# THE DETERMINATION OF TRACE ELEMENTS IN SQUIDS USING ICP-MS/INAA AND ITS APPLICATION TO THE MARINE RADIOACTIVITY MONITORING

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## 1. INTRODUCTION

The atmospheric nuclear testing of nuclear weapon conducted in the late 1950s and 1960s increased the level of environmental radioactivity in the ecosystem. Moreover, since the accident of Chernobyl nuclear power plant in 1986, radioactive fallout had been world-widely spreaded out, and much more attention has been directed to monitoring the environmental radioactivities in the ecosystem and in the food in aspect of radiological hazard. As the number of nuclear power plants in many countries were continuously increased in the recent years, there might exist the discharge of a large amount of radionuclides into environments and of their environmental contamination.

In the marine ecosystem, some marine organisms such as algae and shellfish are the first concentrators of metals or radionuclides and, through the food chain, those substances are transferred to fishes and finally human being. It is well accepted that the analysis of trace elements in marine organisms is very important for evaluating the environmental contamination of radionuclides as well as estimating their behaviors in the marine ecosystem.

In 1965, Folsom and Young found $^{60}Co$ and $^{108m/110m}Ag$ in the viscera of squid collected from the North Pacific. After his discover, we had continuously surveyed the long lived radionuclides including $^{60}Co$ and $^{108m/110m}Ag$ in the various kind of squid collected from around Japan during 1978-1989. As the results of analysis of squid, we have found that squid is useful material to investigate the radioactivity level of marine environment.

In this paper, we describe the analytical results on the trace elements in squids and their organs by inductively coupled plasma-mass spectrometry(ICP-MS) and instrumental neutron activation analysis (INAA) as well as the radioactive nuclides($^{60}Co$, $^{108m/110m}Ag$ and $^{137}Cs$) by $\gamma$-spectrometry.

## 2. EXPERIMENTAL

### 1) Sample collection and preparations

Three varieties of squids(*Todarodes pacificus*, *Loligo edulis*, *Sepia officinalis*) had been collected from the eight local fishery cooperative unions in Japan during 1981-1988, dried at 105°C and ashed for 24 hour at 450°C. Especially, *Todarodes pacificus* collected from Chiba fishery cooperative union in 1996 was divided into edible part, backbone, liver, stomach including diets, and other viscera.

### 2) Determination of trace elements in squids

#### (1) *ICP-MS analysis*

0.5 gram of squid ash samples was taken in the teflon beaker and 5 ml of 7 M $HNO_3$ was added, heated to dryness. The residue was dissolved in 20 ml of 1 M $HNO_3$ and boiled for 10 min. The sample solution was transferred to 100 ml teflon

**Table 1. Isotopes and internal standards used for analysis of biological samples.**

| Element | Mass number of isotope used | Internal standard | Scan time (msec) | Element | Mass number of isotope used | Internal standard | Scan time (msec) |
|---|---|---|---|---|---|---|---|
| V | 51 | Sc | 120 | Mo | 98 | Y | 120 |
| Cr | 53 | Sc | 120 | Ag | 107 | Rh | 80 |
| Mn | 55 | Sc | 120 | Cd | 111 | In | 80 |
| Fe | 57 | Sc | 120 | Cs | 133 | In | 80 |
| Co | 59 | Sc | 120 | Ba | 137 | In | 80 |
| Ni | 62 | Sc | 120 | Tl | 205 | Tb | 50 |
| Cu | 63 | Sc | 120 | Pb | 207 | Tb | 50 |
| Zn | 66 | Sc | 120 | Bi | 209 | Tb | 50 |
| Se | 77 | Y | 120 | Th | 232 | Tb | 50 |
| Rb | 85 | Y | 120 | U | 238 | Tb | 50 |
| Sr | 88 | Y | 120 | | | | |

flask with 1 M $HNO_3$. When required, samples were diluted 10 or 50 times with 18.2 megaohm pure water produced freshly by Milli-Ro60 (Millipore). The sample solutions were analyzed for V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Rb, Sr, Mo, Ag, Cd, Cs, Ba, Tl, Pb, Bi, Th and U. The mass number of isotopes used for ICP-MS measurement are presented in table 1. 10 ng/ml of Sc, Y, Rh, In and Tb was separately added to the sample solutions as an internal standard.

The standard stock solution of 10 mg/l(SPEX multi-element plasma standard, SPEX chemical, USA) was diluted to prepare a series of standard solution(0, 0.05, 0.5, 2.5, 5, 50, 100, 200 ng/ml).

