Development of low level plutonium measurement by ICP mass spectrometry and its application to marine environment: Pu isotopes and heavy metal elements in Surume squid

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January 2007

Doctoral dissertation

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January 2007

博士論文

ICP質量分析計による極微量Pu同位体測定法の開発と海洋環境試料への応用

－海産生物試料中のPu同位体および重金属元素－

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平成19年1月

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ABSTRACT

As a biological indicator in tracing the levels and fate of contaminants such as toxic metals and radionuclides in marine environment, squids, especially Surume squid, were selected since their life span was only a year and trace elements were remarkably concentrated in their organs. The losses of trace elements in marine organisms during thermal decomposition were at first investigated with emphasis on the development of low level plutonium measurement by inductively coupled plasma mass spectrometry (ICP-MS). These findings were applied to the measurements of plutonium isotopes and some stable elements (V, Mn, Fe, Co, Cu, Zn, Rb, Sr, Ag, Cd, Cs, Th and U) in liver of Surume squid collected in the coastal sea areas of Japan. The Pu and other 13 elements were concentrated with concentration factor (CF) ranging from 10^0 *to as high as* 10^7*. Transition metal elements, Mn, Fe, Co, Cu, Zn, Ag and Cd were concentrated with high CF values (*10^6*). Plutonium, as well as V and Th, were concentrated in liver with CFs of* 10^2 *to* 10^4*. The* $^{240}Pu/^{239}Pu$ *atomic ratios 0.177 to 0.237 which were slightly higher than 0.178 ± 0.014 for global fallout were found in squid liver. Based on the habitat of the Surume squid and ocean currents, the Pu found in the liver might be due to a mixture of global fallout Pu and close-in fallout Pu with high* $^{240}Pu/^{239}Pu$ *atomic ratio around Bikini Atoll. By assuming the two sources mixing model, Bikini close-in fallout Pu accounts for ca. 35% of the whole plutonium amounts. The results strongly indicate that the squid liver is very usefully biological indicator for evaluating marine pollution of Pu and some other trace elements.*

CHAPTER 1

CHAPTER 1 : General Introduction.

1.1. General background

The man-made long-lived radionuclides, such as ^{90}Sr, ^{137}Cs and Pu isotopes, are now in distributed world wide as a result of global fallout from atmospheric nuclear weapons tests. The total oceanic inventories of selected fission products and transuranium elements produced in atmospheric nuclear weapons tests are reported by Hamilton (2004). However, plutonium has a lot of isotopes as shown in Table 1.1, regarding Pu isotopes, it was estimated that, since 1945, about 12 PBq of $^{239+240}$Pu has been deposited on the oceans as global fallout from 543 atmospheric nuclear weapons tests (UNSCEAR 2000). According to the report, the Arctic, Atlantic, Indian and Pacific Oceans contain about 0.1 PBq, 2.3 PBq, 1.0 PBq and 8.6 PBq of $^{239+240}$Pu, respectively. These data predict that a significant fraction of the plutonium present in the Pacific Ocean comes from local and regional injections rather than global fallout deposition. Water column inventories in the North Pacific do reflect an excess of plutonium above what is expected from global fallout depositions (Bowen et al., 1980).

Artificial radionuclides ^{110m}Ag and ^{60}Co appear in marine organisms as a result of metabolism during a growth processes (Folsom et al., 1965). This finding is useful for evaluating toxic metal elements and radionuclide pollution in marine environment (Folsom et al., 1970). Seawater is the most significant medium to migration processes in the marine environment. Instead of seawater, marine organism which inhabits inshore sea areas around our country will be useful bio-indicator for environmental radioactivity monitoring. Surume squid (*Todarodes pacificus*), one of the squid classifies as shown in Fig. 1.1 are convenient for our purpose from view point of landing things in a nationwide scale and developed a channel of distribution in our country.

The main island of Japan (Honshu) is surrounded by the Pacific Ocean and the Sea of Japan, which are different in their current and open/close areas. About 400 to 600 thousand tons of squids were caught in each of the last five years, and the Surume squid represents about half (or more) of the catch, and they are easily caught everywhere on the coast around Japan’s islands (Living Information Center, 2003). Since their life span is only a year and trace elements are remarkably concentrated in their organs, levels of trace elements in seawater can be monitored by measuring these elements in their organs (Abe and Honma, 1997). In contrast to flat fish, seaweed and benthos which inhabit in quite small area, the squid moves long distance and pathways depending mainly on seawater temperature (Abe and Honma, 1997). Therefore, the squid may be useful for monitor of larger sea area. Although the habitable sea area is not uniform since Surume squid is migrant marine organism depending on sea temperature and ocean current (Fig. 1.2). Surume squid is a kind of invertebrate marine organism which has a three parts of the body (Fig 1.3). Surume squid liver is the largest internal organ and it is easy to confirm and remove liver from other internal organs (Fig. 1.4). Surume squid liver, largest internal organs is suitable for natural samples in the field of environmental radioactivity monitoring (Folsom et al., 1965).

1.2. Practical use of inductively coupled plasma mass spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) is arguably the most versatile trace elemental analysis technique available today. Depending on the individual instrument configuration, sample types ranging from seawaters and rock digests to ultra pure semiconductor grade chemicals can be routinely analyzed, almost all the element in the Periodic Table, from "low pg ml^{-1}" to "high ug ml^{-1}" concentration levels. It is this versatility that has led to the rapid acceptance and subsequent growth of the technique. Since the launch of the first commercial quadrupole ICP-MS instrument in 1983, the technology has evolved from large, floor-standing, manually operated systems, with limited functionally and relatively poor detection limit capabilities, to compact, sensitive and highly automated routine analytical instruments. From the outset, it was observed that although ICP-MS spectra were much less complex than ICP optical emission spectra, interferences were nonetheless present and as ICP has grown, considerable attention has been focused on achieving wholly interference-free analysis. The first step towards achieving this objective was the development of high resolution ICP-MS in the late of 1980s, whereby analytes could be resolved from interferences using a magnetic field, by virtue of the mass differences between analyte/interference pairs. This technology, although effective in resolving a wide range of polyatomic interferences, lacks the power to the resolve isobaric interferences (*i.e.* overlap between isotopes of the same nominal mass, such as ^{87}Rb and ^{87}Sr). Recently years, the advent of collision/reaction cell technology has revolutionized quadrupole ICP-MS. Born out of existing technology for triple quadrupole organic mass spectrometers; collision/reaction cells have taken interference reduction a dramatic step forward. Through collision and reaction with appropriate gases in a cell preceding the analyzer quadrupole, interferences such as $^{40}Ar^{2+}$ can be completely eliminated while leaving analyte ions (^{80}Se in this case) relatively unaffected.

Recently, ICP-MS instrument has become a powerful tool for the determination of both long-lived radionuclides and trace levels of heavy metal elements in environmental samples. Naturally occurring and artificial radionuclides present in environment are useful indicators in many field of science. From a view point of radiation protection of the general public, these radionuclides need to be analyzed in different environments at natural levels and at elevated concentrations, following accidents at nuclear facilities. When radionuclides are released after accidents, they will be transported by air and water. Since the half-lives of many released radionuclides are very long, people will be radiated internally and externally for long periods by contact with the environment, by food intake and etc. Plutonium isotopes are especially important in ecotoxicology since it seems that they significantly affect the human body.

Plutonium has accumulated in the environment from several sources, such as atmospheric nuclear weapons tests, the accidental burn-up of satellites carrying nuclear batteries and discharges from nuclear facilities. The isotopic composition of Pu is characteristics for each origin, and so it is possible to estimate the source location from the ^{240}Pu/^{239}Pu atomic ratio in the samples. In addition, Pu isotopic ratio gives important geochemical information about the behavior of Pu in marine and terrestrial water environments. Usually, the ^{240}Pu/^{239}Pu isotopic composition cannot be measured by conventional alpha-ray spectrometry. For isotope measurement of Pu, thermal ionization mass spectrometer (TIMS) has been the most commonly used method, although occasionally the fission track (FT) method has been applied. The first paper reporting Pu determination and isotopic composition measurement in environmental samples using ICP-MS was published by Kim et al. (1989). Since then, ICP-MS was only just starting to gain recognition in the field of analytical chemistry; they applied the technique to analysis of long-lived radionuclides in environmental samples. Following this work, a number of papers discussing on the measurement of long-lived radionuclides, particularly Pu isotopes, using ICP-MS increased rapidly, and it is not an exaggeration to say that this technique is now regarded as a standard approach for analysis of these isotopes in a broad range of samples.

1.3. The aim of this study

In the field of radioactivity monitoring for Pu isotopes commissioned with Japanese government, routine analysis for Pu isotopes in seawater is carried out by radiochemical analysis using a large volume (100 L) of seawater samples according as standardized radiochemical method. However, a large volume seawater samples are hard to handling through routinely chemical separation schemes without elemental losses as low as possible. Instead of seawater sample, marine organism, especially Surume squid is found to be useful for environmental radioactivity monitoring as living indicators.

Therefore the sample preparation method was studied from view point of ashing processes to the meaning of elemental losses. A rapid chemical separation procedure using anion exchange resin disk are developed for the determination of Pu isotopes by alpha-ray spectrometry and ICP-MS in standard reference materials. Before radioactivity monitoring by using marine organisms, chemical behavior and concentration levels of trace elements concerning radioactivity monitoring (*i.e.* ^{60}Co-stable Co, ^{90}Sr-stable Sr, ^{110m}Ag-stable Ag, etc.) were determined by neutron activation analysis and ICP-MS to compare both method for estimation of the validation. Finally, obtained knowledge through this study are applied to Surume squid liver collected in the coastal sea area in Japan, and discussion on the possibility of the usefulness of squid liver for environmental radioactivity monitoring in marine environment.

1.4. Content and findings of the dissertation

In this CHAPTER, general introduction of the investigation including a general background, practical advantages of the inductively coupled mass spectrometry, the aim of the study.

CHAPTER 2 described ash content of foodstuff samples in environmental radioactivity analysis. Statistical data of the ash content in various kind of foodstuff samples obtained from an environmental radioactivity survey project commissioned by Japanese government of Science and Technology Agency (at present Ministry of Education, Culture, Sports, Sciences and Technology) during the past decade are expressed for establishing a standard ash content in foodstuff samples based on environmental radioactivity analysis.

CHAPTER 3 described a rapid separation technique of plutonium in environmental samples using an anion exchange resin disk. A rapid analytical method of plutonium in environmental samples by alpha-ray spectrometry and sector field inductively coupled plasma mass spectrometer using an anion exchange resin disk 3M Empore^{TM} for solid phase extraction has been developed.

CHAPTER 4 described determination method of trace elements in squid organs by inductively coupled plasma mass spectrometry and neutron activation analysis with the aim for an analytical validation of the inductively coupled plasma mass spectrometry method by neutron activation analysis.

CHAPTER 5 described the radioanalytical and mass spectrometric analysis by a sector field inductively coupled plasma mass spectrometer of plutonium concentration in Surume squid liver collected from the coastal sea areas of Japan. Emphasis is put on the ^{240}Pu/^{239}Pu atomic ratio of plutonium in the liver. In addition to plutonium, levels of 13 elements (V, Mn, Fe, Co, Cu, Zn, Rb, Sr, Ag, Cd, Cs, Th and U) were measured for comparison. These data are discussed with emphasis on the potential use of plutonium signatures in squid liver to trace the radioactive and marine contamination of plutonium.

Finally, CHAPTER 6 described a conclusion of this dissertation.

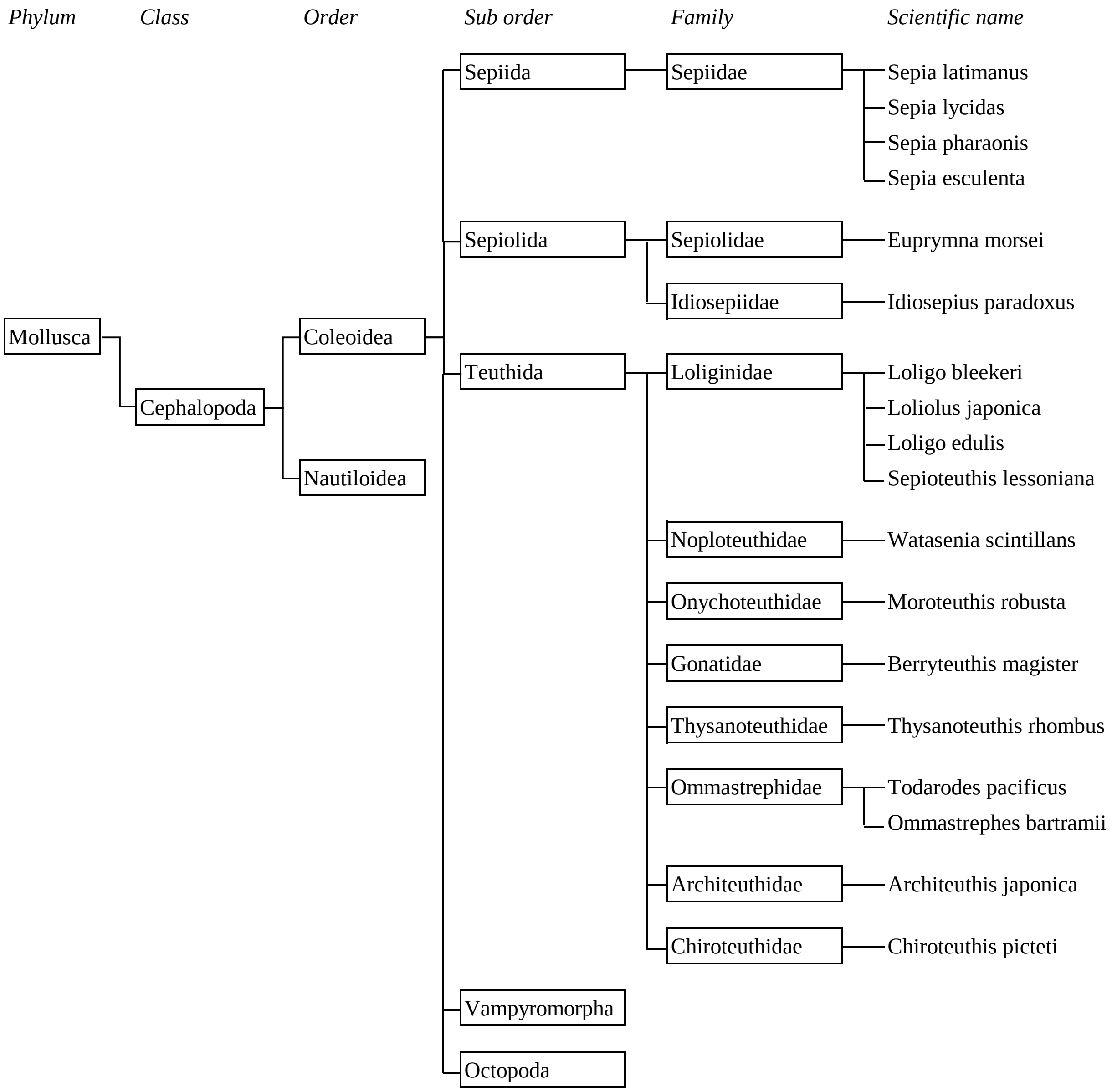

Fig. 1.1 Typical scientific classification of the squids.

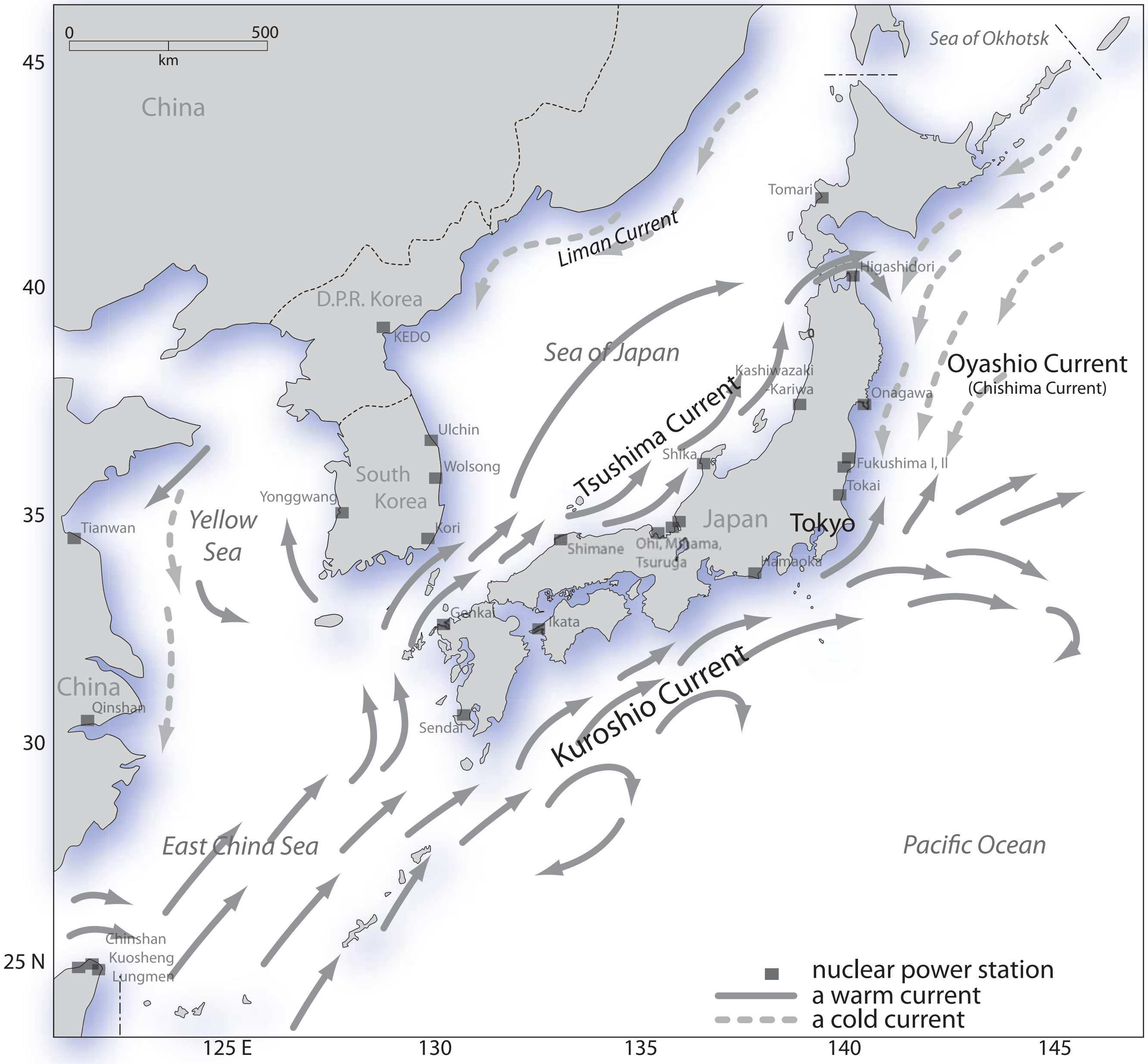

Fig. 1.2 The Janan islands surrounding sea, Sea of Japan, East China Sea, Sea of Okhotsk and Pacific Ocean with the schemitic ocean current flowing patterns.

