efficiency(%)= 100xactual count/ theorical count of standard source

5.4. Background of total procedure

prepare not less than 5 blank U and Th apha scurces according to procedure III to meausre their background counts .Their measuring times should be greater than 15 hours.The mean count of these background counts is regraded as background value of total procedure.

5.5. Measurement of sample

Fristly,calculate measuring time(t) according to the relative error (ε) and sample counting rate(N) shown as follows:

$$t=1/(N\varepsilon^2),$$

then set uranium or thorium apha source of sample into the chamber and pump vaccum till 13 Pa , measure its apha spectrum referred to measuring time calculated mentioned above. Read peak integrating areas of ^{238}U, ^{234}U, ^{232}Th and ^{230}Th based on the spectra.

IV. Calculation

Isotopic ratios are shown as follows:

$$RU={}^{234}U/{}^{238}U=x/y(1+\sigma),$$

$$RTh={}^{230}Th/{}^{232}Th=x/y(1+\sigma),$$

where ^{234}U , ^{238}U, ^{230}Th and ^{232}Th are peak areas(minus backgroung) of , each isotope; x is peak area of ^{234}U or ^{230}Th; y is peak area of ^{238}U or ^{232}Th; σ is relative standard deviation expressed as:

$$\sigma = \sqrt{\left(\frac{\delta x}{x}\right)^2 + \left(\frac{\delta y}{y}\right)^2}$$

where δx is $\sqrt{x}$, δy is $\sqrt{y}$.

APPENDIX F: Chemical Analysis of Uranium at CNNC-BRIUG

Determination of Trace Uranium in Geological Samples
by Standard Addtion Laser Fluorimetry

I. Introduction

A. Purpose and Applicability

This method is used for the assay of trace uranium in geological samples without any separation and preconcentraation.

B. Summary of Method

Samples are digested in open mixed acids HNO_3-$HClO_4$-HF and prepared in PH=7 solution for determination using laser fluorimetry with standard addition technique. The key is that employed SPECIAL FLUORESCENT REAGENT, which was developed by Zhang Yan'an et.al.(Beijing Research Institute of Uranium Geology),reacts with uranium to form a complex that can emit intensive fluorescence by excitation of nitrogen molecular laser.The fluorescence intensity is direct proporational to concentration of uranium.

C. Descriptive Information

The assay must be run with appropriate quality control standards. Samples with high content uranium (500 µg/g in solid sample) must be run with a large dilution factor.Consequentially,the accuracy and precision are worse. We recommend that other methods such as Ferrous-ammonium vanadate titrimetric method and TOPO extraction separation-Br-PADAP spectrophotometry be replaced in that case.

II. Reagents and Apparatus

A.Reagents
1. HNO_3 ,$HClO_4$, HF
2. U standard solution
3. J-22 Special fluorescent reagent

B.Apparatus
1. Laser Uranium Analyzer:JU-1,made in China
2. Other common analytical appartus.

III. Procedure

A.Sample Preparation - Open Mixed Acids Digestion

0.1 g sample was weighed in a 50-ml PTFE crucible. 5 ml HNO_3 ,1 ml $HClO_4$ and 1.5-2 ml HF were added and mixed in homogeneity.The mixture was set on an electric plate-heater to be heated to incipient dryness.And then 5 ml HNO_3(1+2) was added to dissolve the mixture. The mixture solution was transferred into a 50-ml volumetric flask and made to volume with deioned water and shaken,awaited one night untill it could be measured.