The data obtained from ICP-MS were calculated by spreadsheet software "Quattro Pro(Boland)" installed in personal computer.

(2) *INAA analysis*

For the analysis of V, Mn and Cu, 100 mg of squid ash samples or the standards impregnated with filter paper were sealed in polyethylene bag, irradiated for 2 min by TRIGA Mark II reactor(100 kW, flux of thermal neutron; $1.5x10^{12}$n $cm^{-2}sec^{-1}$) of RIKKYO University in Japan. After the sample was cooled down for 6 min, radioactivities of $^{52}V$, $^{66}Cu$ and $^{56}Mn$ were counted for 300 sec using the multichannel analyzer with Ge detector with 19 and 35% relative efficiency for 1.332 MeV gamma rays of $^{60}Co$. The measurement of $^{56}Mn$(half life: 2.58h, 0.8438 meV) was made after $^{27}Mg$ (half life:9.46m, 0.8468 meV), interfering $^{56}Mn$ counting had decayed out (about 1 hr)(Morrison and Potter, 1972).

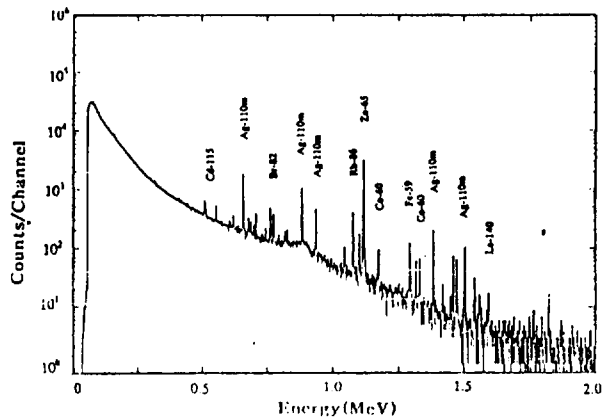


**Figure 1. $\gamma$-ray spectrum of squid ash sample counted by Ge detector one month after neutron irradiation**

For the analysis of Fe, Cs, Ag, Co and Zn 200 mg of samples and standards were irradiated for 12 hr at the flux of $5x10^{11}$n $cm^{-2}sec^{-1}$. After the sample was cooled down for 2 weeks - 1 month, radioactivities of $^{59}Fe$, $^{60}Co$, $^{65}Zn$, $^{86}Rb$, $^{110m}Ag$, $^{115m}In$ and $^{115m}Cd$ were counted for 600-4000 sec under the

conditions of plastic plate inserted between detector and sample to reduce intensity of the gamma rays induced from intense $^{32}P$ in sample(Morrison and Potter, 1972). Figure 1 shows the $\gamma$-ray spectrum of squid ash sample counted by Ge detector 1 month after neutron irradiation.

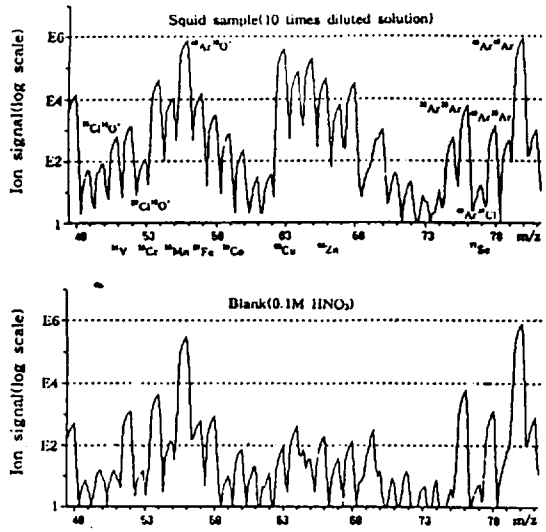


Figure 2. Mass spectrum of squid ash sample solution. After 0.1 g of squid ash sample was taken and dissolved in 20 ml of 1M $HNO_3$ and boiled. The sample was transferred to 100 ml flask with 1M $HNO_3$ and diluted 10 times.

3) $\gamma$-spectrometry

After the ash samples were uniformly packed into a cylindrical vessel of 48 mm diameter, 60 mm height, $^{60}Co$, $^{108m/110m}Ag$ and $^{137}Cs$ activities in squid ash sample were counted for about 80,000 sec by $\gamma$-spectrometry with Ge detector having approximately 20 % relative efficiency for 1.332 MeV gamma rays of $^{60}Co$. The counting efficiency of Ge detector is determined by using a mixed point source and KCl volume source with different height.