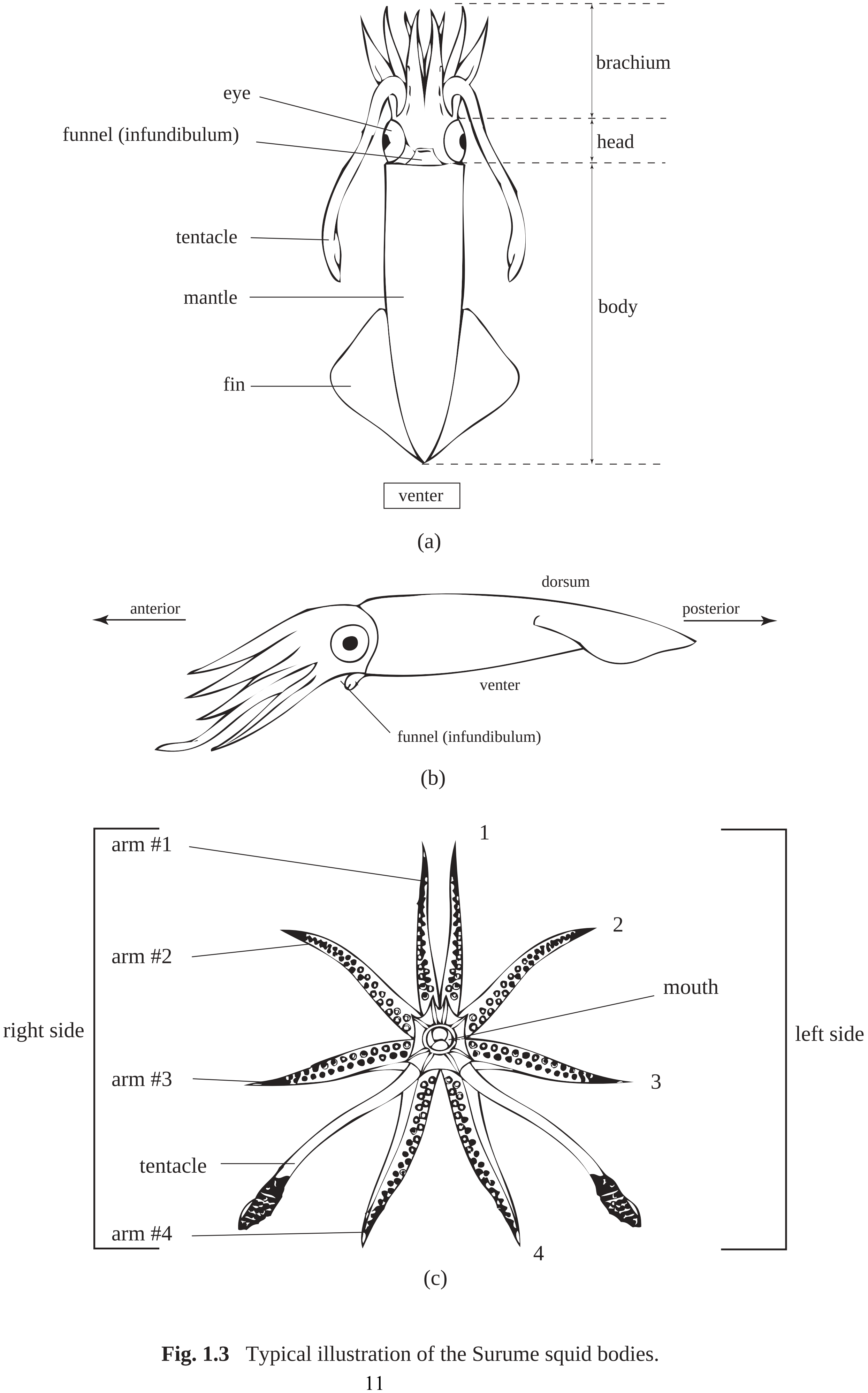

Fig. 1.3 Typical illustration of the Surume squid bodies.

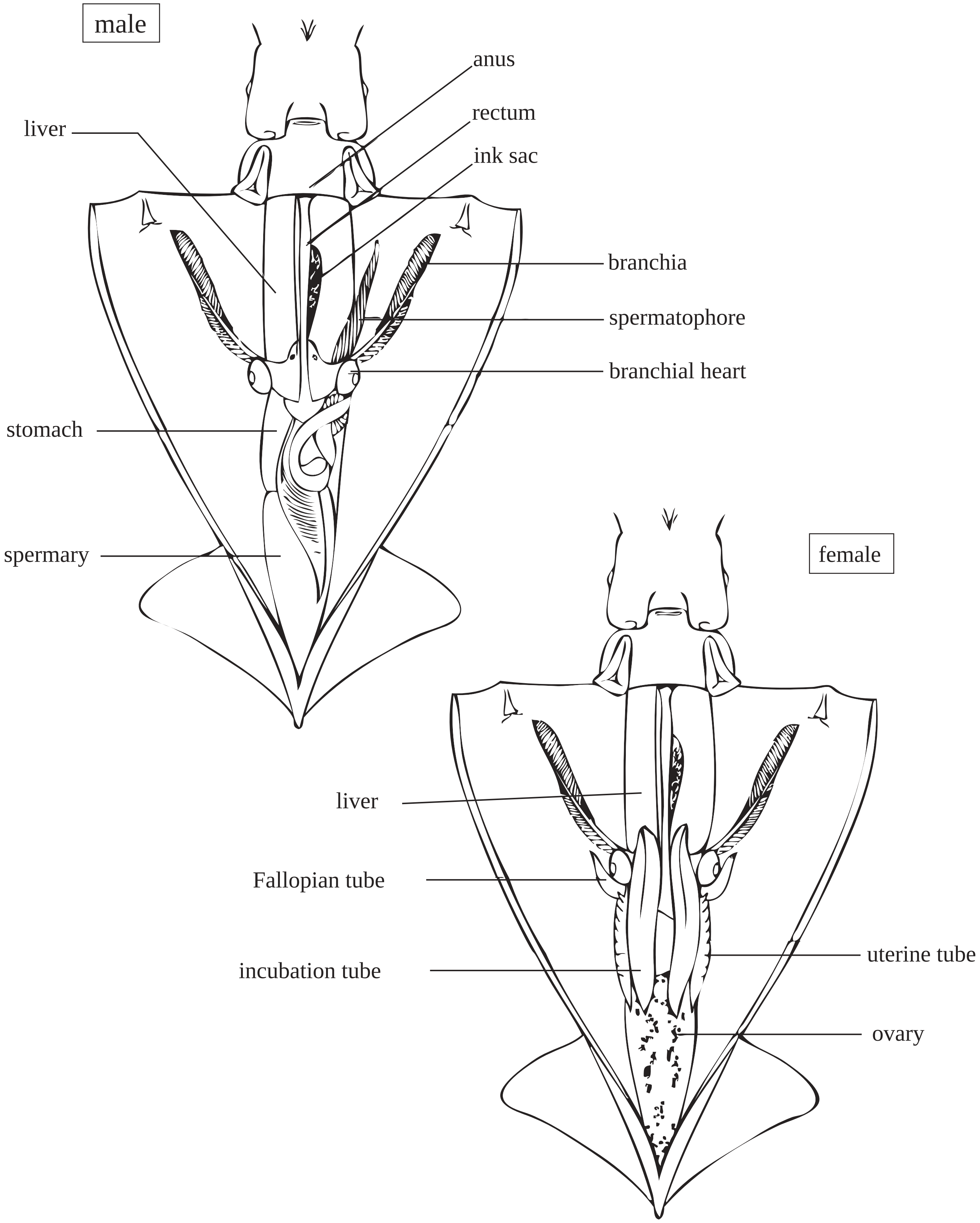

Fig. 1.4 Illustration of typical intenal organs of Surume squid.

Table 1.1 Major plutonium isotopes and its half life, decay type, particle energy and main souce.

Nuclide	Half life	Decay type	Energy(MeV)	Source (reaction)
^{232}Pu	34.1 m	EC(80%), α(20%)	1.060(EC), 6.716(α)	^{232}Am EC, ^{233}U(α, 5n), ^{235}U(α, 7n)
^{233}Pu	20.9 m	EC(99.8%), α(0.12%)	1.900(EC), 6.420(α)	^{233}U(α, 4n)
^{234}Pu	8.8 h	EC(94%), α(6%)	0.388(EC), 6.310(α)	^{234}Am EC, ^{238}Cm α
^{235}Pu	25.3 m	EC(99.99%), α(0.003%)	1.170(EC), 6.000(α)	^{235}U(α, 4n), ^{233}U(α, 2n)
^{236}Pu	2.858 y	α(100%), sf($\approx$0%)	5.867(α)	^{236}Np β^-, ^{240}Cm α, ^{235}U(α, 3nγ)
^{237}Pu	45.2 d	EC(99.99%), α(0.004%)	0.220(EC), 5.750(α)	^{237}Am EC, ^{241}Cm α, ^{237}Pu IT
^{238}Pu	87.7 y	α(100%), sf($\approx$0%)	5.593(α)	^{238}Np β^-, ^{238}Am EC, ^{242}Cm α
^{239}Pu	2.41×10^4 y	α(100%), sf($\approx$0%)	5.244(α)	^{239}Np β^-, Muonic, ^{239}Am EC, ^{243}Cm α
^{240}Pu	6563 y	α(100%), sf($\approx$0%)	5.256(α)	^{240}Np β^-, ^{240}Am EC, ^{244}Cm α
^{241}Pu	14.35 y	β^-(100%), α($\approx$0%)	0.021(β^-), 5.140(α)	^{241}Np β^-, ^{245}Cm α, ^{240}Pu(n, γ)
^{242}Pu	3.733×10^5 y	α(100%), sf($\approx$0%)	4.982(α)	^{242}Np β^-, ^{242}Am EC, ^{246}Cm α
^{243}Pu	4.956 h	β^-(100%)	0.582(β^-), 4.754(α)	^{243}Np β^-, ^{247}Cm α, ^{242}Pu(n, γ)
^{244}Pu	8.08×10^7 y	α(99.9%), sf($\approx$0.1%)	4.665(α)	^{248}Cm α, ^{244}Np β^-, ^{244}Am EC
^{245}Pu	10.5 h	β^-(100%)	1.205(β^-), 0.150(γ)	^{244}Pu(d, p), Fission isomer
^{246}Pu	10.84 d	β^-(100%)	0.401(β^-)	^{244}Pu(t, p)

Reference from the Table of Isotopes 8th edition.

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CHAPTER 2

CHAPTER 2 : Ash content of foodstuff samples in environmental radioactivity analysis.

2.1. Introduction

Radionuclides present in environment can be classifies into two categories, natural and artificial radionuclides from viewpoint of its origins. Based on the nuclear safety, radioactivity monitoring around nuclear facilities are important things due to increasing of the electricity demand following peaceful operations of nuclear power plants. Background survey for the general public is an important thing using a distribution foodstuffs samples from view point of radioactivity monitoring. Particularly, radionuclides present in the environment distributed by nuclear weapons tests conducted in atmospheric environment mainly at the northern hemisphere may potentially ingest to human beings via food chains. Consequently, environmental radioactivity analysis for foodstuff samples has to take a broad and long-term view of things, and the results are used to be background data based on radioactivity monitoring.

In our laboratory, radioactivity analysis has been carried out in environmental food samples such as dietary food, dairy products, root vegetables, green vegetables, fishes, teas and food cereals. From view point of a nationwide background survey project, it should be carried out in uniform pre-treatment, radiochemical and measurement methods. Pre-treatment methods, particular ashing process, applied for environmental radioactivity analysis are deficient in statistical and experiences data nevertheless effective techniques to reducing sample volume. Generally, ashing process is conducted by using an electric furnace. However, ashing efficiency is depending on location in the furnace, or temperature control characteristics of the electric furnace. To avoid elemental losses, especially cesium isotopes, temperature at ashing is routinely up to 450 ˚C for 24 hours. The temperature at 450 ˚C is lower than the literature values and different in the method. Thus, information on ashing and ash content at the temperature 450 ˚C is a problem to be solved from view point of environmental radioactivity analysis (Nonaka et al., 1981; 1985).

In this chapter, statistical data of the ash content in various environmental samples obtained from an environmental radioactivity survey project commissioned by the Japanese government of Science and Technology Agency (at present the Ministry of Education, Culture, Sports, Sciences and Technology) cooperate with prefectural hygiene centers during the past 10 years are expressed for establishing a standard ash content in environmental samples based on radioactivity analysis.

2.2. Methods

Environmental foodstuff samples subjected of our survey was selected from a standpoint of our daily life; dietary foods, milk, spinach, Japanese radish, edible part of fishes, whole fishes, green tea, cabbage, Chinese cabbage, potato and onion. Those samples were obtained from commercial market in cooperate with the 47 prefectures of prefectural hygiene center in every fiscal year from 1993 to 2002. Raw samples were ashed at 450 ˚C for 24 hours at the prefectural hygiene center and then an aliquot of ash was sent to our laboratory. The ash samples were aliquot about one gram and then ashed again at 450 ˚C for 5 hours. Ash content C_{ash} was calculated by following equation;

$$C_{ash} = \frac{W_{ash}}{W_{raw}} \times 100 \quad (\%) \qquad \cdots (1)$$

where W_{ash} is weight of ash (g), W_{raw} is weight of raw sample before ashing (g). In the case of dietary food sample, it is difficult to interpretation as a uniform sample due to differ from place to place, manners and customs and an age bracket. Consequently, dietary food samples were obtained by "set a meal for an absent person" thanks to the cooperation with participants. Daily meals collected into vinyl bag and then ashed at 450 ˚C for 24 hours. Ash content was calculated by equation (1) and result was converted to "g/person/d" unit.

2.3. Results and discussions

2.3.1. Differences in ash content

Remarkable progress in electronic devices past few decades has brought about a revolution in many aspects of our daily life. Electric furnace used in environmental radioactivity analysis is also useful tools for sample preparation. However, sample preparation skills are still not entirely in agreement on ash content. As an example of spinach sample, relative deviations of ash content between the 47 prefectures of prefectural hygiene center and our laboratory (JCAC) are shown in Fig. 2.1. This difference may be caused mainly by incomplete calcinations of the samples containing unburned charcoal dust.

2.3.2. Ash content of foodstuff samples

It is difficult to classify of the ash content every foodstuff samples which includes many different fields. To evaluation of ash content from overview classifications, foodstuff sample was categorized 12 groups as dietary food, milk, spinach, Japanese radish, fish (edible part), fish (whole), green tea, cabbage, Chinese cabbage, potato and onion. The result of statistical calculation of the above 12 groups from fiscal year of 1993 to 2002 are summarized in Table 3.1 together with confidence intervals (three sigma standard deviation).

Depending on personal dietary habits, dietary food is heterogeneousness sample. However, the results of mean ash content and its statistics obtained from the past decades were 15.0 ± 2.8 g/person/d (n=1862) as shown in Fig. 2.2. Ash content of the dietary food "15.0 ± 2.8 g/person/d" can be interpreted as an average ash content of the Japanese meals and also meals of dietary habits/culture in our country. Although dietary food sample is heterogeneousness from view point of individuals, it is homogeneousness from point of the ash content after sample calcinations.

In the case of milk, it is the most homogeneousness sample in 12 categories. Ash content of the milk was 0.724 ± 0.0340 % with the coefficient of variation of 4.7 % (n=1359), as shown in Fig. 2.2. The reason milk ash content uniformed that a whole milk sample was carbonized and then being reduced to ashes without human experiences.

In the case of Japanese radish and spinach samples from green vegetables and root vegetables categories, a part of the foods such as edible part of the Japanese radish (e.g. leaves include edible part or not) depend on regional dietary cultures. In the case of fish (edible part) sample, ash content was 1.39 ± 0.300 % with the coefficient of variation of 21.6 % (n=216). This is because that cut and divide the fish techniques are requires a great deal of skill, so that coefficient of variation might be derived mainly on human skills. On the other hand, fish (whole) were directly ashed in electric furnace without special (such as cut and divide) processes. However, ash content was 3.49 ± 1.09 % (n=110) and coefficient of variation (31.2 %) is higher than that of fish (edible part) (21.6 %). This variance may be caused by difference of the percentage of muscle, born and internal organs based on maturities.

Ash content obtained from Green teas and Chinese cabbage is relatively lower than that of above categories of food samples. Green tea, commercially available Japanese tea leaves and raw green tea such as Yabukita tea leaves are likely to homogeneous sample from view point of ash content.

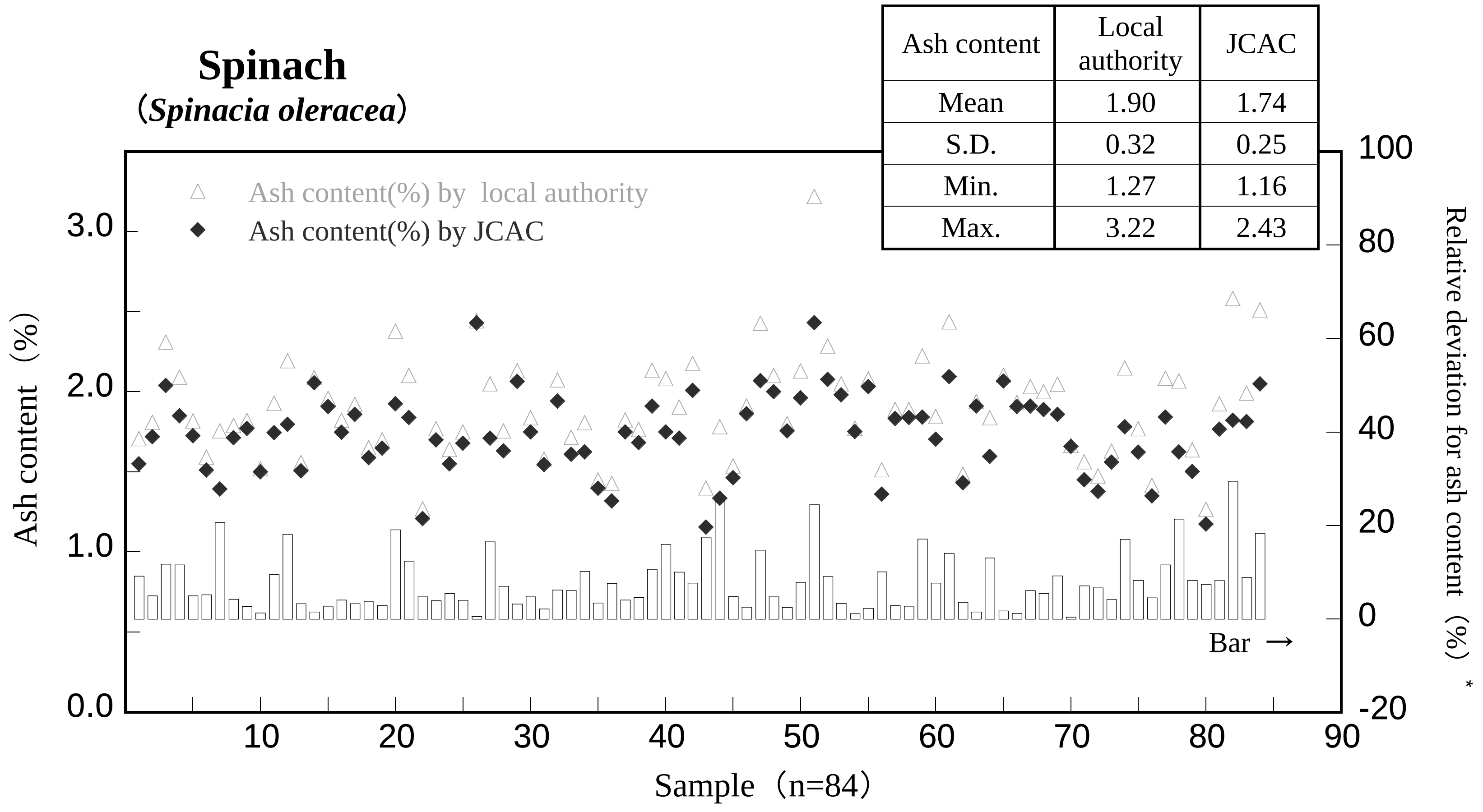
As a whole, coefficient of variation seems to be depending on technical skill under sample preparation such as cut, divide and rend of the part of sample. Ash content shown in Table 2.2 is an average ash content at 450 ˚C for 24 hours.

2.3.3. Ash content of fish samples

Ash content of fish sample describing as mentioned above were typical ash content obtained from various kinds of fishes. However, ash content was a great difference every kind of fish. Ash content of twelve kinds of fish obtained from past decades radioactivity analysis project are summarized in Table 2.3. There is 5-10 % higher than that of ash content reported in Standard Tables of Food Composition (2000) (ashed at 550 ˚C).

2.4. Conclusions

Pretreatment of environmental samples especially ashing processes are important from the view point on environmental radioactivity analysis, which is one of the especial fields on analytical chemistry. Statistical reviewed data obtained in this chapter may useful for sample preparation on environmental radioactivity analysis.



Spinach
（***Spinacia oleracea***）

Ash content	Local authority	JCAC
Mean	1.90	1.74
S.D.	0.32	0.25
Min.	1.27	1.16
Max.	3.22	2.43

*Relative deviation for ash content were calculated by the equation: $\frac{\text{(Local authority - JCAC)}}{\text{(JCAC)}} \times 100$

Fig. 2.1 Relative deviations of ash content between the local authority and JCAC.