B.Measurement With Standard Addition Technique

1. Turn on the Analyzer and wait for 8-10 min.
2. Turn on Laser switch and adjust PMT to let the meter of energy of laser indicate 60%-70% and wait for 40 min.
3. Take V ml (e.g. 0.5 ml) blank solution in the reaction cell and add Special Fluorescent Reagent till total volume of the cell to be 5.0 ml and mix them. Set the cell in light path position. Clear zero and set the counter on and recorde the intensity of fluorescence Fo.
4. Take out the cell and add b' ml uranium standard solution which concentration is Cs' and stir the mixture. Set the cell in light path position again, clear counter zero and push the counter on to recorde the intensity of fluorescence Fo'.
5. Blank solution and Fo are replaced by sample solution and F1 in step 3 above respectively and repeat the step.
6. b',Cs' and Fo' are replaced by b,Cs and F2 in step 4 above respectively

and repeat the step.

IV. Calculations

The uranium content in solid sample is

$$C(ug/g)=50[F1bCs/(F2-F1)-Fob'Cs'/(Fo'-Fo)]/(VG),$$

where "50" is dilution volume(ml); G is weight of sample(g);Fo,F1,F2, b,b',Cs,Cs'and V are represented as stpe 3-6 mentioned above.

APPENDIX G: Chemical Analysis of Thorium at CNNC-BRIUG

Determination of Trace Thorium in Geological Samples by N263 Extraction Chromatographic Separation ArsenazoIII Spectrophotometry

I. Introduction

A. Purpose and Applicability

This method is used for the assay of trace thorium in geological samples with separation and preconcentraation.

B. Summary of Method

Samples are decomposed by alkali fusion or mixed ammonium salts and dissolved in nitric acid.The solution is passed through chromatographic column.Thorium is absorbed in this way and separated from a large amount U,REE,Zr,Hf,Ti,Fe,Nb,and Ta.Thorium is eluted with 4N HCl and determined with ArsenazoIII spectrophotometry, which is based on a well-known reaction, mean that ArsenazoIII reacts with thorium in more concentrated hydrochloric acid medium(4-6N HCl) to form a blue-green complex which has a maximum absorption at wave length 660 nm and get a molar absorption coefficient up to 1.27E5. However, Zr,Hf,Ti and U(IV) combine also with ArsenazoIII, separation must be performed prior to measurement of thorium.

II. Reagents and Apparatus

A. Reagents

Following items for mixed ammonium salts decomposition :

1. Mixed ammonium salts,proporation is as follows:
   $NH_4F:(NH_4)_2SO_4:NH_4Cl:NH_4NO_3=3:0.5:1:1$,dried(<70 ℃),ground.
2. Aqua regia,$HClO_4$,15% HNO_3

Following items for alkali fusion :

3.Na_2O_2,$MgCl_2$
4.2%NaOH ,HNO_3(1+2)

Following items for both mixed ammonium salts and alkali fusion:

5. 4N HCl
6. Mixed solutions:15%HNO_3+15%$Al(NO_3)_3$+2%tartaric acid
7. N263 column(7x70mm).
8. V.C,40% urea,5% oxalic acid
9. 0.05% ArsenazoIII aquous solution.

B. Apparatus

1. Spectrophotometer,Model 721,made in China.
2. Other general apparatus used in laboratory.

III. Procedure

i. Preparation of N263 column

a. Purity of D201

60-80 mesh D201 (commerical name,a kind of resin) is taken in a beaker and non aquous alcohol is added and stirred and transferred into a direct tube.

The alcohol is continually added to wash impurities till non yellow colour. After lique is out ,the resin is taken out and laid in an open vessel and dried at 70-80 C till non alcohol exists.Finally,the pure D201 is stored in a clean glass bottle and sealed.

b. 10g N263 is weighed in a clean beaker 15 ml 200# kerosene is added and stirred to dissolve N263 .3-4 drops 2-octanol are added to assist dissolve and stirred till uniform.N263 solution is obtained.

c. 10g pure D201 is weighed and poured quickly into N263 solution prepared in step b and stirred immediately till uniform. 10 minutes later ,a solid N263-D201 resin will be gotten. Let it dry in natural condition untill non kerosene exists. The resin (called CL-N263) should be sealed in a glass container.

d. Pour Cl-N263 into 2N HCl to equalize for 2 hours.

e Pack column(8x100mm) with CL-N263 which has been prepared in step d above, add 15% HNO to equalize it. Now, it has been ready to use.