## 3. RESULT AND DISCUSSIONS

### 1) Elimination of spectral interferences of ICP-MS

Inductively coupled plasma-mass spectrometry (ICP-MS) is now a well-established analytical technique that provides with very low detection limits(1 ug/L or less) for most of the elements in the periodic table. Also it allows multi-element analysis with rapid sample throughput(Dams *et al.*, 1995). This technique has, however, some difficulties associated with analytical performance such as matrix effect and molecular ion interference.

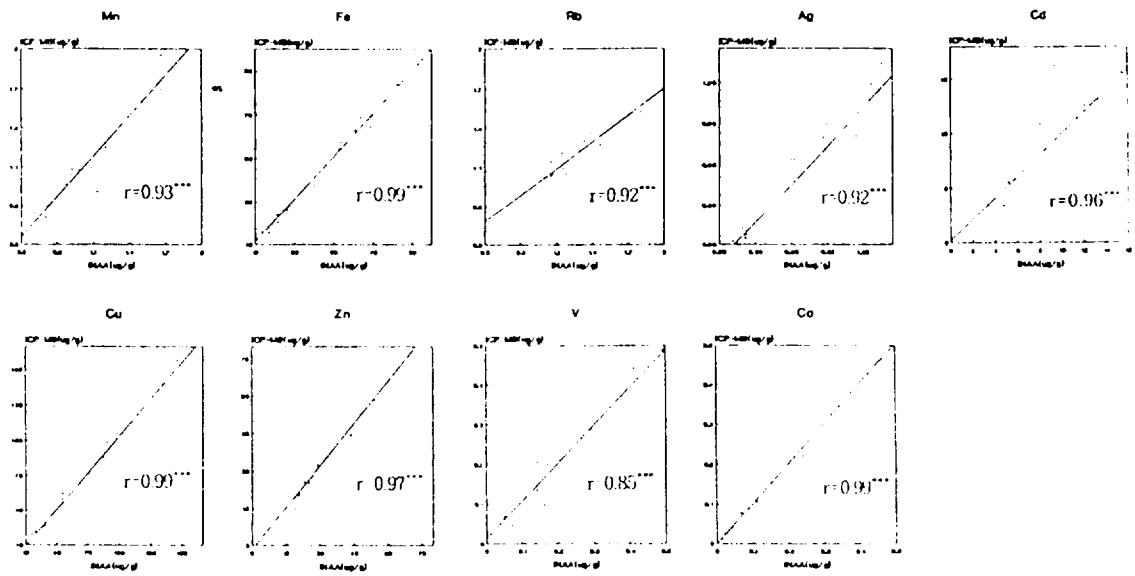


Figure 3. Comparison of ICP-MS and INAA results, as determined the concentrations of trace elements in squid by their techniques.

The problems of the background spectral interference(e.g. $ArO^+$, $Ar_2$ etc.) of blank sample can be solved to some extent by optimizing ICP-MS performance. However, the contribution of polyatomic ions and oxides from biological sample matrix on m/z peak of elements($^{35}ClO^+$, $ArC^+$, $^{37}ClO^+$, $ArO^+$, $PO_2$, $ArNa^+$, $^{35}Cl_2$ or $Ar_2$ occurred as a result of combinations of C, Cl, S, O, P and Na) is the most severe problem for the determination of lighter elements(m/z < 80)(Houk and Thompson, 1988; Dams *et al.*, 1995), giving higher background to reduce the accuracy and precision of analysis because the peaks of some polyatomic ions and oxides are overlapped with those from analytes. Therefore, in squid sample possible interferences may be caused by Na, K, Ca, Mg, Cl, S or P. The peaks of polyatomic ions and oxides generated from those matrixes were identified by introducing the solution containing Na, K, Ca, Mg, Cl, P or S(data not shown). The important spectral overlapping related to the determination of squid samples occurred on peaks of $^{51}V(^{35}Cl^{16}O^+)$, $^{53}Cr$ $(^{37}Cl^{16}O^+)$, $^{77}Se(^{40}Ar^{37}Cl^+)$ (figure 2), thus being limited to Cl effect. However, as the contribution of Cl on $^{35}Cl^{16}O^+$, $^{37}Cl^{16}O^+$ and $^{40}Ar^{37}Cl^+$ at the different Cl concentrations(0 - 50 mg/l) was very small, those spectral interferences can be eliminated by diluting sample solution to be below 20 mg/l.