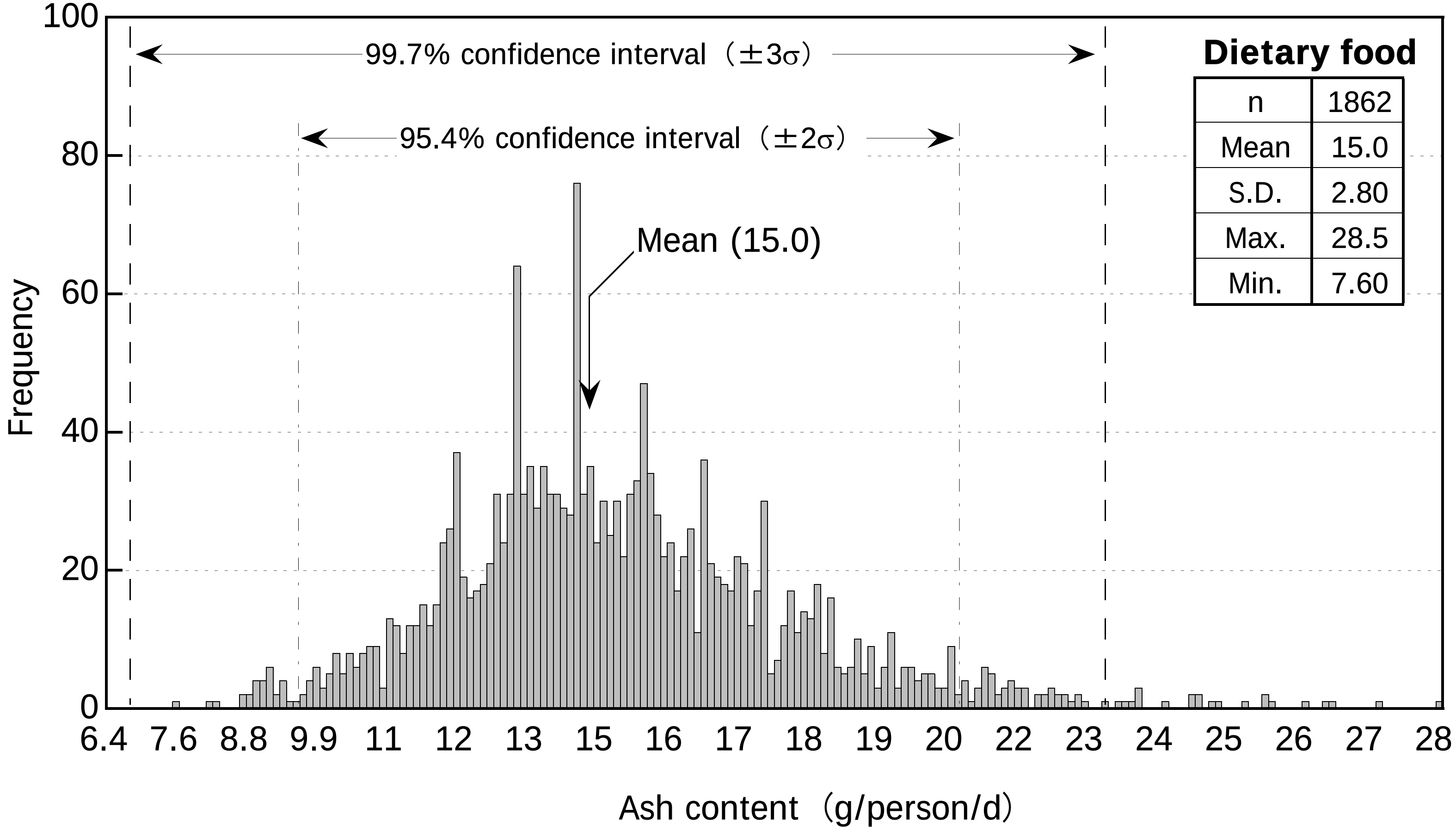
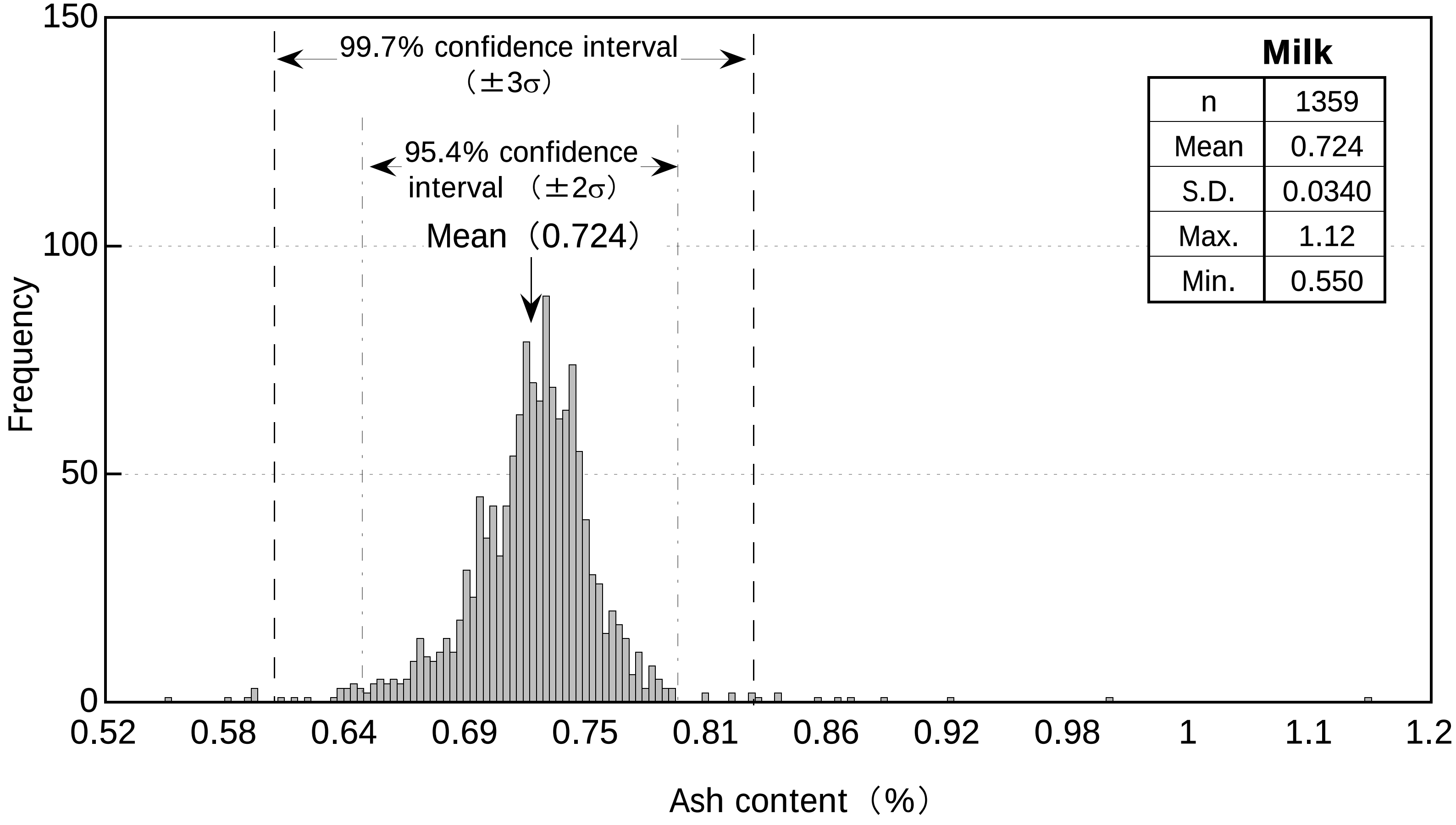


Fig. 2.2 Frequency distribution of ash content for dietary food samples collected from a nationwide in Japan during 1993 to 2002.



n	1359
Mean	0.724
S.D.	0.0340
Max.	1.12
Min.	0.550

Fig. 2.3 Frequency distribution of ash content for milk samples collected from a nationwide in Japan during 1993 to 2002.

Table 2.1 Ash content for foodstuff samples during 1993-2002.

Sample category	n	Ash content (%)[1]		C. V.[3]	Confidence interval
		Arithmetic mean	S. D.[2]	(%)	(±3 sigma S. D.)
Dietary food	1862	15.0	2.80	18.7	6.60 ～ 23.4
Milk	1359	0.724	0.0340	4.7	0.622 ～ 0.826
Japanese radish (*Raphanus sativus longipinnatus*)	469	0.533	0.102	19.1	0.227 ～ 0.839
Spinach (*Spinacia oleracea*)	419	1.70	0.270	15.9	0.890 ～ 2.51
Fish (edible part)	216	1.39	0.300	21.6	0.490 ～ 2.29
Fish (whole)	110	3.49	1.09	31.2	0.220 ～ 6.76
Green tea (commercially Japanese tea leaves)	140	5.26	0.370	7.0	4.15 ～ 6.37
Green tea (raw) (ex. Yabukita tea leaves)	20	1.33	0.110	8.3	1.00 ～ 1.66
Cabbage	43	0.636	0.231	36.3	－ ～ 1.33
Chinese cabbage	30	0.595	0.0728	12.2	0.377 ～ 0.813
Potato	10	0.865	0.0560	6.5	0.697 ～ 1.03
Onion	10	0.375	0.0167	4.5	0.325 ～ 0.425

[1] Ash content given in "%" except for Dietary food "g/person/d".

[2] Standard deviation from ash content of each sample.

[3] Coeficient of variation.

Table 2.2 Ash content for Pisces samples during 1993-2002.

Sample		n	Ash content (%)		C. V.[2]	Confidence interval
			Arithmetic mean	S. D.[1]	(%)	(±3 sigma S. D.)
Spotted chub mackerel[3] (*Scomber australasicus*)	Edible part	50	1.23	0.166	13.5	0.728 ～ 1.72
Red sea bream snapper (*Pagrus major*)	Edible part	39	1.42	0.266	18.8	0.619 ～ 2.22
Stone flounder[4] (*Kareius bicoloratus*)	Edible part	38	1.50	0.297	19.8	0.612 ～ 2.39
	Whole	19	3.09	0.434	14.1	1.78 ～ 4.39
Yellowfin horse mackerel (*Trachurus japonicus*)	Edible part	24	1.45	0.230	15.8	0.763 ～ 2.14
	Whole	15	3.05	0.591	19.4	1.28 ～ 4.82
Japanese pilchard (*Sardinops melanosticta*)	Edible part	4	2.49	0.416	16.7	1.24 ～ 3.74
	Whole	16	2.38	0.290	12.2	1.51 ～ 3.25
Darkbanded rockfish (*Sebastes inermis*)	Whole	10	4.82	0.254	5.3	4.05 ～ 5.58
Skipjack tuna (*Katsuwonus pelamis*)	Edible part	10	1.24	0.0598	4.8	1.06 ～ 1.42
Rock trout (*Hexagrammos otakii*)	Edible part	10	1.55	0.241	15.5	0.827 ～ 2.27
Japanese sand lance (*Ammodytes personatus*)	Whole	10	2.24	0.135	6.0	1.84 ～ 2.65
Striped mullet (*Mugil cephalus cephalus*)	Edible part	20	1.25	0.206	16.4	0.635 ～ 1.87
Goldenbanded fusilier (*Pterocaesio diagramma*)	Whole	10	3.81	0.506	13.3	2.29 ～ 5.32
Banded blue-sprat (*Spratteloides gracilis*)	Whole	10	2.96	0.171	5.8	2.45 ～ 3.47
Japanese amberjack (*Seriola quinqueradiata*)	Edible part	10	1.35	0.231	17.1	0.655 ～ 2.04

[1] Standard deviation from ash content of each sample.

[2] Coeficient of variation.

[3] include Chub mackerel (*Scomber japonicus*)

[4] include Brown sole(*Limanda herzensteini*)

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CHAPTER 3

CHAPTER 3 : Rapid separation techniques for the determination of plutonium in environmental samples by using an anion exchange resin disk.

3.1. Introduction

Various analytical methods have been applied to the chemical separation and determination of plutonium in environmental samples. Recently days, much interest has been shown in replacing conventional solvent extraction and ion exchange techniques for separating environmental radionuclides. Rao and Cooper applied selective oxidation-reduction and co-precipitation with NdF_3 to the separation of actinides (Rao and Cooper, 1995). Horwitz et al. developed several new extraction chromatographic resins (commercialized by Eichrom Industry) and applied to the separation of actinide elements (Horwitz et al., 1993, 1993b ; Maxwell, 1993). Bunzl and Kracke determined the concentration of plutonium isotopes in human tissues and soil samples using extraction chromatographic resin, TEVA spec^{TM}, Eichrom Industries Ltd, USA (Bunzl and Kracke, 1994).

The extraction chromatographic resin is usually used in slow flow rate (0.5-1.0 ml min.$^{-1}$) and sometimes the loaded extractant on inert polymeric substrate bleed with the effluent during the separation procedure. The bleed extractant interfere the determination of actinides by absorptiometry and electrodeposition of actinides for alpha-ray spectrometry. In contrast, a 3M Empore^{TM} anion exchange resin disk consists of fine resin particles (average particle size, 1.2×10^{-7} m) tightly held in polytetrafluoroethylene (PTFE) fiber. In addition, the disk ca be used under fast flow rate (150-200 ml min.$^{-1}$) (Hagen et al., 1993 ; Miura et al., 2000).

The aim of this study is to develop a rapid analytical method for Pu isotopes in environmental samples using a 3M Empore^{TM} anion exchange resin disk. The elution behavior of Pu and the decontamination factors of Th, U and Am in the procedure of Pu separation using the disk were investigated. The present method was applied to the determination of Pu isotopes in the certified reference material (IAEA-135, Irish Sea sediment) and the forest soil sample by alpha-ray spectrometry and high resolution ICP-MS. The results obtained were compared with the literature values.

3.2. Experiment

3.2.1. Instruments for alpha-ray spectrometry

The silicon semiconductor detector, an ORTEC model 576A alpha spectrometer (with 450 mm^2 active area) was used for alpha-ray measurement. Counting efficiencies were 20 to 30 %, and energy resolutions were 20-40 keV full width at the half-minimum peak height (FWHM) at 5.47 MeV of ^{243}Am alpha-ray peak. Radioactivity measurement of $^{239+240}$Pu and ^{238}Pu were calculated from the count ratios of $^{239+240}$Pu and ^{238}Pu to ^{242}Pu, which was added as a yield tracer. The detection limit of Pu by alpha-ray spectrometry was 1 mBq/sample, based on the three times counting statistics for a counting time of 70,000 s.

3.2.2. Instruments for mass spectrometry

A sector field double focusing high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS), model JMS-PLASMAX2 (Japan Electron Optics Laboratory, Tokyo, Japan) was applied for the measurement of Pu isotopes. After chemical separation and purification of Pu, the sample solution was introduced into the HR-ICP-MS through CETAC ultrasonic nebulizer, model U-5000AT$^+$ (CETAC Technologies, Toms River, USA). The operating conditions are summarized in Table 3.1. The concentrations of Pu isotopes, especially ^{239}Pu and ^{240}Pu, in the sample solution were determined from the peak abundance ratios of m/z 239 and 240 to 242, which was added as a yield tracer of known amounts of ^{242}Pu, on the basis of the isotope dilution method.

The detection limit of Pu in sample solution by HR-ICP-MS measurement estimated to be 21 fg ml^{-1} (^{239}Pu: 0.05 mBq ml^{-1}, ^{240}Pu: 0.18 mBq ml^{-1}), based on standard deviation at three times replicated measurements. To check the interference of hydrogen coupling isobar

$^{238}U^{1}H^{+}$ ions and up-mass tailing of $^{238}U^{+}$ at the mass *m*/*z* 239, the mass *m*/*z* 238 was measured.

3.2.3. Anion exchange resin disk

Anion exchange resin disk, an Empore™ anion exchange-SR resin disk was obtained from the 3M Company (St. Paul, USA). Specifications of the disk is 47 mm diameter, 0.5 mm thickness, 90 wt.% resin particle and 10 wt.% fibrillated polytetrafluoroethylene (PTFE), styrenedivinylbenzene copolymer resin, strongly basic quaternary ammonium functional group, 350 m^2 g^{-1} surface area, 12 micrometer average particle size, >0.2 mEq per disk exchange capacity. The disk was successively washed with 10 ml of methanol, 50 ml of pure water, 20 ml of 1M HCl, 50 ml of pure water, and finally with 20 ml of 8M HNO_3 to convert the NO_3^- form.

3.2.4. Apparatus, reagents and standard solutions

The 47 mm glass filtering apparatus provided from 3M and triple-stage extraction manifold assembly was used for solid phase extraction procedures. The aspirator, model Shibata WJ-15 was used for vacuum source. Gelman Science polysulfone filtering funnels (200 ml capacity), a polysulfone filter holder, a polysulfone support screen and SUPOR™ membrane filter (polysulfone, 25 mm diameter, 0.1 micrometer pore size) were applied for preparation of alpha-ray counting using NdF_3 coprecipitation method.

All reagents used were of reagent grades. Pure water was purified with Milli-Q plus (Japan Millipore Ltd., Shinagawa, Japan). The ultra pure nitric acid used for preparing the final solution for HR-ICP-MS measurement was of super analytical grade reagent Tamapure AA-100, provided from Tama Chemical Ltd., Japan.

The ^{242}Pu standard solution, SRM-4334E, supplied by National Institute of Standard and Technology (NIST, Gaithersburg, USA) was diluted to activity concentration of approximately 20 mBq ml^{-1} in 7M HNO_3, and stored in the Teflon bottle. The thorium and uranium standard solution were prepared from $Th(NO_3)_4 \cdot 4H_2O$ and $UO_2(NO_3)_2 \cdot 4H_2O$ reagent provided from Merck Inc. The solution was standardized by gravimetric techniques. The ^{243}Am standard solution was obtained from Isotope Products Laboratories (Burbank, USA). The $^{239+240}Pu$ solution was prepared from 10 g of sea sediment reference material, IAEA-135 certified reference material (Irish Sea sediment) by HNO_3 leaching and purified with anion exchange resin column method. The concentration of $^{239+240}Pu$ in the solution was determined with alpha-ray spectrometry.

3.2.5. Determination of the decontamination factors

Decontamination factor (*DF*) through the chemical separation procedure was determined by using following equation;

$$DF = \frac{C_{added}}{C_{sample}}$$

where C_{added} is added amount of ion to the sample, C_{sample} is measured amount of ion after separation of interference elements (Th, U and Am) in the anion exchange resin disk separation procedure.

3.2.6. Measurement of the elution behavior of Pu in the procedure

A known amount of $^{239+240}Pu$ in 8M HNO_3-0.03M $NaNO_2$ sample solution (100 ml volume) was prepared using the 20 ml of the $^{239+240}Pu$ standard solution. The solution was treated with the procedure using a 3M Empore^{TM} anion exchange resin disk. All of the fractions were stored and $^{239+240}Pu$ was measured in those fractions with HR-ICP-MS.

3.2.7. Building of chemical separation procedure

The recommended chemical separation procedure consists of following three steps; (1) preparation of the load solution, (2) chemical separation of Pu with anion exchange resin disk,

(3) coprecipitation of Pu with NdF_3 and alpha-ray spectrometry, or measurement of Pu with HR-ICP-MS.

An aliquot of 0.5-1.0 g sample was weighed for analysis. If the sample amount is up to 5 g, the sample was ashed at 500 ˚C for 2-4 hours. The sample was leached with 8M HNO_3 at 180 ˚C for 2 hours after a spiked about 30 mBq of ^{242}Pu as a yield tracer. The sample was cooled down to 50 ˚C, the insoluble substance was filtered. The filtrate was then adjusted to 200 ml of 8M HNO_3-0.03M $NaNO_2$ solution to keep Pu in tetravalent chemical state (Keder et al., 1960; Rao and Cooper, 1995).

The sample solution was passed through the 3M Empore^{TM} anion exchange resin disk for adsorption of Pu(IV) at flow rate of 150-200 ml min.$^{-1}$ under vacuum conditions. After the disk was washed with 10 ml of 8M HNO_3 (5 ml × 2) and 12 ml of 9M HCl (4 ml × 3), Pu(IV) on the disk was then reduced to Pu(III) and eluted with 15 ml of 1M HNO_3-0.03M ascorbic acid solution (3 ml × 5).