2. Sample preparation

a. Mixed ammonium salts decomposition

0.3g sample is weighed in a 150-ml beaker.and.10g.mixed in uniform.Set it on an electric furance be heated untill non white smoke exists.Cool till 50-60°C, add 10 ml aqua regia and 1 ml $HClO_4$,and heat till non white smoke exists again. Cool till 50-60°C,add mixed solution(II.A.6) 15 ml to disslove the mixture.

b. Alkali fusion

3-5g Na_2O_2(which is relevent to 8-10 times of sample weight) is added in a corundum crucible,0.3g sample is weighed in it and 1-2g $Na_2O_2$is added again and mixed. Set it into a muffle furance whose temperature has already been 800°C and maintain 10 minutes then cool till 50-60°C. Lay it in a 150-ml beaker and add 100-120 ml hot deioned water(60-70°C).Wash the crucible with the hot water and a few drops of HCl(4 mol/L). Set it on an electric plate-heater to boil. Remove from the heater and cool till precipitate deposited. Filter and wash the precipitate and beaker with 2% NaOH.Filtrate is discarded. The precipitate is dissloved in 10-20 ml hot HNO_3(1+2) in the beaker,and 2 ml 2% tartaric acid is added to complex Zr.

3. Separation

The sample solution prepared in either step a or step b is poured into the column prepared in (III.1.e). After the solution passed,wash it with 15 ml mixed solution(II.A.6) and 5 ml 15% HNO_3. Add 2 ml 4N HCl to wash NO_3^-. 20 ml4N HCl (as eluate) is eluted and collected in a 25-ml volumetric flask which has already been added 1 ml 40% urea and 1-2mg V.C.

4. Measurement

2 ml 5% oxalic acid and 2 ml 0.05% ArsenazoIII aquous solution are added and made to volume in the flask prepared in (III.3). Using a spectrophotometer(e.g. Model 721) at wave length 660 nm,measure absorbance of the complex.

5. Calibration

Take thorium standard solution series instead of sample solution in (III.3) and repeat (III.3) and (III.4).

IV. Calculation

1. Calibration curve is

$$A=a+bC \ ,$$

where a and b are coefficients of the linear calbriation,
A is absorbance ,C is concentration of the complex determined.

2. Thorium content in solid sample is

$Th(ug/g)=C.V/G$,

where C is concentration(ppm) of sample calculated from equation (IV.1)
G is weight of sample (g),V is dilution volume(ml) .

Impression

Japan, just like her flag, the place of the sun rising, has been making the world warmed up and enriched. If you have seen the TOYOTA's automobile production lines and the staffs' works, you may know why Japan achieced the miraculous progress in the last decades and became a supereconomical nation. I think, the best words for Japanese people are well-educated, diligent,hard-working and harmonizing. Whatever I saw, wherever I visited, the industrial production lines,the telecommunication system, the transportation system,the education system, the PNC facilities, the daily life facilities as well as the friendly Japanese people and their doing, all have given me a deep impression.

And during my 3-month stay at PNC Chubu Works, I was becoming more familiar with PNC, especially PNC-Chubu Works and the staffs, as the time flying. Now, I have completely fulfilled my expected subject of STA Scientist Exchange Program on schedule and very satisfied with it. Besides, I am also very satisfactory with what PNC and the staffs have done for me and enjoyed my life in Japan. I dare say, if without their helps, the schedule would not proceed so smoothly. I was greatly impressed by them and their doing. I never forget them.

Staying in Japan, I can feel many Japanese people have good feeling to China and Chinese people. And also ,I like both Japan and her diligent people very much. Thanks to the STA program, the mutual understanding, the friendship and the feeling between us increased a lots. So,this is a good way for us. If I could have another chance staying in the overseas of China, I would select Japan, especially PNC, as a favourable one.

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