### 2) Analysis of trace elements

Under the optimum condition of ICP-MS measurement previously mentioned, the simultaneous multi-analysis of 21 elements(V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Rb, Sr, Mo, Ag, Cd, Cs, Ba, Tl, Pb, Bi, Th, U) in the squid sample was tried. As there are no available certified values for trace elements in the squid, the method of INAA was applied to compare with the results of ICP-MS. In the practical measurement, besides spectral interference by polyatomic ions derived from matrix elements such as Na, Ca and Cl, the count rates of analytes can be affected by high level of salts or heavy matrix ions themselves(Houk and Thompson, 1988). Orifice plugging is also, a problem for the samples with high solid contents(> 0.5 %). Hence, internal standard was adapted to ICP-MS to deal with matrix effects. Five elements(Sc, Y, In, Tb, Rh) well-known as internal standard were used.

Three biological reference samples(SRM 1572 citrus leaves, SRM 1577 bovine liver, NIES No. 9 sargasso) were analyzed to obtain the validity of our ICP-MS results, and in general our analytical data were well agreed with the certified values in all standard materials(data not shown). On the other hand, the concentrations of V, Mn, Fe, Co, Cu, Zn, Rb, Ag and Cd determined by ICP-MS were closely correlated with those of INAA as shown in figure 3.

The reason why the analytical result of Ag by ICP-MS is less than that by INAA could be explained from the fact that Ag is apt to absorb on teflon vial wall and its concentration can be decreased as time elapsed. This is one of the difficulties of Ag determination by ICP-MS.

The concentration of trace elements in squids was shown in table 2. The concentrations of Fe, Ni, Cu, Zn, Mo, Cd, Pb and U in *Todarodes pacificus*, a migratory squid, were higher than those in other varieties. *Sepia officinalis*, a sedentary one, had higher concentration of V, Co, Se, Sr. However, there were no differences among the varieties in the concentrations of other elements. The concentrations of trace elements in *Todarodes pacificus* were influenced by the sampling sites.

Based on these results, there might be physiologically different characteristics among squid varieties. It might be considered that the different Cd values in *Todarodes pacificus* among sampling sites represents some possibility of environmental contamination.

Table 2. The concentrations(μg/g) of trace elements in squids as determined by ICP-MS and INAA.