In the preparation of counting sample, Pu was coprecipitated with NdF_3 precipitation according the procedure reported by Rao and Cooper (1995). The Pu fraction was evaporating to dryness and the organic compounds were decomposed with a few ml of HNO_3 and $HClO_4$. After the decomposition, the residues were dissolved with 10 ml of 1M HCl-0.03M ascorbic acid solution containing 0.1 mg amount of Nd^{3+}. Neodymium fluoride was precipitated by addition of a one ml of HF. The solution was allowed to stand for 30 minutes and filtered with a SUPOR^{TM} membrane filter under vacuum conditions. The filter was removed and dried at 105 ˚C for 30 minutes. Subsequently, the filter was mounted on a stainless steel disk (25 mm diameter) using a double-side adhesive tape. The mounted sample was counted for 70,000 s by alpha-ray spectrometry.

For HR-ICP-MS measurements, the Pu fraction was evaporated to dryness and the organic matter were decomposed with a few ml of HNO_3. After decomposition, the residue was dissolved into ultra pure 20 ml of 1M HNO_3. The concentration of Pu isotopes were measured by HR-ICP-MS.

3.3. Results and discussion

3.3.1. Elution behavior of Pu and the decontamination factor of interference elements

The elution behavior of Pu is presented in Fig. 3.1. It was found that tetravalent state Pu was quantitatively adsorbed on the Empore^{TM} anion exchange resin disk even at the high flow rate, 150-200 ml min.$^{-1}$. Chemical recovery of Pu in this procedure was found to be 90-97%. According to the procedure, plutonium in the sample solution can be separated from the other matrix elements within 20 minutes. Decontamination factors of Th, U and Am were 4.4×10^2, 6.6×10^3 and 2.1×10^3, respectively. These results showed that the anion exchange resin disk is useful for chemical separation of Pu in environmental samples because it gives rapid and large volume successive separation and enough decontamination capabilities.

3.3.2. Application to environmental samples

A certified reference material, IAEA-135 Irish Sea sediment was analyzed in order to examine the reproducibility and accuracy of the present method. The concentration of Pu isotopes in IAEA-135 reference material was determined by alpha-ray spectrometry and HR-ICP-MS after chemical separation method mentioned above. The analytical results are summarized in Table 3.2, together with recommended and literature values, chemical recovery, mean and standard deviations. Mean concentration values of $^{239+240}$Pu and ^{238}Pu were in well agreement with the recommended values within statistics, and high chemical recovery (70-83%). Atomic ratio of ^{240}Pu/^{239}Pu was 0.23±0.04, which is comparable with the ratio (0.211±0.004) reported by Muramatsu et al. (1999).

We also applied the method to environmental soil sample. The sample was collected from a forest in Fukui prefecture, Hokuriku region, Japan. Analytical results were comparable to the value by conventional anion exchange column method and determined by HR-ICP-MS, as shown in Table 3.3.

3.4. Conclusions

From the results of present studies, it was found that Pu was quantitatively extracted with the anion exchange resin disk at high flow rate of 150-200 ml min.$^{-1}$. These results showed that Pu could be rapidly, effectively and easily separated from other interfere elements such as Th, U and Am by using anion exchange resin disk. The time needed to separate Pu from other interfere elements in environmental samples by the present method was only 20 minutes. The operation time of chemical separation of the present method is less than for the method using an anion exchange resin column, extraction chromatographic resin cartridge and solvent extraction. Measurement time of Pu isotopes are 70000 s for alpha-ray spectrometry, 10-20 min. for HR-ICP-MS. The combination of Pu separation by Empore^{TM} anion exchange resin disk and the measurement by HR-ICP-MS is more rapid than the alpha-ray spectrometry. After the preparation of load solution, the concentration of Pu could be determined with HR-ICP-MS in less than 2 hours. Using a 10 g sample, the detection limits of $^{239+240}$Pu and ^{238}Pu are 0.1 mBq g^{-1} by alpha-ray spectrometry, and those of ^{239}Pu and ^{240}Pu are 0.1 and 0.36 mBq g^{-1} by HR-ICP-MS, respectively.

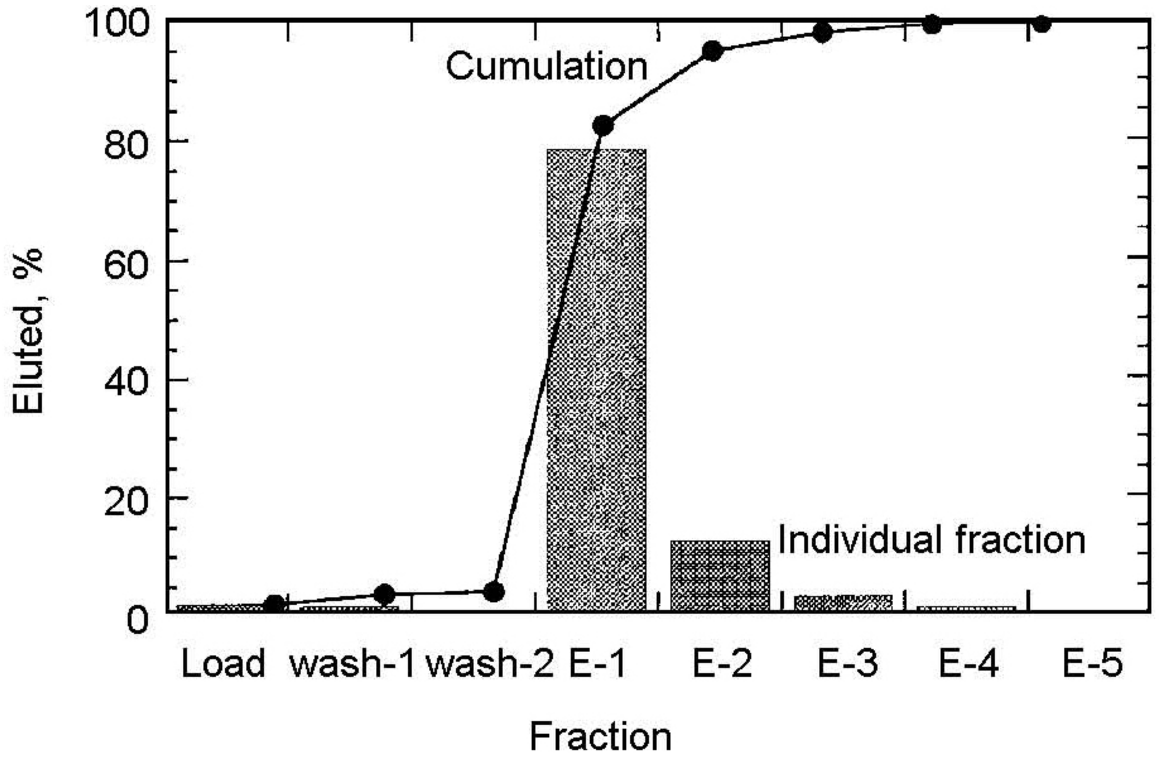

Fig. 3.1 Elusion behavior of Pu with 3M Empore™ anion exchange resin disk. Disk: 3M Empore anion exchange-SR, 47 mmϕ. $^{239+240}$Pu: 200 mBq. Effluent: Load; 8M HNO_3-0.03M $NaNO_2$ 200ml, wash-1; 8M HNO_3 15ml (5ml×3), wash-2; 10M HCl 12ml (3ml×4), E-1～5; 1M HNO_3-0.03M ascorbic acid 15ml (3ml×5). Instrument: JEOL JMS-PLASMAX2 high resolution ICP-MS.

Table 3.1 Operating conditions of HR-ICP-MS (PLASMAX2).

RF power	1.2 kW
Plasma gas flow rate	14 L/min.
Auxiliary gas flow rate	0.3 L/min.
Nebulizer gas flow rate	1.0 L/min.
Mass analyzer	
Acceleration voltage	6.0 kV
Mass resolution	M/ΔM= 500
Data acquisition	
Mass range (m/z)	238 (^{238}U), 239 (^{239}Pu) 240 (^{240}Pu), 242 (^{242}Pu)
Dwell time	6000 ms/channel
Number of sweeps	10
Number of replicates	3
Ultrasonic nebulizer	
Solution uptake rate	1.2 mL/min.
Heater temperature	140 ℃
Condenser cooling temperatur	3 ℃

Table 3.2 Analytical results of Pu in IAEA-135 (Irish Sea sediment)

Run No.	Sample weight (g)	Recovery (%)	$^{239+240}$Pu cocn. (Bq/kg)	^{240}Pu/^{239}Pu atomic ratio	^{238}Pu cocn. (Bq/kg)	Method
1	1.12	83	190 ± 14[*1]	-	40 ± 3.4[*1]	alpha-ray spectrometry
2	1.16	70	200 ± 17[*1]	-	45 ± 4.2[*1]	
3	1.00	79	190 ± 15[*1]	-	43 ± 3.8[*1]	
4	0.503	n.d.[*2]	240 ± 19[*3]	0.255 ± 0.05	-	HR-ICP-MS
5	0.503	n.d.[*2]	220 ± 13[*3]	0.195 ± 0.05	-	
Mean $\pm 1\sigma$			210 ± 22		42 ± 2.7[*3]	
Reccomended value			213		43	
Literature value[*4]				0.211 ± 0.004		ICP-MS

[*1] Propagated counting statistics

[*2] Not determined

[*3] Standard deviation

[*4] Muramatsu et al., 1999.

Table 3.3 Analytical results of Pu in forest soil collected from Okuetsu plateau, Fukui, Japan.

Run No.	Sample weight (g)	$^{239+240}$Pu cocn.[*1] (Bq/kg)	Method
1	10.0	2.81 ± 0.23	HR-ICP-MS
2	10.1	2.52 ± 0.26	
3	10.1	2.64 ± 0.35	
Mean ±1σ		2.66 ± 0.14	
		2.83 ± 0.26[*2]	HR-ICP-MS

[*1] standard deviation (n=3)

[*2] The determined values (n=3) of $^{239+240}$Pu was obtained by convensional separation method coupled with HR-ICP-MS.

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CHAPTER 4

CHAPTER 4 : Determination of trace elements in squid organs by inductively coupled plasma mass spectrometry and neutron activation analysis.

4.1. Introduction

It is well known things that trace elements in seawater concentrate in specific marine organisms. In 1965, Folsom et al. reported that radionuclides such as ^{60}Co and ^{110m}Ag derived from atmospheric nuclear explosion tests were detected from marine organisms collected from Pacific Ocean (Folsom et al., 1965; 1970). There were simultaneously pointed out that concentration of above mentioned radionuclides were not agreement with the squids which is one of the migrant marine organism (Fukatsu et al., 1982, Imazawa et al., 1982).

Environmental radioactivity monitoring for seawater is one of the most important things due to location of the nuclear power station or nuclear reprocessing plant along with coastal sea area in Japan. However, concentration of radionuclides in seawater is not easily to determine without any chemical separation and concentration processes, a large volume (more than 100 L) of seawater are required for the determination of radionuclides. Instead of any chemical pre-concentration, marine organisms may be useful to determine extremely low level radionuclides presented in seawater.

In Japanese people, squids is the most popular fish and shellfish (fishery : about an half million tons every year). Surume squid (*Todarodes pacificus*) is most popular squids in Japan, which occupies about a half of fishery. The habitat sea area of Surume squid is throughout inshore sea area around Japan islands. In addition, life span of Surume squid is about a year that is born generally in winter season at East China Sea moves northward along the coast of the Japan islands in the Pacific Ocean and the Sea of Japan. Consequently, Surume squid may be able to applied environmental radioactivity monitoring as a biological indicator for a wide range of sea area. However radionuclides detected now in the neighboring seawater are limited such as long-lived radionuclides released from nuclear explosion tests mainly conducted in northern hemisphere, controlled-releasing from nuclear facilities. Before radioactivity analysis for Surume squid, an aspect of trace elements in seawater concentrated into Surume squid are necessary to investigation subject from viewpoint of the field of analytical chemistry.

There is main purpose of this study that methods for heavy metal elements present in internal organs determined by ICP-MS after appropriate pre-treatment and get the knowledge relation to the concentration mechanism by compared with the average concentration of trace element in seawater. Stable elements are selected for 13 elements, according to environmental radioactivity, such as ^{60}Co, ^{110m}Ag and ^{137}Cs.

4.2. Experimental

With the aim for an analytical validation of the ICP-MS method by neutron activation analysis, Surume squid collected from Japanese inshore during 1981 to 1996 (Table 4.1). Internal organs obtained from the Surume squid samples were dried at 105 ˚C for overnight and ashed for 48 hours at 450 ˚C. Ashed samples were pulverized and homogenized. On the other hand, squids were collected in 1996 for the purpose of concentration factor. The squid was cautiously divided into edible, born, craw, liver and others by using Teflon scissors and forceps. These samples were also ashed. Determination of nine elements (V, Mn, Fe, Co, Cu, Zn, Rb, Ag and Cd) in the ash and standard reference material, SRM 1572 citrus leaves, SRM 1577b bovine liver and NIES No. 9 sargasso, was carried out by instrumental non destructive neutron activation analysis (INAA) at the TRIGA Mark II reactor of Rikkyo University with the flux of 5×10^{11} n cm^{-2} s^{-1}. The standards were prepared by impregnating an aliquot of certified reference material, SPEX standard solution (SPEX CertiPrep, Inc.), into filter paper.

For ICP-MS, an aliquot of 0.5 g of ash sample and SRMs were dissolved into 7M HNO_3 and then evaporated to dryness. The residue was completely dissolved into 1M HNO_3 and diluted with pure water. Concentration of 13 elements (V, Mn, Fe, Co, Ni, Cu, Zn, Rb, Ag, Cd, Cs, Ba and Pb) was determined after an addition of internal standard solution to avoid any instrumental drift (Table 4.2 & Table 4.3).

4.3. Results and discussion

4.3.1. Elemental losses following ashing process

Elemental losses at ashing process had been studied for 23 and 26 elements used standard reference materials such as orchard leaves (Nonaka et al., 1981; 1985). In those elements, transition metal and alkali earth metal elements such as V, Mn, Fe, Co, Zn, Cd and Ba were not caused elemental losses used by any shapes of crucibles at 800 ˚C. Because mentioned above, it may be caused no elemental losses at 450 ˚C for those of elements.

Rubidium may cause approximately 10 % of elemental loss at 450 ˚C by using quartz crucible due to silicate constituent (Nonaka et al., 1981; 1985). This is because alkali earth metal element may react with quartz crucible, and then transition into crucible. While the trend of elemental losses applied by platinum plate or ceramic dish used at 600 ˚C were Cs > Rb > K > Na, lower than 5% of losses.

Ashing procedure applied in this study, it may be caused no elemental losses for almost elements even Cs and Rb.

4.4. Comparison ICP-MS with INAA method

To estimate an analytical validation of the ICP-MS method by INAA, eight squid samples collected from Japanese inshore during 1981 to 1996 were analyzed to determine 13 elements in internal organs. In these 13 elements, nine elements, V, Mn, Fe, Co, Cu, Zn, Rb, Ag and Cd were also determined by INAA, and then compared ICP-MS results with INAA (Fig. 4.1). In Table 4.4 summarized an analytical result of nine elements in squid internal organs by ICP-MS and INAA. It is difficult to make a comparison ICP-MS with INAA by using different eight squid samples due to inhomogeneous elemental concentrations. Therefore the ratio of analytical results (ICP/INAA) was applied for more discussions. Determined value of Fe was ranging from 40 to 100 μg g^{-1} with a ratio of 1.04 ± 0.07 (n=8, average ratio and one sigma standard deviation). Also V was ranging from 0.05 to 0.5 μg g^{-1} with a ratio of 1.12 ± 0.38. The other elements were ranging from 0.94 to 150 μg g^{-1} with a ratio of 0.94 to 1.13. Consequently, determined values by ICP-MS were agreed well with INAA, and then it was not affected by polyatomic ions peculiar to the spectrometer with ICP ion source. Analytical results of the other four elements (Ni, Cs, Ba and Pb) were also confirmed by ICP atomic emission spectrometry, atomic absorption spectrometry and flame photometry techniques.

4.5. Concentration of metal elements in squid organs

4.5.1. Distribution of metal elements in squid and its concentration factors

According to the Standard Tables of Food Composition in Japan (2000), Surume squid constituent is 75 to 80 % of moisture, about 20 % of crude proteins, about 1.5 % of crude adipose. Ash content including internal organs is about 2 % by weight. Analytical results of 13 elements in each part in Surume squid collected in 1996 were summarized in Table 4.5, together with concentration factor calculated from average concentration in seawater. It was difficult to cut and divide exactly due to classification of Surume squid in invertebrate on systematics. However, liver which is the largest internal organ in Surume squid seems to be the most concentrate trace elements from seawater. Chemical behaviors in seawater relate to the nutrient elements such as V, Fe, Ni, Cu, Zn, Ag, Cd and Ba were specific for concentrated in liver with a concentration factor of 10^4 to 10^6. Therefore Surume squid inhabit in Japanese inshore may be useful as a living indicator for marine pollution or environmental radioactivity monitoring. Actually, large quantities of radioactive materials as radioactive fallout due to Chernobyl accident occurred in 1986 are introduced into Japan and neighboring countries (including land and sea area) via the prevailing westerlies. For several years after the accident, radionuclides such as ^{60}Co and ^{110m}Ag derived from the accident had been detected from squid liver collected from Japanese inshore sea area. While the element related to scavenged element such as Mn, Co and Pb were also concentrated into each parts with a concentration factors of 10^3 to 10^6. The tendency of concentration for conservative element such as Rb and Cs were not clear, with a factor of just 10^2.

4.5.2. Distribution of metal elements in squid organs

In the part of five (edible, born, craw, liver and others), heavy metal element such as Mn, Fe, Co, Cu, Ag and Pb were distinguishing concentrate into liver as shown in Fig. 4.2. Compared to fishes and Mollusca, Cu and Zn were also distinguishing concentrate into liver. Particularly, cupper with a large concentration factor is due to electively combined by complexing with respiratory pigment of hemocyanin. For same element with different concentration factor in the part such as V, Mn, Fe, Co, Cu, Ag, Cd and Pb seems to be concentrating and distinguish associated with metabolism. The important things in environmental radioactivity monitoring are a) rapid distinction of radionuclide at emergency, b) concentration and distinction of radionuclide for long-term monitoring. At the time of accident in nuclear facilities with a release of radionuclide such as ^{60}Co and ^{137}Cs, short-term evaluation used by Surume squid liver may useful to be medium.

4.6. Conclusions

Trace elements concerning with radioactive contamination such as V, Mn, Fe, Co, Ni, Cu, Zn, Rb, Ag, Cd, Cs, Ba and Pb in squid organs were determined by ICP-MS after ashing and acid decomposition. An ICP-MS is a powerful tool for trace element determination with a simultaneous measurement. Analytical validation of ICP-MS results were confirmed by INAA for nine elements (V, Mn, Fe, Co, Cu, Zn, Ag, Cd and Cs).

This paper describes the usefulness of ICP-MS for trace elements in squid organs, and an application to determine the concentration factors. Particularly, Co, Zn, Ag and Cd were concentrated into liver with concentration factors of 10^5 to 10^6. The analysis of trace elements in squid organs was found to be a useful method for studying heavy metal or radioactive contamination in a marine environment.

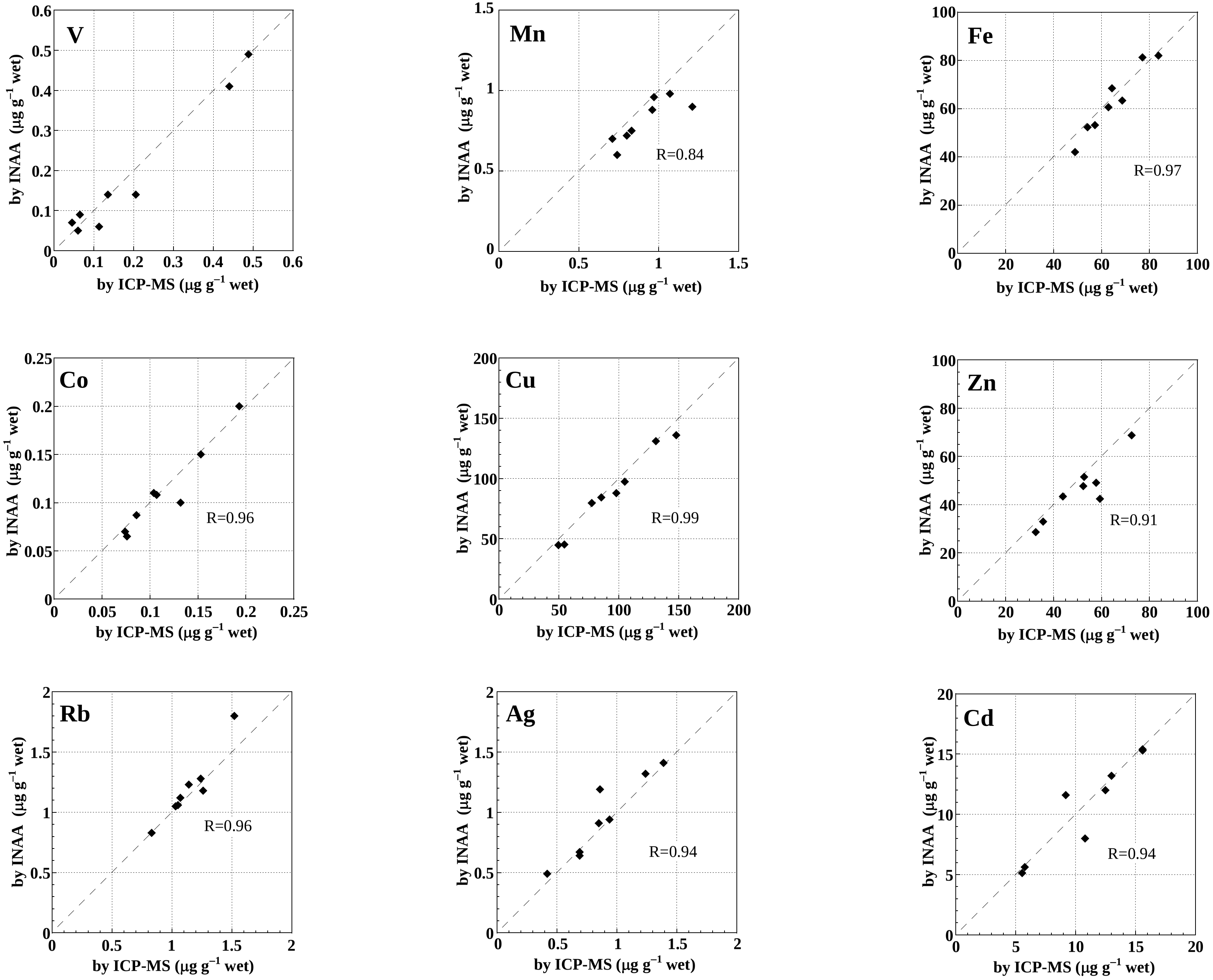

Fig. 4.1 Relationship of analytical results between ICP-MS and INAA.

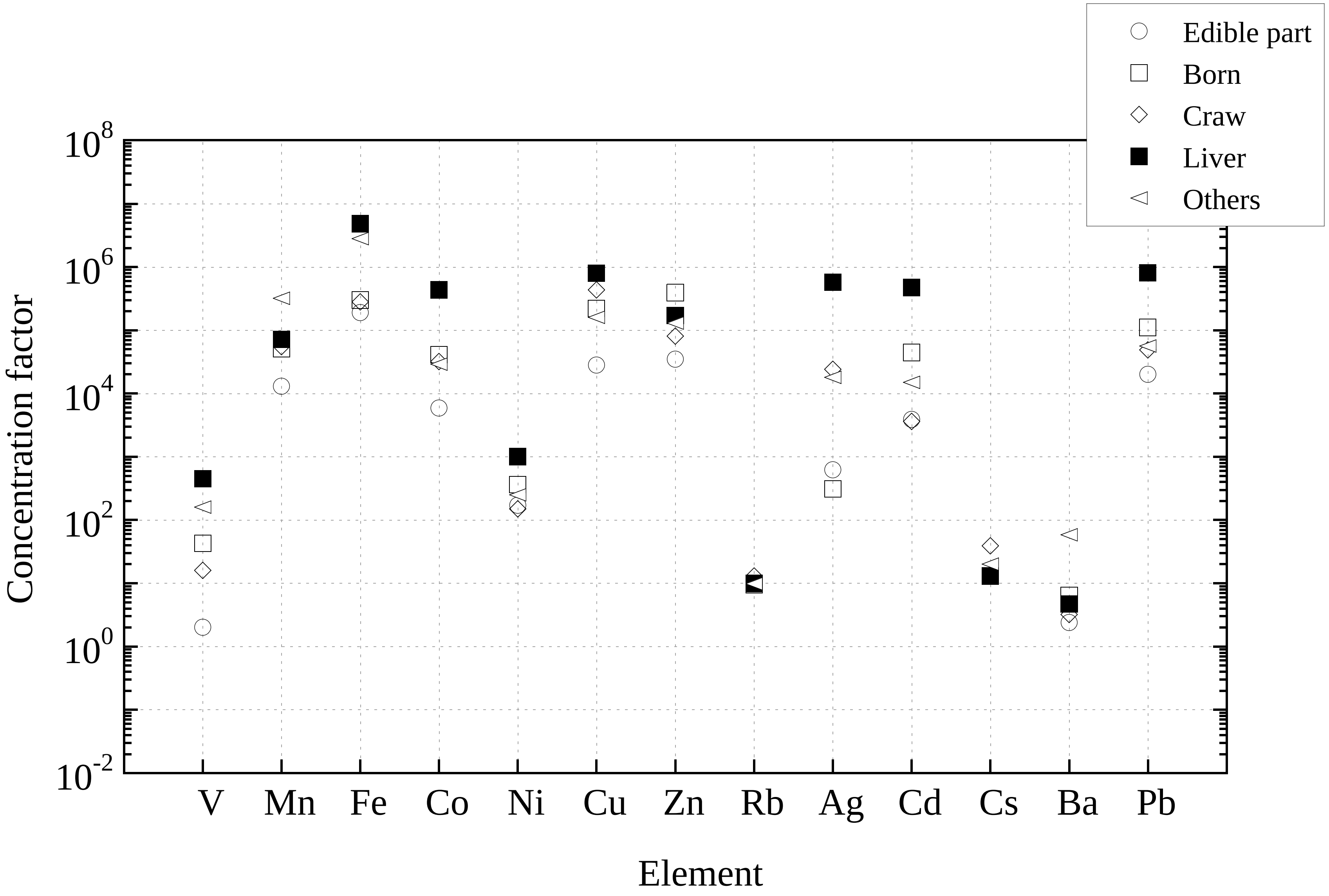

Fig. 4.2 Concentration factor of the elements in part of squid sample.

Table 4.1 Sampling year and region of Surume squid.

Sampling Year	Sampling region and month			
	Hokkaido	Miyagi	Chiba	Niigata
1981				⑥ （Jul.）
1986	① （Nov.）		④ （Jun.）	⑦ （Jun.）
1988	② （Nov.）	③ （Sep.）	⑤ （Jul.）	⑧ （Jun.）
1996			⑨ （Jun.）	

Table 4.2 Operating conditions of ICP-MS

RF power	1.25 kW
Frequency	27.12 MHz
Ar gas flow rate	15 L min^{-1}
Auxillary Ar gas flow rate	1.15 L min^{-1}
Carrier Ar gas flow rate	0.45 L min^{-1}
Nebulizer type	Coaxaial
Uptake rate	0.15 mL min^{-1}
Splay chamber tempearture	0 ℃

Table 4.3 Mass number and integration time of element using ICP-MS measurements.

Element	*m/z*	Internal standard	*m/z*	Integration time (ms)
V	51	Sc	45	120
Mn	55	Sc	45	120
Fe	57	Sc	45	120
Co	59	Sc	45	120
Ni	60	Sc	45	120
Cu	63	Sc	45	120
Zn	66	Sc	45	120
Rb	85	Y	89	120
Ag	107	Rh	103	80
Cd	111	In	115	80
Cs	133	In	115	80
Ba	137	In	115	50
Pb	208	Tb	159	50

Table 4.4 Analytical results of nine elements in squid organs by ICP-MS and INAA.

Element	Sample No.	ICP-MS	INAA	ICP/INAA	Average ratio	**Element**	Sample No.	ICP-MS	INAA	ICP/INAA	Average ratio	**Element**	Sample No.	ICP-MS	INAA	ICP/INAA	Average ratio
V	①	0.44	0.41	1.07	1.12 ± 0.38	**Co**	①	0.15	0.15	1.02	1.06 ± 0.12	**Rb**	①	1.26	1.18	1.07	0.97 ± 0.06
	②	0.07	0.09	0.72			②	0.10	0.11	0.95			②	1.03	1.05	0.98	
	③	0.49	0.49	1.00			③	0.19	0.20	0.97			③	1.52	1.80	0.84	
	④	0.11	0.06	1.88			④	0.07	0.07	1.06			④	0.83	0.83	1.00	
	⑤	0.21	0.14	1.46			⑤	0.13	0.10	1.32			⑤	1.24	1.28	0.97	
	⑥	0.05	0.07	0.64			⑥	0.08	0.07	1.17			⑥	1.05	1.06	0.99	
	⑦	0.14	0.14	0.96			⑦	0.11	0.11	0.99			⑦	1.14	1.23	0.93	
	⑧	0.06	0.05	1.20			⑧	0.09	0.09	0.99			⑧	1.07	1.12	0.96	
Mn	①	0.96	0.88	1.09	1.13 ± 0.10	**Cu**	①	85.4	84.3	1.01	1.13 ± 0.18	**Ag**	①	0.85	0.91	0.93	0.94 ± 0.10
	②	0.71	0.70	1.01			②	54.6	45.3	1.21			②	0.69	0.67	1.03	
	③	1.07	0.98	1.09			③	131	131	1.00			③	0.86	1.19	0.72	
	④	0.74	0.60	1.23			④	49.6	44.8	1.11			④	0.69	0.64	1.08	
	⑤	1.21	0.90	1.34			⑤	168	106	1.58			⑤	0.42	0.49	0.86	
	⑥	0.80	0.72	1.11			⑥	77.5	79.7	0.97			⑥	0.94	0.94	1.00	
	⑦	0.97	0.96	1.01			⑦	105	97.4	1.08			⑦	1.39	1.41	0.99	
	⑧	0.83	0.75	1.11			⑧	97.9	87.9	1.11			⑧	1.24	1.32	0.94	
Fe	①	83.8	82.0	1.02	1.04 ± 0.07	**Zn**	①	72.6	68.8	1.06	1.12 ± 0.12	**Cd**	①	15.6	15.3	1.02	1.04 ± 0.14
	②	68.7	63.4	1.08			②	57.8	49.1	1.18			②	5.77	5.63	1.02	
	③	77.1	81.3	0.95			③	43.9	43.4	1.01			③	13.0	13.2	0.98	
	④	57.3	53.2	1.08			④	32.6	28.6	1.14			④	5.55	5.13	1.08	
	⑤	49.0	42.0	1.17			⑤	59.4	42.4	1.40			⑤	10.8	8.00	1.35	
	⑥	54.2	52.3	1.04			⑥	35.7	33.0	1.08			⑥	9.19	11.6	0.79	
	⑦	62.9	60.6	1.04			⑦	52.8	51.5	1.03			⑦	12.5	12.0	1.04	
	⑧	64.4	68.5	0.94			⑧	52.4	47.7	1.10			⑧	15.6	15.4	1.01	

Table 4.5 Concentrations of elements in parts of squid organs.

Site	Element and its concentration（μg g^{-1}）												
	V	Mn	Fe	Co	Ni	Cu	Zn	Rb	Ag	Cd	Cs	Ba	Pb
Edible part	0.0040	0.22	6.3	0.007	0.082	3.6	14	1.3	0.0020	0.33	0.0040	0.039	0.054
Born	0.088	0.84	9.9	0.048	0.17	28	152	1.2	0.0010	3.8	0.0040	0.11	0.29
Craw	0.033	0.90	9.3	0.038	0.069	55	31	1.6	0.077	0.30	0.012	0.053	0.13
Liver	0.92	1.2	161	0.51	0.47	101	68	1.2	1.9	39	0.0040	0.078	2.2
Others	0.32	5.2	92	0.034	0.12	21	50	1.2	0.058	1.3	0.0060	0.97	0.15
Sea water*1（ng g^{-1}）	2.0	0.016	0.034	0.0012	0.47	0.13	0.39	124	0.0032	0.084	0.31	17	0.0027

*1The mean concentrations of elements in sea water（Nozaki, 1992）.

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CHAPTER 5

CHAPTER 5 : Plutonium concentration and $^{240}Pu/^{239}Pu$ atomic ratio in liver from squid collected in the coastal sea areas of Japan.

5.1. Introduction

Artificial radionuclides ^{110m}Ag and ^{60}Co appear in marine organisms as a result of metabolism during a growth processes (Folsom et al., 1965). This finding is useful for evaluating toxic metal elements and radionuclide pollution in marine environment (Folsom et al., 1970). Seawater is the most significant medium to migration processes in the marine environment. The man-made long-lived radionuclides, such as ^{90}Sr, ^{137}Cs and Pu isotopes, are distributed world wide as a result of global fallout from atmospheric nuclear weapons tests. Regarding Pu isotopes, it was estimated that, since 1945, about 11 PBq of $^{239,240}Pu$ has been deposited on the oceans as global fallout from 543 atmospheric nuclear weapons tests (UNSCEAR 2000).

The main island of Japan (Honshu) is surrounded by the Pacific Ocean and the Sea of Japan, which are different in their current and open/close areas. About 400 to 600 thousand tons of squids were caught in each of the last five years, and the Surume squid (*Todarodes pacificus*) represents about half (or more) of the catch, and they are easily caught everywhere on the coast around Japan’s islands (Living information center, 2003). Since their life span is only a year and trace elements are remarkably concentrated in their organs, levels of trace elements in seawater can be monitored by measuring these elements in their organs (Abe and Honma, 1997). In contrast to flat fish, seaweed and benthos which inhabit in quite small area, the squid moves long distance and pathways depending mainly on seawater temperature (Abe and Honma, 1997). Therefore, the squid may be useful for monitor of larger sea area. In our country, the Surume squid seems to be suitable for biological indicator for Pu in seawater, as shown from its habitats in Fig. 5.1. However, the habitable sea area is not uniform since Surume squid is migrant marine organism depending on sea temperature and ocean current.

We proposed that the Surume squid was a useful biological indicator for evaluating oceanic environments for pollution and radioactivity (Oikawa et al., 2003). Recently, Pu isotopes were measured in organs of squid collected over the last 20 years from the coast of Ishikawa, Japan sea side, and the coast of Chiba, Pacific Ocean side (Kishimoto et al., 2002). However, this investigation was carried out using squid samples cached in broadly sea area at the different time. Surume squid samples landing in a nationwide at the same time are indispensable to get expand data concerning oceanic environments for pollution and radioactivity.

In this paper, a detailed work is reported on the radioanalytical and mass spectrometric analysis (by a sector-field high resolution ICP-MS) of Pu concentration in Surume squid liver collected from the coastal sea areas of Japan in 2002. Emphasis is put on the ^{240}Pu/^{239}Pu atomic ratio in Surume squid liver. In addition to Pu, levels of 13 elements (V, Mn, Fe, Co, Cu, Zn, Rb, Sr, Ag, Cd, Cs, Th and U) were measured for comparison. These data are discussed with emphasis on the potential use of Pu signatures in squid liver to trace the radioactive and marine contamination of Pu.

5.2. Materials and methods

5.2.1. Sampling and pretreatment method

Surume squid samples were obtained from nine landing ports in Japanese inshore during fishery season from September to December 2002 as shown in Fig. 5.2, along with the location of nuclear power stations in/around our country. Surume squid that were born in winter season at East China Sea moves northward along the coast of the Japan islands in the Pacific Ocean and the Sea of Japan. Other groups born in summer or autumn around Japan islands also move northward in the Sea of Japan. An egg-laying area and season may be overlapped with each group. Thus, Surume squid samples landing during the autumn to winter season are ones which were born mainly at around East China Sea in winter season (Abe and

Honma, 1997). Refrigerated Surume squid samples were defrosted at room temperature and their livers were removed using polytetrafluoroethylene coating scissors and forceps. For plutonium analysis, raw livers were dried overnight at 105 °C and carefully ashed at 450 °C for 48 hours. Ashed samples were mixed well, sealed in polypropylene bags and stored in desiccators.

5.2.2. Measurements of Pu isotopes by sector field ICP-MS

Aliquots of 50 g ash were dissolved in 8M nitric acid with a few drops of hydrogen peroxide, with the addition of known amounts of ^{242}Pu standard solution as a tracer (about 0.2 ng per sample). The ^{242}Pu standard solution was Standard Reference Material 4334G Plutonium-242 radioactivity standard, provided from National Institute of Standards and Technology. The sample solution was evaporated to dryness and dissolved in 8M nitric acid. Plutonium was separated by anion exchange resin column (Dowex 1-X8, 100-200 mesh, 5.5 ml volume). Plutonium adsorbed on the resin was successively washed by 8M nitric acid and 10M hydrochloric acid to remove interference elements such as Fe, Th and U. After washing, plutonium was eluted with 5% NH_4I-10M HCl solution. Finally, eluate was evaporated to dryness and then, to remove U completely, residue was dissolved in 4M acetic acid, and then passed through anion exchange resin column (Dowex 1-X8, 100-200 mesh, 2 ml volume). The eluate was evaporating to dryness and was dissolved into about 10 ml of 1M nitric acid (Kishimoto et al., 2002).

A sector field high resolution ICP-MS, Finnigan Element 2, Thermo Electron, Inc., Germany, working in the single collector, was used to measure Pu. The instrument was optimized for Pu measurement, also tuned for high sensitivity and low background.

Since a major problem in determining Pu isotopes by ICP-MS is the interference of $^{238}U^{1}H^{+}$ ion on ^{239}Pu peak area (Yamamoto et al., 2002), additional purification was performed using anion exchange resin from acetic acid solution before measuring ^{239}Pu and

^{240}Pu. Since resolution (M/ΔM) more than 40,000 is required for accurate measurement, it is not possible to separate interference from ^{239}Pu peak at the resolution achievable with our instrument. Therefore, we assessed the influence of U on ^{239}Pu measurement. The increase in the *m*/*z* 239 mass peak was measured using a uranium standard solution. If the U content in the final solution was assumed to be 0.1 ng ml^{-1}, the expected influence was approximately 5 fg ml^{-1} for ^{239}Pu, which corresponds to the same order as the detection limit.

Through the measurements, the instrument was operated in the electric scanning (e-Scan) mode by varying the accelerating voltage. Sample solution was introduced into the instrument at 0.3 ml min^{-1} using a pneumatic nebulizer. Measurements were carried out in the low resolution mode (M/ΔM = 300).

For Pu isotopic measurements, ion signals were collected at *m*/*z* 239, 240 and 242 using fixed magnetic field. The magnetic field can be held constant very accurately by means of current control of the magnet, measurement of the peak-centered voltages provides a very accurate method for measuring differences in masses. Also, acceleration voltages can be scanned much faster than magnetic fields. The drawback to this method of operation is that a systematic error for the measurement of peak intensities is introduced because instrumental sensitivity also is a function of acceleration voltage (Montaser, 1998). Therefore, measuring parameters was configured to improve mainly statistical error, considering final sample volume. Total measurement time was about 20 minutes for each sample under following conditions; sample time of 0.1 s, 100 peaks per 10% mass window and 100 passes scans. The optimized operation conditions are summarized in Table 6.1.

Concentrations of ^{239}Pu and ^{240}Pu were calculated by isotope dilution method from the results of isotopic ratios relative to the ^{242}Pu spike. To check the accuracy of determination, certified reference material IAEA-135 (Irish Sea sediment) with a known ^{239,240}Pu concentration and ^{240}Pu/^{239}Pu atomic composition was used (Muramatsu et al., 1999 ; Miura, 2001). In case that any U is not contained in the sample, detection limit was about 1 fg ml^{-1} at final solution. Using a 50 g ash sample, detection limits as g-ash unit are achieved to be 0.5 μBq g^{-1} for ^{239}Pu and 2 μBq g^{-1} for ^{240}Pu.

5.2.3. Measurement of major metal elements

Aliquots of 5g raw liver sample were dissolved for measuring stable elements in concentrated nitric acid with a few drops of hydrogen peroxide. The solution was evaporated to dryness and the residue was dissolved in 1 M ultra pure nitric acid. A quadrupole ICP-MS, Agilent 7500ce was used for 13 elements, except for Fe. An ICP-AES, Seiko SPS7800 was used for Fe measurement. An internal standard element was added to the sample solution to correct signal drift. Standard solution was XSTC-332 or XSTC-662 multi elements standard solution, and PL series single element standard solution provided from SPEX CertiPrep, Inc. The 13 elements were determined by interpolation method using a working curve with internal standard correction mode. For the purpose of internal standard correction, it was changed every target element as shown in Table 5.2. The internal standard correction techniques are one of the practicable and useful methods for the determination of trace elements by ICP instruments (Montaser, 1998).