| Location | Variety | Mn | Fe | Cu | Zn | Rb | Sr | Ag | V | Cr | Co | Ni | Se | Mo | Cd | Cs | Ba | Tl | Pb | Bi | Th | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hokkaido | *Todarodes pacificus* | 0.96* | 83.8 | 85.4 | 72.6 | 1.26 | 4.09 | 0.85 | 0.440 | 0.023 | 0.153 | 0.229 | 0.039 | 0.054 | 15.6 | 0.004 | 0.146 | 0.0001 | 0.339 | 0.0025 | 0.0004 | 0.0347 |
| | | 0.88** | 82.0 | 84.3 | 68.8 | 1.18 | | 0.91 | 0.410 | | 0.150 | | | | 15.3 | | | | | | | |
| Hokkaido | // | 0.71 | 68.7 | 54.6 | 57.8 | 1.03 | 2.63 | 0.69 | 0.065 | 0.017 | 0.104 | 0.077 | 0.027 | 0.012 | 5.77 | 0.003 | 0.013 | 0.0000 | 0.213 | 0.0028 | 0.0001 | 0.0237 |
| | | 0.70 | 63.4 | 45.3 | 49.1 | 1.05 | | 0.67 | 0.090 | | 0.110 | | | | 5.63 | | | | | | | |
| Miyagi | // | 1.07 | 77.1 | 131 | 43.9 | 1.52 | 5.22 | 0.86 | 0.488 | 0.037 | 0.193 | 0.393 | 0.074 | 0.017 | 13.0 | 0.005 | 0.073 | 0.0001 | 0.094 | 0.0007 | 0.0002 | 0.0615 |
| | | 0.98 | 81.3 | 131 | 43.4 | 1.80 | | 1.19 | 0.490 | | 0.200 | | | | 13.2 | | | | | | | |
| Chiba | // | 0.74 | 57.3 | 49.6 | 32.6 | 0.83 | 5.85 | 0.69 | 0.113 | 0.009 | 0.074 | 0.166 | 0.028 | 0.009 | 5.55 | 0.003 | 0.043 | - | 0.095 | 0.0014 | 0.0001 | 0.0167 |
| | | 0.60 | 53.2 | 44.8 | 28.6 | 0.83 | | 0.64 | 0.060 | | 0.070 | | | | 5.13 | | | | | | | |
| Chiba | // | 1.21 | 49.0 | 168 | 59.4 | 1.24 | 10.9 | 0.42 | 0.205 | 0.021 | 0.132 | 0.643 | 0.076 | 0.026 | 10.8 | 0.004 | 0.198 | 0.0002 | 0.119 | 0.0022 | 0.0003 | 0.0222 |
| | | 0.90 | 42.0 | 106 | 42.4 | 1.28 | | 1.09 | 0.140 | | 0.100 | | | | 8.00 | | | | | | | |
| Niigata | // | 0.80 | 54.2 | 77.5 | 35.7 | 1.05 | 3.66 | 0.94 | 0.045 | 0.016 | 0.076 | 0.076 | 0.034 | 0.007 | 9.19 | 0.003 | 0.026 | 0.0001 | 0.299 | 0.0016 | 0.0002 | 0.0158 |
| | | 0.72 | 52.3 | 79.7 | 33.0 | 1.06 | | 0.94 | 0.070 | | 0.065 | | | | 11.6 | | | | | | | |
| Niigata | // | 0.97 | 62.9 | 105 | 52.8 | 1.14 | 4.93 | 1.39 | 0.135 | 0.016 | 0.107 | 0.179 | 0.013 | 0.011 | 12.5 | 0.003 | 0.036 | 0.0000 | 0.292 | 0.0036 | 0.0002 | 0.0297 |
| | | 0.96 | 60.6 | 97.4 | 51.5 | 1.23 | | 1.41 | 0.140 | | 0.108 | | | | 12.0 | | | | | | | |
| Niigata | // | 0.83 | 64.4 | 97.9 | 52.4 | 1.07 | 3.46 | 1.24 | 0.060 | 0.029 | 0.086 | 0.129 | 0.027 | 0.012 | 15.6 | 0.003 | 0.038 | 0.0001 | 0.429 | 0.0036 | 0.0003 | 0.0255 |
| | | 0.75 | 68.5 | 87.9 | 47.7 | 1.12 | | 1.32 | 0.050 | | 0.087 | | | | 15.4 | | | | | | | |
| Submean(ICP-MS) | | 0.91 | 64.7 | 96.1 | 50.9 | 1.14 | 5.09 | 0.88 | 0.194 | 0.021 | 0.116 | 0.237 | 0.040 | 0.019 | 11.0 | 0.003 | 0.072 | 0.0001 | 0.235 | 0.0023 | 0.0002 | 0.0287 |
| CV(%) | | 17.8 | 16.9 | 38.2 | 24.2 | 16.8 | 47.2 | 32.8 | 84.3 | 39.2 | 33.5 | 76.3 | 54.4 | 76.5 | 33.5 | 19.5 | 85.6 | 87.2 | 49.7 | 42.5 | 45.6 | 47.6 |
| Submean(INAA) | | 0.81 | 62.9 | 84.5 | 45.6 | 1.19 | | 1.02 | 0.181 | | 0.111 | | | | 10.8 | | | | | | | |
| CV(%) | | 15.9 | 20.9 | 32.1 | 25.2 | 22.0 | | 25.9 | 88.0 | | 37.5 | | | | 35.4 | | | | | | | |