5.3. Results and discussion

5.3.1. Concentrations of Pu isotopes and 13 elements in Surume squid liver

The liver of mature Surume squid is its largest internal organ and corresponds to about 10% of the squid's body weight. Plutonium isotopes were measured in liver samples, and the concentrations of the individual ^{239}Pu and ^{240}Pu isotopes and sum (^{239,240}Pu) of these isotopes were found in the range from 1.5 to 28, 1.1 to 24 and 2.5 to 53 mBq kg^{-1} raw liver (wet weight), respectively (Table 5.3). The concentrations of ^{239,240}Pu in the squid liver show a large variation. This seems due to the difference of the squid samples themselves rather than the difference of ^{239,240}Pu concentrations in seawater every landing port. The ^{239,240}Pu levels in liver at Pacific Ocean and Sea of Japan sides are about 10^3 times higher than typical levels (^{239,240}Pu; about 15 mBq m^{-3}) for seawater found in about 200 m depth of the sea area (Yamada et al., 1996 ; Hirose et al, 1999 ; Livingston et al., 2001). While the mechanism is unknown, Surume squid concentrates Pu in their liver from seawater during growth. As a result, it is a useful organism for evaluating ^{239,240}Pu levels of larger sea area. Compared with the other marine products such as mussels, seaweeds and benthos, which habit in quite small coastal area, the Surume squid seems to surpass these marine products with regard to its relatively high concentration of ^{239,240}Pu within a year (Hirose and Haraguchi, 1990). In addition, in a brief life of a year Surume squid moves northward between nuclear power stations as shown in Fig. 5.2. Therefore, Surume squid is a useful for ^{239,240}Pu monitoring.

To know the relationship between Pu and trace elements, a comparison of trace elements found in squid liver and seawater is plotted as a logarithmic function together with the concentration factors (Fig. 5.3). The concentration factor (*CF*) in squid liver for each element compared to its mean seawater concentration was calculated as follows:

$$CF = \frac{C_{Liver}}{C_{SW}}$$

where C_{Liver} is elemental contents of the Surume squid liver (μmol kg^{-1}, raw liver, wet weight) and C_{SW} mean seawater concentrations of each element. The concentrations of trace elements in seawater vary with region, depth and other environmental factors. It is difficult to evaluate the C_{SW} mean seawater concentrations of each element every sampling area because data on these elements with depth profiles are not available. Therefore, the C_{SW} mean seawater concentrations of each element were represented for convenience by data from the Pacific Ocean (μmol kg^{-1}) estimated by Nozaki (1992).

The *CFs* found for Pu and the other 13 elements ranged from 10^0 to 10^7, although the content of each element varied within a factor of 1.2 to 2.4. Alkali metal and alkali earth metal elements, such as Rb, Sr and Cs, had *CFs* of 10^0 to 10^2 and were not generally concentrated in liver. Also U was barely concentrated in liver. On the other hand, transition metal elements, Mn, Fe, Co, Cu, Zn, Ag and Cd had high *CF* values and were remarkably concentrated in liver. The *CF* for Pu, which are nearly same order as the *CFs* for V and Th, were found in the range from 10^2 to 10^4. Based on the chemical behavior of dissolved trace elements in seawater, the elements can be divided into three categories. These categories are (1) conservative elements (V, Rb, Sr, Cs and U), (2) nutrient elements (Fe, Cu and Zn) and (3) scavenged elements (Mn, Fe, Co, Cu, Ag, Cd and Th). The scavenged elements were selectively concentrated in Surume squid liver. Since Pu is well known to be particle reactive nuclides and is good tracer for the study of particle scavenging process, it was expected that Pu might be classified into scavenged element groups. However, as can be seen from the *CF* values for Pu, Pu had an intermediate *CFs* between conservative and scavenged elements. This difference can not be explained at present. One probable reason of this may be due to the following fact. Surume squid is an aggressive carnivorous species, and it feeds mainly on zooplankton species. The concentrations of major metals in zooplankton species are similar to those in squid liver. Therefore, most of metal elements concentrated in squid liver are derived from seawater via zooplankton species (Masuzawa et al., 1988) and fixed in liver tissue by proteins such as ferritin and metallothioneins (Durand et al., 1999, 2002). Probably, the same mechanism serves in case of Pu.

5.3.2. ^{240}Pu/^{239}Pu atomic ratio in Surume squid liver

As shown in Table 3, ^{240}Pu/^{239}Pu atomic ratios in squid liver ranged from 0.177 to 0.237, which are slightly higher than 0.178±0.014 for global fallout (Krey et al., 1976), except for Wakayama. The ^{240}Pu/^{239}Pu ratio observed in Wakayama seems different from those observed in another 8 sampling ports. This may be due to the difference of egg-lying and born area between Surume squid landing in Wakayama and in another 8 landing ports. The ^{240}Pu/^{239}Pu ratios in liver from Surume squid collected from the Sea of Japan side appear to be a little higher than those from the Pacific Ocean side. Slightly higher ^{240}Pu/^{239}Pu values than in global fallout have been reported for sea sediments, seawater and marine products (Yamada et al., 1996 ; Buesseler, 1997 ; Kim et al., 2003 ; Kim et al., 2004 ; Zheng et al., 2004 ; Zheng et al., 2006).

The major origin of Pu isotopes in Surume squid liver is presumably due to global fallout from nuclear explosion tests. If Pu isotopes detected in their liver is only due to the global fallout, the ^{240}Pu/^{239}Pu atomic ratios are expected to have nearly the same values as those (0.178±0.014) observed in land. There are three large ocean currents flowing around Japan. These currents are the Kuroshio and Tsushima Currents that flow from the south and the Oyashio Current that flows from the north. The Kuroshio Current is a warm water current suitable for Surume squid. The principal axis of Kuroshio Current depends on seawater temperature in the depth from 100 to 200 m. The Kuroshio Current advances northward at 2-3 knot in east of Taiwan, East China Sea, the coastal sea area at Pacific Ocean side. The Tsushima Current advances northward at 0.5-1 knot along the coastal sea area in the Sea of Japan (Rika Nenpyo, 2006). Most of the Surume squids are born in East China Sea and move northward riding Kuroshio Current and/or Tsushima Current as they grow.

Along the path of the Kuroshio and Tsushima Currents, nuclear power stations and nuclear facilities are located in neighboring countries such as Taiwan, China and Korea. However, as far as we know, radionuclides, especially Pu, have not been released, based on environmental monitoring conducted in the countries. The Bikini Atoll is another potential source of Pu. The Kuroshio and Tsushima Currents are confluent current of the North Pacific Current passing through Bikini Atoll, which was contaminated by strategic explosion tests conducted in the 1950s. Annual discharge of Pu (as ^{239,240}Pu) from Bikini Atoll (and Enewetak) is estimated to be approximately 0.2 TBq (Hamilton et al., 1996), and its ^{240}Pu/^{239}Pu atomic ratios are in the range of 0.30-0.36 (Buesseler, 1997 ; Muramatsu et al., 2001). Contaminated particles with Pu isotopes deposited on lagoons, surrounding slopes and basin sediments have formed a reservoir and source for the marine environment after they are solubilized and transported in water. It seems likely that close-in fallout Pu with high ^{240}Pu/^{239}Pu atomic ratios are continuously transported through the solubilization and water transport from the North Equatorial Current to Kuroshio and its branch, the Tsushima Current (Kim et al., 2004; Zheng et al., 2006).

Therefore, it seems reasonable to assume that the Pu found in Surume squid liver is a mixture of global fallout Pu and close-in fallout Pu with high ^{240}Pu/^{239}Pu atomic ratio around Bikini Atoll (Muramatsu et al., 2001 ; Yamamoto et al., 2002). An attempt was made using simple two sources mixing model (Krey et. al., 1976) to resolve global fallout and Bikini close-in fallout Pu in Surume squid liver. Plutonium atomic ratio ^{240}Pu/^{239}Pu derived from global fallout was regarded as 0.178±0.014. For the Bikini close-in fallout ^{240}Pu/^{239}Pu atomic ratio, the values of 0.30 - 0.36, as mentioned above, were used for convenience. In case that global fallout ^{240}Pu/^{239}Pu atomic ratio was 0.178, except for Wakayama, the Bikini close-in fallout Pu accounts for ca. 35% (mean, ranges from 30-41%) of the whole plutonium in Surume squid liver using identification calculation method applied by Zheng and Yamada (2004). Identification of Bikini close-in fallout Pu in Surume squid liver will allow model calculations for better understanding oceanic transport of close-in fallout Pu from Bikini Atoll.

5.4. Conclusions

Plutonium isotopes and 13 stable elements (V, Mn, Fe, Co, Cu, Zn, Rb, Sr, Ag, Cd, Cs, Th and U) were measured in liver of Surume squid collected in the coastal sea areas of Japan using ICP-MS/ICP-AES. Plutonium isotopes ^{239}Pu and ^{240}Pu were detected in liver samples. The concentrations of ^{239}Pu and ^{240}Pu and sum (^{239,240}Pu) ranged from 1.5 to 28, 1.1 to 24 and 2.5 to 53 mBq kg^{-1} raw liver, respectively. The Pu and the other 13 elements were concentrated with concentration factors (*CF*) ranging from 10^0 to 10^7. Alkali metal and alkali earth metal elements, such as Rb, Sr and Cs, were rarely concentrated with *CF* values of 10^0 to 10^2. Uranium was barely concentrated in liver. On the other hand, transition metal elements, Mn, Fe, Co, Cu, Zn, Ag and Cd were concentrated with high *CF* values. Plutonium, as well as V and Th, were concentrated in liver with *CFs* of 10^2 to 10^4. Scavenged elements (Mn, Fe, Co, Cu, Ag and Cd) were selectively concentrated in liver. Most metal elements concentrated in squid liver were probably derived from seawater via zooplankton species and fixed in tissues by proteins such as ferritin and metallothioneins. The same mechanism probably serves for Pu.

The ^{240}Pu/^{239}Pu atomic ratios 0.177 to 0.237 which were slightly higher than 0.178±0.014 for global fallout were found in squid liver. The ocean currents with their different source functions were an essential consideration in the interpretation of high ^{240}Pu/^{239}Pu atomic ratios. Three large ocean currents are flowing around Japan: Kuroshio and Tsushima Currents from south and Oyashio Current from north. Based on the habitat of the Surume squid, the Pu found in the liver is probably a mixture of global fallout Pu and close-in fallout Pu with high ^{240}Pu/^{239}Pu atomic ratio around Bikini Atoll. By assuming the two sources mixing model, Bikini close-in fallout Pu accounts for ca. 35% of the whole plutonium amounts. The results strongly indicate that the squid liver is very useful oceanic biological indicator for studying marine pollution of Pu and some other elements.

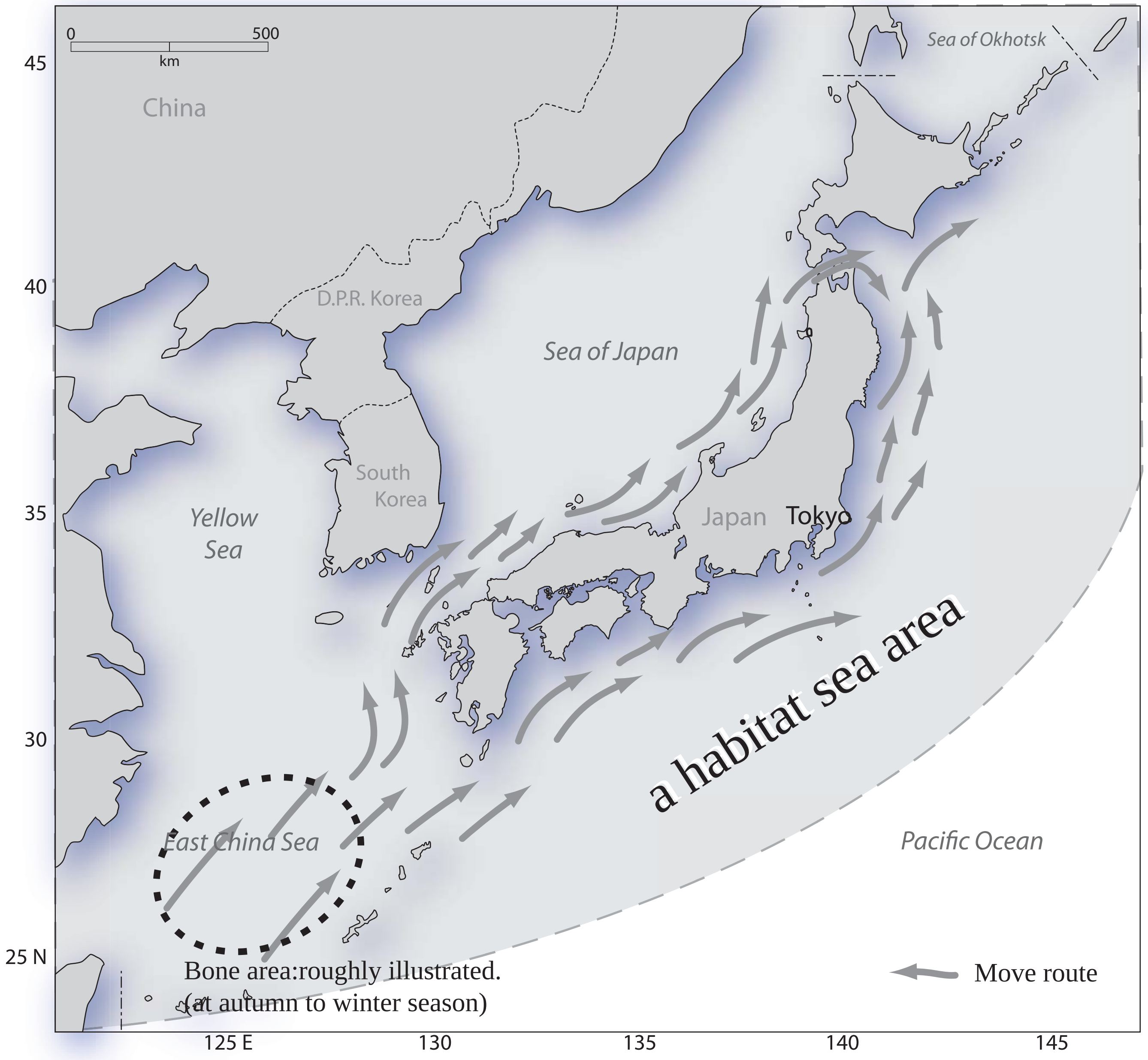

Fig. 5.1 Map of the location of born sea area of Surume squid with the schematic route to move northward.

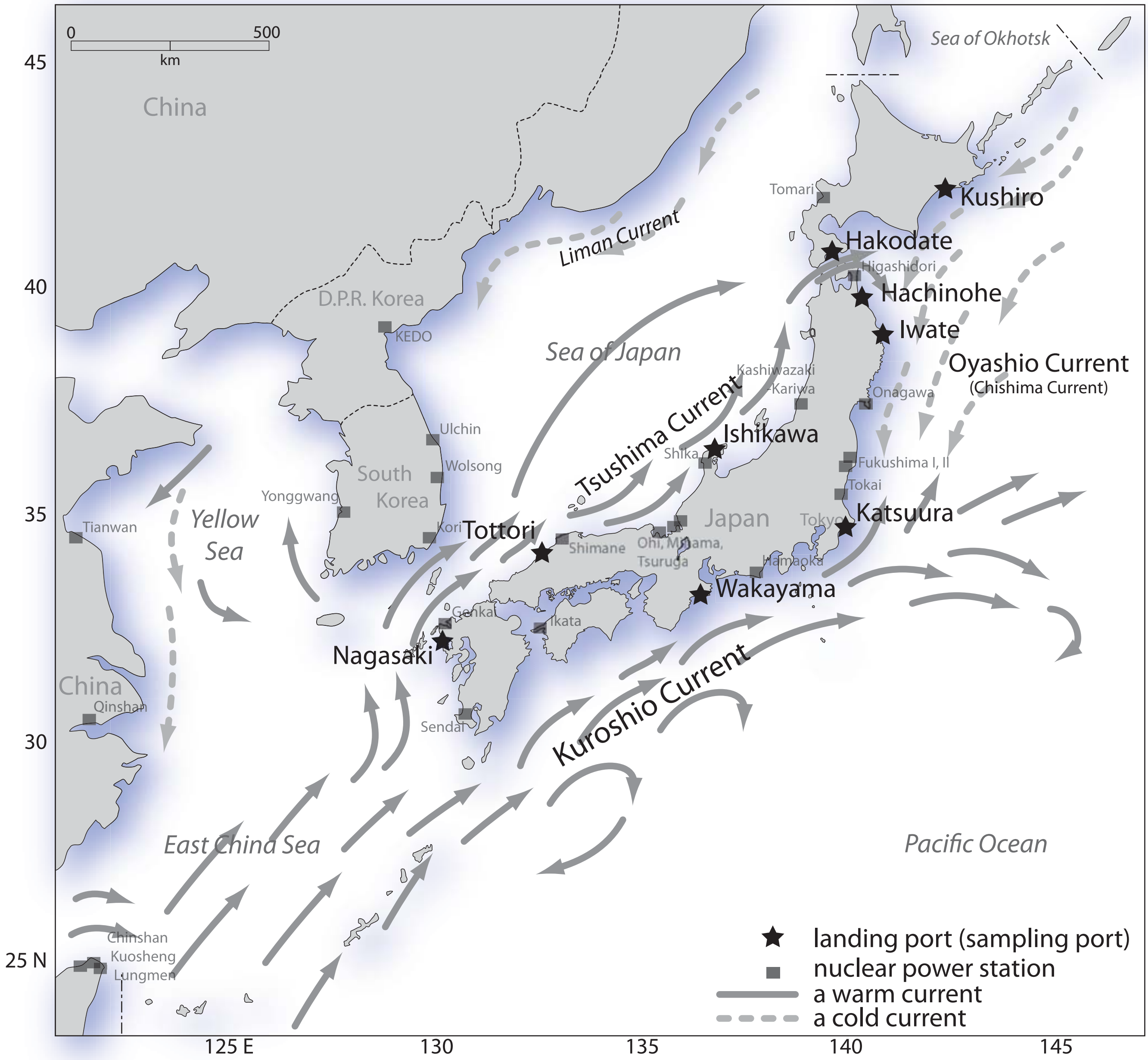

Fig. 5.2 Map of the location of Surume squid landing port (sampling port) in Japan and surrounding sea, Sea of Japan, East China Sea, Sea of Okhotsk and Pacific Ocean with the schemitic ocean current flowing patterns.

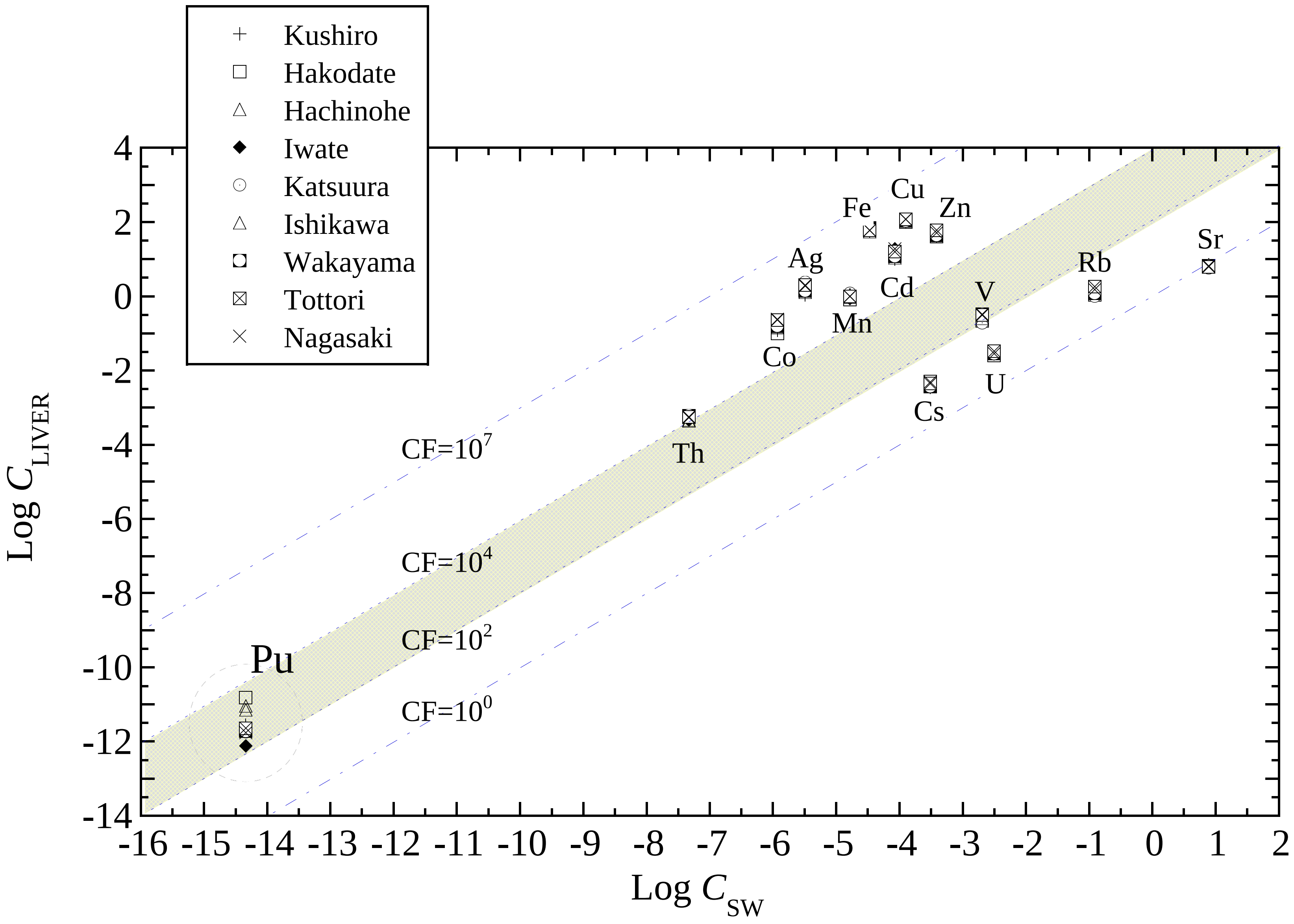

Fig. 5.3 Relationship between mean seawater concentration (C_{SW}) and elemental contents of the Surume squid liver (C_{Liver}) for plutonium and 13 elements in logarithmic scale.

Table 5.1 : Operational conditions of ELEMENT 2 for Pu isotope measurements.

Plasma gas flow rate (L min.$^{-1}$)	16
Auxiliary gas flow rate (L min.$^{-1}$)	0.9
Plasma operation power (W)	1200
Peristaltic pump uptake rate (mL min.$^{-1}$)	0.3
Resolution	Low resolution mode (M/ΔM = 300)
Scan mode	e-Scan
Accurate mass & range (a.m.u.)	^{238}U ; 238.0502 (238.011 - 238.090) ^{239}Pu ; 239.0517 (239.012 - 239.092) ^{240}Pu ; 240.0533 (240.013 - 240.093) ^{242}Pu ; 242.0582 (242.018 - 242.099)
Magnet mass (a.m.u.)	238.050
Settling time per peak (s)	^{238}U ; 0.300 ^{239}Pu, ^{240}Pu, ^{242}Pu ; 0.001
Sample time per point (s)	^{238}U ; 0.0250 ^{239}Pu, ^{240}Pu, ^{242}Pu ; 0.100
Samples per peak	100
Mass window (%)	10
Segment duration (s)	^{238}U ; 0.250 ^{239}Pu, ^{240}Pu, ^{242}Pu ; 1.000
Detection mode	Counting, Analogue
Number of passes	100
Replicates	3

Table 5.2 : Internal standard element for ICP-MS/ICP-AES measurment.

Target element	*m* /*z*	Internal standard	*m* /*z*	Note
V	51	Sc	45	
Mn	55			
Fe	(238.204 nm)	Y	(371.030 nm)	by ICP-AES
Co	59	Sc	45	
Cu	62			
Zn	66			
Rb	85	Y	89	
Sr	88			
Ag	107	Rh	103	
Cd	111	In	115	
Cs	133			
Th	232	Bi	209	
U	238			

Table 5.3 : Concentration and atomic ratio of Pu isotopes in Surume squid liver collected from the coastal sea areas in Japan, 2002.

Landing port		Pu concentration（mBq/kg-raw）[*1]		$^{240}Pu/^{239}Pu$ atomic ratio[*2]	RSD (%)
		^{239}Pu	^{240}Pu		
Pacific Ocean side	Kushiro	5.23 ± 0.07	4.09 ± 0.25	0.213 ± 0.011	5.2
	Hachinohe	16.7 ± 0.16	14.1 ± 0.39	0.230 ± 0.005	2.1
	Iwate	1.45 ± 0.07	1.07 ± 0.03	0.196 ± 0.015	7.4
	Katsuura	3.46 ± 0.10	2.56 ± 0.09	0.202 ± 0.002	1.0
	Wakayama	3.69 ± 0.06	2.37 ± 0.07	0.177 ± 0.007	4.1
Sea of Japan side	Hakodate	28.2 ± 0.7	24.2 ± 0.9	0.234 ± 0.006	2.4
	Ishikawa	13.0 ± 0.2	11.4 ± 0.1	0.237 ± 0.002	0.63
	Tottori	4.24 ± 0.32	3.56 ± 0.32	0.230 ± 0.003	1.2
	Nagasaki	3.22 ± 0.02	2.67 ± 0.15	0.226 ± 0.012	5.4

[*1] Calcurate from isotope dilution method by using known amount of ^{242}Pu spike.

[*2] Standard deviation at three replicates acquisition (total 300 passes scans).

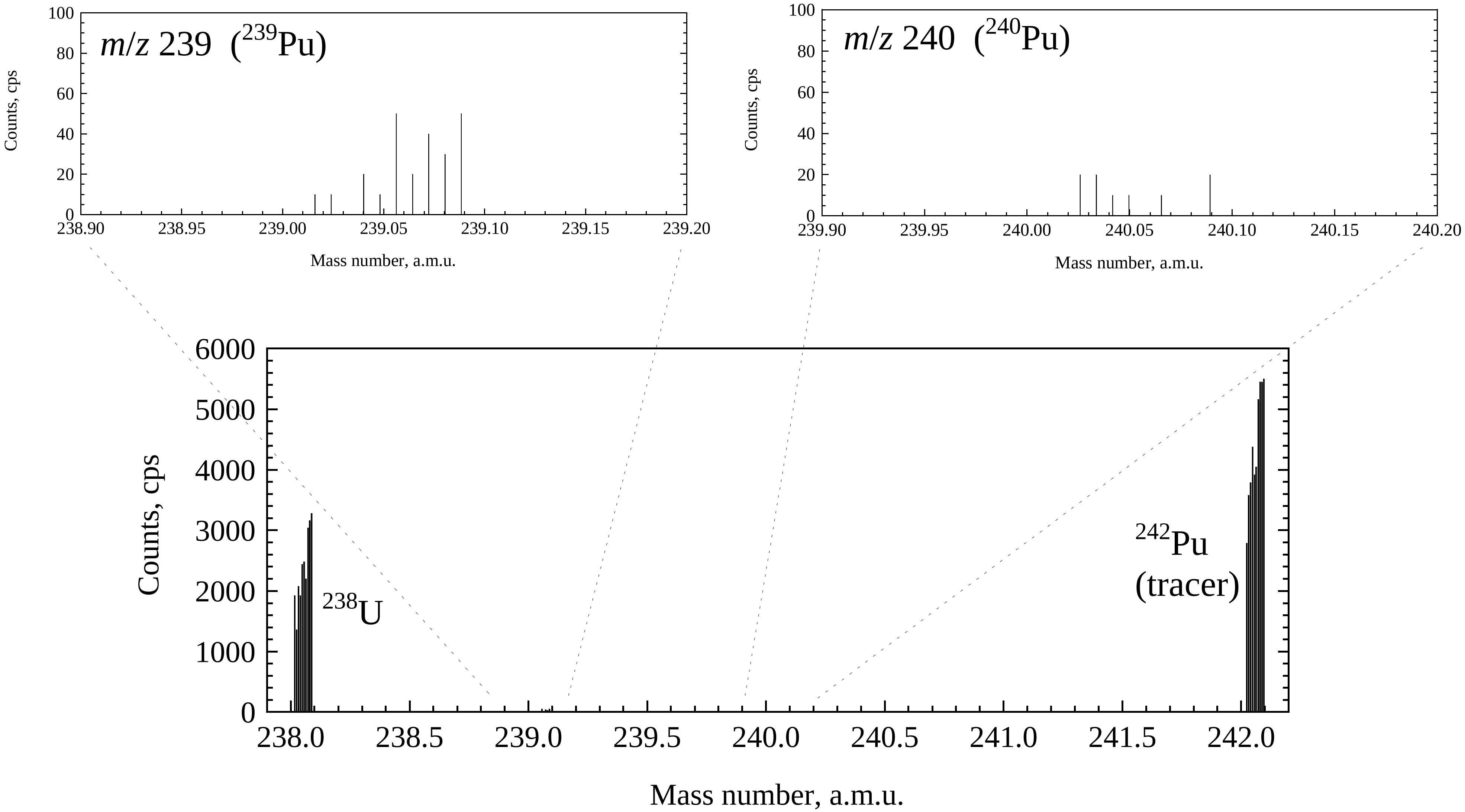

Fig. 5.A An example of plutonium mass spectra observed from Surume squid liver samples after chemical separation.

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CHAPTER 6

CHAPTER 6 : Conclusions.

Pretreatment of environmental samples especially ashing processes are important from the view point on environmental radioactivity analysis, which is one of the especial fields on analytical chemistry. Statistical reviewed data obtained in this chapter may useful for sample preparation on environmental radioactivity analysis.

From the results of present studies, it was found that Pu was quantitatively extracted with the anion exchange resin disk at high flow rate of 150-200 ml min.$^{-1}$. These results showed that Pu could be rapidly, effectively and easily separated from other interfere elements such as Th, U and Am by using anion exchange resin disk. The time needed to separate Pu from other interfere elements in environmental samples by the present method was only 20 minutes. The operation time of chemical separation of the present method is less than for the method using an anion exchange resin column, extraction chromatographic resin cartridge and solvent extraction. Measurement time of Pu isotopes are 70000 s for alpha-ray spectrometry, 10-20 min. for HR-ICP-MS. The combination of Pu separation by Empore^{TM} anion exchange resin disk and the measurement by HR-ICP-MS is more rapid than the alpha-ray spectrometry. After the preparation of load solution, the concentration of Pu could be determined with HR-ICP-MS in less than 2 hours. Using a 10 g sample, the detection limits of $^{239+240}$Pu and ^{238}Pu are 0.1 mBq g^{-1} by alpha-ray spectrometry, and those of ^{239}Pu and ^{240}Pu are 0.1 and 0.36 mBq g^{-1} by HR-ICP-MS, respectively.

Trace elements concerning with radioactive contamination such as V, Mn, Fe, Co, Ni, Cu, Zn, Rb, Ag, Cd, Cs, Ba and Pb in squid organs were determined by ICP-MS after ashing and acid decomposition. An ICP-MS is a powerful tool for trace element determination with a simultaneous measurement. Analytical validation of ICP-MS results were confirmed by INAA for nine elements (V, Mn, Fe, Co, Cu, Zn, Ag, Cd and Cs). This result describes the usefulness of ICP-MS for trace elements in squid organs, and an application to determine the concentration factors. Particularly, Co, Zn, Ag and Cd were concentrated into liver with concentration factors of 10^5 to 10^6. The analysis of trace elements in squid organs was found to be a useful method for studying heavy metal or radioactive contamination in a marine environment.

Plutonium isotopes and 13 stable elements (V, Mn, Fe, Co, Cu, Zn, Rb, Sr, Ag, Cd, Cs, Th and U) were measured in liver of Surume squid collected in the coastal sea areas of Japan using ICP-MS/ICP-AES. Plutonium isotopes ^{239}Pu and ^{240}Pu were detected in liver samples. The concentrations of ^{239}Pu and ^{240}Pu and sum (^{239,240}Pu) ranged from 1.5 to 28, 1.1 to 24 and 2.5 to 53 mBq kg^{-1} raw liver, respectively. The Pu and the other 13 elements were concentrated with concentration factors (*CF*) ranging from 10^0 to 10^7. Alkali metal and alkali earth metal elements, such as Rb, Sr and Cs, were rarely concentrated with *CF* values of 10^0 to 10^2. Uranium was barely concentrated in liver. On the other hand, transition metal elements, Mn, Fe, Co, Cu, Zn, Ag and Cd were concentrated with high *CF* values. Plutonium, as well as V and Th, were concentrated in liver with *CFs* of 10^2 to 10^4. Scavenged elements (Mn, Fe, Co, Cu, Ag and Cd) were selectively concentrated in liver. Most metal elements concentrated in squid liver were probably derived from seawater via zooplankton species and fixed in tissues by proteins such as ferritin and metallothioneins. The same mechanism probably serves for Pu. The ^{240}Pu/^{239}Pu atomic ratios 0.177 to 0.237 which were slightly higher than 0.178±0.014 for global fallout were found in squid liver. The ocean currents with their different source functions were an essential consideration in the interpretation of high ^{240}Pu/^{239}Pu atomic ratios. Three large ocean currents are flowing around Japan: Kuroshio and Tsushima Currents from south and Oyashio Current from north. Based on the habitat of the Surume squid, the Pu found in the liver is probably a mixture of global fallout Pu and close-in fallout Pu with high

^{240}Pu/^{239}Pu atomic ratio around Bikini Atoll. By assuming the two sources mixing model, Bikini close-in fallout Pu accounts for ca. 35% of the whole plutonium amounts. The results strongly indicate that the squid liver is very useful oceanic biological indicator for studying marine pollution of Pu and some other elements.

Finally, marine organism, Surume squid has a great potential as a useful medium for marine radioactivity monitoring in large sea area. By using suitable pretreatment method, radiochemical separation techniques, and ICP mass spectrometer, rapid method for the determination of plutonium isotopes (and isotopic composition) and other heavy metal elements including short or long lived radionuclides in Surume squid can be applied for routine and in emergency analysis.

APPENDIX

Appendix : Historical review of plutonium and origin of plutonium isotopes in the environment.

A.1. Historical background of plutonium

The element plutonium occupies a unique place in the history of chemistry. With the discovery and isolation of plutonium, the age-old dream of the alchemist of transmuting the elements was fulfilled with a vengeance, for this element is now manufactured by transmutation in huge industrial establishments on a large scale, and has become available in ton quantities. The fascination exercised by this element is not diminished by the knowledge that it presents two aspects: one, beneficent, promises treasures by the peaceful applications of nuclear energy; the other, grim, threatens man's survival by nuclear and thermonuclear weapons. When the first of transuranium elements, neptunium was discovered, it was realized that the decay of ^{239}Np should lead to the formation of element 94. The scale of the experiments at that time, however, precluded its identification. The element 94 was named to be "plutonium" associated with dwarf planet "Pluto". Plutonium (in the form of the isotope ^{238}Pu) was first produced late in 1940 by bombarding uranium with deuterons (Seaborg, et al., 1946):

$$^{238}_{92}\mathrm{U} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{238}_{93}\mathrm{Np} + 2\mathrm{n}$$

$$^{238}_{93}\mathrm{Np} \xrightarrow[2.1\ \mathrm{d}]{\beta^-} {}^{238}_{94}\mathrm{Pu}\ (\alpha\ \text{emitter},\ T_{1/2} = 87.7\ \text{y})$$

Because of the short half-life of ^{238}Pu, tracer studies are feasible, and as a result of such studies by Seaborg, Wahl, and Kennedy, considerable chemical information was obtained. The isotope of major importance, ^{239}Pu, was discovered in 1941 as the decay product of ^{239}Np produced with cyclotron neutrons. Experiments established the fissionability of ^{239}Pu with slow neutrons (Kennedy et al., 1946). This critical experiment revealed the potentialities of ^{239}Pu as a nuclear energy source. On August 20, 1942, Cunningham and Werner isolated approximately 10^{-6} g of a pure plutonium compound from 90 kg of uranyl nitrate, which had been bombarded with cyclotron neutrons. The first weighing of a plutonium sample was carried out by Cunningham on September 10, 1942. This historic sample, which is now at the Lawrence Hall of Science in Berkeley, California, consisted of 2.77×10^{-6} g of plutonium oxide. A detailed first-hand account of the early history of plutonium is given in the proceedings of the 1963 Plutonium Chemistry Symposium held in Chicago.

Ever since the discovery and the first isolation of plutonium, all phases of plutonium chemistry and metallurgy have been subjected to such intensive examination that plutonium is now among the best understood of the actinide elements.

A.2. The production and use of plutonium

Almost plutonium isotope has been produced in natural uranium fueled, thermal, heterogeneous reactors. The development of large-scale nuclear power reactors will require more extensive studies, since plutonium created by fuel irradiation will be an important constituent of any power reactor using natural or near-natural uranium fuel. A high rate of production of plutonium is desirable, as this tend to lengthen the fuel life in the reactor. In addition, the use of plutonium as initial fuel enrichment in power reactors is another possible application of plutonium. The letter possibility has been actively explored in the Plutonium Recycle Program at Hanford Laboratories for a number of years. Still a further use of plutonium in reactor system is found in the fast breeder reactor concept, as this may greatly extended the world’s supply of nuclear fuels by breeding more ^{239}Pu from ^{238}U than the fast reactor consumes. Many other applications are being considered for certain plutonium isotopes, *e.g.*, ^{238}Pu has been used for heat generation in power systems for space flights.

A.3. Historical review of plutonium production

The history of the production of plutonium from the first synthesis to the advent of large scale production reactors has been told in a fascinating story in a volume prepared for the

Second International Conference on the Peaceful Uses of Atomic Energy (Seaborg, 1958). Plutonium does occur in nature in uranium ores as a result of the neutron capture in ^{238}U from spontaneous fission and alpha-neutron reactions. The concentrations of plutonium which are found are extremely minute order of one part in 10^{11} of the uranium present.

The first synthesized plutonium was ^{238}Pu produced by the bombardment of uranium with 16 MeV deuterons from the University of California 60 inch cyclotron and identified on February 23, 1941. Plutonium-239 was produced shortly thereafter by the capture in ^{238}U of neutrons produced by (d, n) reactions using the cyclotron. All of the neutron deficient isotopes from mass number 232 to 238 have been produced by charged particle irradiations. Some of the heavier isotopes have also been produced in this way to obtain samples of high isotopic purity.

Plutonium is a silvery metal which melts at 692.5 C, boils at 3235 C, and has a density of 19.8 $g\cdot cm^{-3}$ at 25 C. It is chemically reactive, dissolves in acids, and has six chemical oxidation states of 0, +III, +IV, +V, +VI and +VII. All plutonium isotopes are radioactive. The most important isotope is ^{239}Pu because it is fissionable, has a relatively long half-life of 2.411×10^{4} years, and can be readily produced in large quantities in uranium reactors by neutron irradiation of non-fissionable ^{238}U. The critical mass of ^{239}Pu is considered to be about 300 g, while that of ^{235}U is about 1kg.

A.4. Production of plutonium in nuclear reactor

Plutonium is produced as the result of neutron capture in ^{238}U and subsequent beta decays to ^{239}Pu. The isotopes 240, 241, 242 and 243 are formed from successive neutron captures as shown; the short half-life of ^{243}Pu essentially terminates the plutonium isotope production at ^{242}Pu. Plutonium-238 is also formed in small quantities from (n, 2n) reactions in ^{239}Pu and ^{238}U. An alternate scheme for production of ^{240}Pu by neutron capture in ^{239}Np ($T_{1/2}$ = 2.3 d, beta decay). The relative production rate of ^{240}Pu from ^{239}Np neutron capture depends on neutron flux level and becomes 1 % of the total production rate of ^{239}Pu at flux of about 4×10^{14} n cm^{-2} s^{-1}.

Plutonium may be produced from ^{238}U in a reactor with any type of neutron spectrum: thermal, intermediate, or fast. There is a large variation in the ratio of the plutonium isotopes produced. The variation is a result of differences in the average cross sections of the various plutonium isotopes over the different neutron spectra. Generally, more fission per atom of plutonium occurs in the fast neutron spectrum than in the intermediate of thermal neutrons. Thus, plutonium formed in a fast reactor is predominantly ^{239}Pu, whereas as significant quantities of the higher isotopes may be present in plutonium from thermal or intermediate reactors. Indeed, isotopic composition of plutonium from a nuclear reactor depends on the design of the reactor and its operating history. Thus, calculations must be made for each specific case. Thermal and intermediate spectrum reactors are not currently considered as potential breeders, i.e., capable of producing more ^{239}Pu than the ^{235}U or ^{239}Pu that is consumed. Fast reactors are, however, good breeders when ^{239}Pu is used as the fuel.

A.5. Production of plutonium in nuclear weapons tests

Most of what we know about fallout from the explosion of nuclear weapons has been learned from studies of the effects of the test explosions that have taken place in various part of the world since the first atomic bomb was detonated on a New Mexico desert in July 1945 (19 kiloton device was fired from a 30 m steel tower). In the intervening 40 years, hundreds of explosions have been conducted by United States and the former Soviet Union, and also United Kingdom, India, France, and the people's republic of China. The yields of nuclear explosions that have been announced by the various countries (total 423 tests: estimated yield; 218 megatons fission, total 547 megatons) (UNSCEAR, 1982). The nuclear weapons explosion tests have been conducted on land and sea, hundreds of miles above the earth's surface, and thousands of feet underground.

Plutonium injected into the atmosphere by nuclear explosion tests originates from volatilization of both unfissioned plutonium and plutonium produced by neutron irradiation of ^{238}U. Several isotopes are produced, ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu. The ^{239}Pu and ^{240}Pu are the most abundant of these nuclides, and because they cannot be distinguished by alpha spectrometry, two nuclides are usually reported together as "plutonium; $^{239+240}$Pu". It has been estimated that about 320 kCi of plutonium has been distributed globally, mainly from nuclear explosion of megaton-range weapons tests that took place before 1963. In 1974 it was reported that another 4 kCi remained in the stratosphere. Transfer from the stratosphere and deposition from the troposphere to the earth's surface proceed at the same rates as for ^{90}Sr, with the results that the ratio of ^{239}Pu to ^{90}Sr has been remarkably constant since the cessation of large scale tests in 1963.

A.6. Man-made plutonium in the environment

Since the birth of the nuclear age in 1945, about 6 tons of ^{239}Pu have been released the earth's atmosphere, predominantly by the atmospheric nuclear weapons testing carried out in the 1950s and 1960s (Harley, 1980). The fallout plutonium from nuclear weapons testing was distributed unevenly between the northern and southern hemispheres, with the deposition in the northern hemisphere being more than three times greater than that in the southern hemisphere (Harley, 1980). Based on the relative areas of land and sea, about two thirds of the fallout plutonium would have been deposited in the oceans (Harley, 1980). Hardy et al. (1973) published a global inventory of the concentrations of $^{239+240}$Pu and ^{238}Pu in the top 30 cm earth's crust at the end of 1960s, this being based on measurements made at 60 locations worldwide. The average concentrations are re-calculated from the results of Hardy et al. (1973) (Taylor, 2001). This demonstrates that the $^{239+240}$Pu concentrations in the northern hemisphere are in fact nearly an order of magnitude larger than those in the southern hemisphere. The latitudinal pattern of distribution in the two hemispheres is also different, with the northern showing a peak between latitudes 30 N and 70 N, which is an order of magnitude greater than the concentrations observed in the polar and equatorial regions. In the southern hemisphere, a lower and narrower plateau occurs in the band 20 S and 50 S. The air concentrations of $^{239+240}$Pu have been decreasing approximately exponentially since the mid-1960s with an apparent halftime of -4 years (Taylor, 2001).

The concentration of fallout 239+240Pu in the ocean is about 3 orders of magnitude lower than that in soils (Watters, 1980).

A.7. Nuclear properties of plutonium

Numerous isotopes of plutonium have been synthesized, all of which are radioactive. A more detailed description of the nuclear properties of the individual plutonium isotopes may be found in the *Table of Isotopes*. As mentioned above, ^{238}Pu was the first of the plutonium isotopes discovered. Because of its relatively short half-life, it is a particularly useful tracer for plutonium. ^{238}Pu is readily obtained by neutron bombardment of ^{237}Np in the following nuclear reaction:

$$^{237}_{93}\mathrm{Np}\ (n,\gamma)\ ^{238}_{93}\mathrm{Np} \xrightarrow{\beta^-} {}^{238}_{94}\mathrm{Pu}$$

The ^{238}Pu is chemically separated from unreacted ^{237}Np by means of ion exchange column techniques. ^{238}Pu may also be obtained from the alpha decay of ^{242}Cm and subsequent chemical separation from undecayed curium. Because of its electric power density of 6.8-7.3 $W\cdot cm^{-3}$ (specific power 0.45 $W\cdot g^{-1}$), ^{238}Pu was become an important fuel for heat sources (MLM-1441, 1967), heart pacemakers (TID-3336, 1973). For instance, in the Passive Seismic Experiment Package (PSEP) set up on the Moon by Apollo 11 expedition, two radioisotope heaters (Apollo Lunar Radioisotope Heater, ALRH) were used, which contained 37.6 g $^{238}PuO_2$ microspheres, producing 15 W thermal (Kelly and Avona, 1969). The Apollo Lunar Surface Experiments Package (ALSEP), which was set up by the Apollo 12 expedition, is powered by a SNAP (systems for nuclear auxiliary power) 27 generator, fueled with 3735 g

$^{238}PuO_2$ microspheres generating 1480 W thermal (Prosser, 1969).

Plutonium-239 is the most important isotopes of plutonium. From the chemist's point of view, its half-life ($T_{1/2}$ = 2.411×10^4 y, alpha decay) is sufficiently long to permit the preparation of this isotope in large-scale amounts, and to make it feasible to carry out conventional chemical studies. ^{239}Pu has a high cross section for fission with slow neutrons, and it is this isotope that serves as both a nuclear fuel and a nuclear weapon. By far the greater portion of the knowledge of the chemical and physical properties of plutonium has been acquired by the use of ^{239}Pu. While its half-life is long enough to permit chemical studies, nevertheless the half-life of ^{239}Pu is still short enough to present serious problems to the chemist. In handling large quantities of ^{239}Pu, the critically hazard caused by its fissionability becomes an additional problem. Amounts as small as 500 g may become critical under certain conditions.

The higher plutonium isotopes are formed as a result of successive neutron capture by the various plutonium isotopes:

$^{239}_{94}\mathrm{Pu}(n,\gamma)\,^{240}_{94}\mathrm{Pu}(n,\gamma)\,^{241}_{94}\mathrm{Pu}$ etc.

The atomic composition of plutonium produced in a nuclear reactor will thus vary according to the length of time the plutonium formed is allowed to remain the neutron flux. From view point of the chemist, the atomic weight of the plutonium may vary to such an extent that it must be taken into consideration in precise work.

The long-lived isotopes ^{242}Pu ($T_{1/2}$ = 3.733×10^5 y, alpha decay) and ^{244}Pu ($T_{1/2}$ = 8.08×10^7 y, alpha decay) appear to be destined for an important chemical future. Residual plutonium, which has been isolated from ^{239}Pu targets irradiated in a high-flux reactor to more than 90 % burn-up, was found to consist mainly of ^{242}Pu and some ^{244}Pu. Many of the complications arising from the use of the relatively short-lived ^{239}Pu are greatly ameliorated by the use of these long-lived isotopes of plutonium.

A.8. Plutonium in nature

The presence of plutonium in small amounts of uranium in natural origin was first established in 1942 (Seaborg and Perlman, 1948 ; Garner et al., 1948). These workers were able to show that Canadian pitchblende and Colorado carnotite both contain a small amount of alpha activity due to plutonium isotope, presumably ^{239}Pu. Pioneer researchers have made thorough investigations and have conclusively demonstrated the existence of ^{239}Pu in nature (Peppard et al., 1951 ; Lavine and Seaborg, 1951). Also the researchers have determined the plutonium content of a number of uranium ores, and have isolated micrograms amounts of ^{239}Pu from uranium process wastes. No plutonium isotopes other than ^{239}Pu have been found in any of these experiments. Alpha pulse analysis and mass spectrometry have been the experimental methods used to characterize the isotopic composition of plutonium isolated from natural sources.

The half-lives of the plutonium isotopes, with the exception of the very long-lived ^{244}Pu, are so short that it is most unlikely that any plutonium except ^{244}Pu can have survived in nature from primordial times. It is overwhelmingly likely that ^{239}Pu arise in nature by nuclear reactions and represents a steady state concentration:

$$^{238}_{92}\mathrm{U}(\mathrm{n},\gamma)\,^{239}_{92}\mathrm{U} \xrightarrow{\beta^-} {}^{239}_{93}\mathrm{Np} \xrightarrow{\beta^-} {}^{239}_{94}\mathrm{Pu}$$

Neutrons necessary for the formation of ^{239}Pu from ^{238}U may arise from various sources; (a) spontaneous fission of ^{238}U; (b) by neutron multiplication in ^{235}U; (c) from (α, n) reactions caused by alpha particles (from the radioactive decay of uranium and its progeny) on the light elements, lithium, boron, beryllium, fluorine, oxygen, silicon, and magnesium; and (d) neutrons produced by cosmic rays. The neutrons from cosmic rays appear to be of negligible importance, since the neutron production from uranium by the capture of mu mesons is considerably less than 0.1 % of the neutrons arising from spontaneous fission. Spontaneous fission in uranium occurs at the rate of 24.2 ± 0.5 fissions per gram per hour, which produces a neutron flux insufficient to account for the observed plutonium concentration. Neutron multiplication by capture of thermarlized neutron in ^{235}U and the production of fission neutrons will contribute to overcoming the deficiency. The contribution from this source will clearly depend on the uranium concentration, on the composition of the ore, and on the probability that a fission neutron will be showed down to thermal energies. In all probability, the neutrons produced in (α, n) reactions account for a major portion of the neutrons required for ^{239}Pu formation. In thorium ores containing small amounts of uranium, the neutron from (α, n) reactions predominate. The amount of plutonium created depends not only on the number of neutrons produced but also on their subsequent fate. Elements with high neutron capture cross section will compete for neutrons and decrease plutonium formation. In carnotite, potassium and vanadium atoms, and in fergusonite, tantalum atoms capture most of the available neutrons, thus accounting for the unusually low plutonium content found in these minerals.

Quite an interesting sample for the possible formation of ^{239}Pu by neutron multiplication in ^{235}U was found by French scientists in the uranium deposit at Oklo in the Gabon, Africa. From anomalies in the isotopic composition of rare earth elements (especially neodymium) and anomalies in the ^{235}U content, it was concluded that, in at least six different locations of this deposit, a self-sustaining chain reaction must have occurred. It was found that, in these locations, a burn-up of part of the original ^{235}U had occurred, but the depletion found was not as great as one would have expected from the observed anomalies in the isotope composition of other elements. A possible explanation for this phenomenon is that, for each ^{235}U atom fissioned, 0.4 to 0.7 atoms of ^{239}Pu were formed from the ^{238}U present in the matrix. In this decay over the course of time, this ^{239}Pu again replenished a fraction of the ^{235}U, which had been consumed earlier. Since no plutonium was found in the Oklo deposit, one may conclude that the self-sustaining chain reaction must have taken place around 1.9×10^{9} years ago (Kuroda, 1960 ; Cowan, 1976).

A.9. Theoretical solution chemistry of plutonium

A.9.1. Oxidation states in solution

Plutonium ions in solution can exist in the +III, +IV, +V and +VI oxidation states as Pu^{3+}, Pu^{4+}, PuO_2^{+}, PuO_2^{2+}, respectively. Because of the relationship between the equilibria, and the kinetics of converting from one state to another, it is possible for all four oxidation states to coexist in appreciable concentrations in the same solution. Solutions of Pu(III) are blue when viewed by the reflected light; when seen by transmitted light they are blue with a pronounced green tinge. Tetravalent state of plutonium forms brown solutions in dilute acids, in more concentrated acids the color often changes due to formation of colored complexes. For example, Pu(IV) in concentrated HNO_3 yields a spinach-green solution, while H_3PO_4 solutions are pink. Pu(V) is colorless in solution, while Pu(VI) forms a solution whose color ca vary from yellow to pink-orange depending on conditions. The oxidation state produced by dissolution of plutonium metal depends on the acid employed. Thus HCl, HBr, H_3PO_4, and $HClO_4$ in any concentration produce a blue solution containing essentially only the trivalent ion, while HNO_3-HF dissolution forms mainly Pu(IV) and produces a green solutions.

Since there is little or no complexing in $HClO_4$ solutions, these spectra are of the aqua ions of plutonium, containing only water molecules in the coordination sphere. In solutions containing more strongly complexing anions the spectra (except for Pu(III)) are generally different, and for this reason spectrophotometry is a useful tool for determining the presence and identity of plutonium complexes.

A.9.2. Oxidation-reduction equilibria of plutonium ions

Oxidation-reduction relationships of the plutonium ions present one of the most complex and fascinating aspects of the chemistry of plutonium. Multiple oxidation states in solution are by no means unknown among many of the transition elements. Plutonium, however, exhibits behavior unmatched in the periodic table in that it is possible to prepare aqueous solutions in which there are substantial concentrations of four oxidation states in equilibrium with one another. The complications arising from this behavior have been responsible for a considerable amount of all the research that has been devoted to the solution chemistry of plutonium. As is case with other actinide elements, it is difficult to calculate standard potential values of the various couples. In many cases the pertinent data were acquired at an ionic strength too high to allow extrapolation to infinite dilution. Moreover, it is difficult to prepare substantial concentrations of tetravalent plutonium in solutions of low acidity (< 0.5 M) without formation of the colloidal hydroxide "polymer". Tetravalent plutonium also disproportionate into tri-, penta-, and hexavalent plutonium in solutions of low acidity, so it is very difficult to obtain experimental conditions that permit extrapolation of the Pu^{4+} activity to zero ionic strength. Formal potential schemes for selected plutonium couples at 25 C are shown as follows:

1M HCl solution;

$$\begin{tikzcd}
PuO_2^{2+} \arrow[r, leftrightarrow, "0.912"] \arrow[rr, bend right, "1.051"'] \arrow[rrr, bend right=40, "1.024"'] & PuO_2^{+} \arrow[r, leftrightarrow, "1.190"] & Pu^{4+} \arrow[r, leftrightarrow, "0.970"] & Pu^{3+} \arrow[r, leftrightarrow, "-2.03"] & Pu^{0}
\end{tikzcd}$$

1M HNO_3 solution;

$$\begin{tikzcd}
PuO_2^{2+} \arrow[r, leftrightarrow, "0.920"] \arrow[rr, bend right, "1.054"'] \arrow[rrr, bend right=40, "1.006"'] & PuO_2^{+} \arrow[r, leftrightarrow, "1.188"] & Pu^{4+} \arrow[r, leftrightarrow, "0.914"] & Pu^{3+}
\end{tikzcd}$$

1M $HClO_4$ solution;

$$\begin{tikzcd}
PuO_2^{2+} \arrow[r, leftrightarrow, "0.916"] \arrow[rr, bend right, "1.043"'] \arrow[rrr, bend right=40, "1.023"'] & PuO_2^{+} \arrow[r, leftrightarrow, "1.170"] & Pu^{4+} \arrow[r, leftrightarrow, "0.982"] & Pu^{3+} \arrow[r, leftrightarrow, "-2.03"] & Pu^{0}
\end{tikzcd}$$

Natural solution (pH 7);

$$\begin{tikzcd}
\mathrm{PuO_2(OH)_2(aq)} \arrow[r, leftrightarrow, "0.77"] \arrow[rr, bend right, "0.94"'] & \mathrm{PuO_2^+} \arrow[r, leftrightarrow, "1.11"] & \mathrm{PuO_2 \cdot \mathit{x}H_2O(s)} \arrow[r, leftrightarrow, "-0.63"] & \mathrm{Pu^{3+}}
\end{tikzcd}$$

1M OH-;

$$\begin{tikzcd}
\mathrm{PuO_2(OH)_3^-} \arrow[r, leftrightarrow, "0.26"] \arrow[rr, bend right, "\sim\ -0.5"'] & \mathrm{PuO_2}(OH) \arrow[r, leftrightarrow, "0.76"] & \mathrm{PuO_2 \cdot \mathit{x}H_2O(s)} \arrow[r, leftrightarrow, "-0.95"] & \mathrm{Pu(OH)_3 \cdot \mathit{y}H_2O(s)}
\end{tikzcd}$$

The Pu(IV)/Pu(III) and Pu(VI)/Pu(V) couples are reversible, but different ionic structures contribute to the irreversibility of the Pu(V)/Pu(III), Pu(VI)/Pu(III), Pu(V)/Pu(IV), and Pu(VI)/Pu(IV) couples. In contrast to the first two couples, the latter four couples approach equilibrium slowly.

A.9.3. Equilibria between Pu(III), (IV), (V) and (VI) in solution

It is possible for finite concentrations of all four oxidation states of plutonium to exist in equilibrium with one another in the same solution. Such behavior, unique for plutonium among all the elements of the periodic table, is due to the interplay of two phenomena, (1) the tendency of Pu(IV) and Pu(V) ions to disproportionate and (2) the slow rate of reactions involving formation or rupture of plutonium-oxygen bonds (such as exist in PuO_2^+ and PuO_2^{2+}), as compared to the much faster reactions involving only electron transfer. Much research has been done in the equilibria, kinetics, and mechanisms of these reactions, the result have gone a long way toward elucidating plutonium solution chemistry.

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ACKNOWLEDGEMENTS

Acknowledgements

It was very proud of studying at the post doctoral course in Graduate School of Natural Science and Technology, Institute of Nature and Environmental Technology, Kanazawa University. It is great honor for me to apply for the degree of the Doctor of Philosophy in Science. The author is deeply indebted to a lot of people for this doctoral dissertation.

The author is deeply indebted to Professor Dr. Masayoshi Yamamoto of K-INET, Low Level Radioactivity Laboratory, Kanazawa University for a great deal of helpful suggestions, advices, discussions and encouragement during the period of attendance at school.

The author is also deeply grateful to Professor Dr. Kazuhisa Komura, Professor Dr. Takashi Nakanishi of Graduate School of Natural Science and Technology, Kanazawa University, Professor Dr. Ryohei Amano of Graduate School of Medicine, Kanazawa University, Associate Professor Dr. Akihiko Yokoyama of Graduate School of Natural Science and Technology, Kanazawa University.

The author wishes to thanks Dr. Hideo Higuchi and Mr. Nobuhiro Nonaka of Japan Chemical Analysis Center for their helpful and kind cooperation and providing fruitful suggestions. The author also thank my teacher former Professor Dr. Shoichi Kawamura of Kanagawa University, former Professor Kaoru Ueno of Kanazawa University. Very special thanks to Dr. Tsutomu Miura of National Institute of Advanced Industrial Science and Technology (AIST), Dr. Yoshihito Ohtsuka of Institute for Environmental Sciences (IES), Dr. Aya Sakaguchi of Graduate School of Natural Science and Technology, Kanazawa University, and also my seniors and juniors.

Finally, I thank my family, my wife Atsuko, my son Yuuki and my daughter Honoka for their continuous encouragement and support.

謝辞

本論文をまとめるにあたり，金沢大学大学院自然科学研究科物質科学専攻 自然計測応用研究センター 低レベル放射能実験施設 山本 政儀 教授 に終始ご指導賜りましたことを深く感謝申し上げます。また，金沢大学大学院自然科学研究科環境科学専攻 自然計測応用研究センター 低レベル放射能実験施設長 小村 和久 教授 にご指導賜りましたことを深く感謝申し上げます。

本論文の作成ならびに審査にあたり，山本 政儀 教授 (主査)，小村 和久 教授，中西 孝 教授，天野 良平 教授（医学系研究科保健学専攻)，横山 明彦 助教授 の先生方に貴重なご意見やご助言を頂いたことに深謝いたします。

本研究を遂行するきっかけを与えて頂いた，財団法人 日本分析センター 樋口 英雄 博士，野中 信博 氏に感謝申し上げます。また，財団法人 日本分析センターの役職員諸氏に感謝申し上げます。放射化学分析に関してご助言を頂いた，独立行政法人 産業技術総合研究所 三浦 勉 博士に感謝申し上げます。

私が放射化学の道を歩むきかっけは，元 神奈川大学理学部教授 河村正一先生，元 金沢大学理学部教授 上野馨先生の親身かつ興味深いご指導を頂いたことによるもので，心より感謝いたします。

最後に，本研究を進め，また学位論文として取りまとめることは家族からの応援なしでは成し得ないことで，妻 敦子，長男 結貴，長女 穂果 からの心温まる応援を頂いたことに感謝します。

平成 18 年度 博士学位論文（甲）（平成 19 年 3 月受理）（金沢大学）

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