| Kagoshima | *Loligo edulis* | 1.04 | 20.3 | 18.6 | 31.8 | 1.02 | 13.4 | 0.09 | 0.044 | 0.008 | 0.032 | 0.048 | 0.124 | 0.005 | 0.24 | 0.008 | 0.084 | - | 0.012 | 0.0003 | 0.0001 | 0.0061 |
| | | 0.91 | 21.3 | 15.5 | 28.7 | 1.00 | | 0.27 | | | 0.030 | | | | - | | | | | | | |
| Fukui | // | 0.76 | 24.0 | 21.5 | 20.2 | 1.36 | 10.1 | 0.17 | 0.071 | 0.005 | 0.024 | 0.033 | 0.040 | 0.006 | 0.18 | 0.006 | 0.106 | - | 0.009 | 0.0007 | 0.0007 | 0.0031 |
| | | 0.77 | 20.5 | 18.1 | 20.5 | 1.38 | | 0.24 | 0.020 | | 0.020 | | | | - | | | | | | | |
| Nagasaki | *Loligo edulis* | 1.69 | 15.7 | 26.3 | 25.7 | 1.21 | 8.22 | 0.07 | 0.097 | 0.005 | 0.038 | 0.038 | 0.056 | 0.004 | 0.15 | 0.006 | 0.067 | - | 0.023 | 0.0000 | 0.0002 | 0.0056 |
| | | 1.66 | 12.8 | 28.3 | 22.8 | 1.14 | | 0.16 | 0.160 | | 0.040 | | | | - | | | | | | | |
| Nagasaki | // | 1.95 | 17.7 | 28.7 | 25.1 | 1.30 | 7.42 | 0.05 | 0.062 | 0.001 | 0.030 | 0.042 | 0.063 | 0.005 | 0.12 | 0.006 | 0.044 | 0.0003 | 0.033 | 0.0002 | 0.0001 | 0.0048 |
| | | 1.66 | 16.0 | 34.0 | 25.0 | 1.33 | | 0.19 | 0.030 | | 0.030 | | | | - | | | | | | | |
| Kagoshima | // | 1.08 | 37.3 | 20.3 | 27.6 | 1.27 | 7.50 | 0.10 | 0.068 | 0.003 | 0.024 | 0.047 | 0.116 | 0.005 | 0.25 | 0.005 | 0.038 | 0.0004 | 0.019 | 0.0003 | 0.0003 | 0.0066 |
| | | 0.92 | 39.7 | 19.7 | 26.4 | 1.46 | | 0.26 | 0.050 | | 0.025 | | 0.098 | | - | | | | | | | |
| Submean(ICP-MS) | | 1.30 | 23.0 | 23.1 | 26.1 | 1.23 | 9.33 | 0.10 | 0.068 | 0.004 | 0.029 | 0.042 | 0.080 | 0.005 | 0.19 | 0.006 | 0.068 | 0.0001 | 0.019 | 0.0003 | 0.0003 | 0.0052 |
| CV(%) | | 34.0 | 33.4 | 16.4 | 14.4 | 9.60 | 24.1 | 45.0 | 25.1 | 55.0 | 17.8 | 13.5 | 42.4 | 14.7 | 27.5 | 18.2 | 37.0 | 129 | 44.3 | 70.2 | 79.8 | 23.1 |
| Submean(INAA) | | 1.18 | 22.1 | 23.1 | 24.7 | 1.26 | | 0.22 | 0.052 | | 0.029 | | 0.030 | | | | | | | | | |
| CV(%) | | 33.1 | 4.24 | 30.0 | 11.5 | 13.3 | | 18.9 | 108 | | 22.9 | | 125 | | | | | | | | | |
| Okinawa | *Sepia Officinalis* | 1.25 | 27.7 | 71.7 | 58.2 | 1.09 | 23.2 | 0.29 | 0.199 | 0.027 | 0.387 | 0.173 | 0.223 | 0.019 | 3.47 | 0.004 | 0.026 | 0.0001 | 0.064 | 0.0012 | 0.0004 | 0.0122 |
| | | 1.20 | 26.8 | 70.3 | 54.0 | 1.15 | | 0.58 | 0.170 | | 0.370 | | | | 3.35 | | | | | | | |
| Okinawa | // | 1.09 | 26.0 | 25.1 | 44.6 | 1.05 | 27.2 | 0.12 | 0.286 | 0.022 | 0.220 | 0.116 | 0.179 | 0.014 | 3.35 | 0.004 | 0.092 | 0.0002 | 0.260 | 0.0003 | 0.0004 | 0.0118 |
| | | 1.08 | 26.1 | 25.3 | 43.7 | 1.17 | | 0.27 | 0.290 | | 0.239 | | | | 4.77 | | | | | | | |
| Submean(ICP-MS) | | 1.17 | 26.8 | 48.4 | 51.4 | 1.07 | 25.2 | 0.21 | 0.243 | 0.025 | 0.304 | 0.144 | 0.201 | 0.017 | 3.41 | 0.004 | 0.059 | 0.0001 | 0.162 | 0.0007 | 0.0004 | 0.0120 |
| CV(%) | | 6.79 | 3.27 | 48.1 | 13.2 | 1.91 | 7.87 | 40.5 | 17.9 | 9.938 | 27.5 | 19.7 | 11.0 | 15.8 | 1.65 | 9.05 | 56.4 | 62.6 | 60.4 | 65.7 | 3.47 | 1.76 |
| Submean(INAA) | | 1.14 | 26.5 | 47.8 | 48.9 | 1.16 | | 0.43 | 0.23 | | 0.305 | | | | 4.06 | | | | | | | |
| CV(%) | | 5.26 | 1.32 | 47.1 | 10.5 | 0.86 | | 36.5 | 26.1 | | 21.5 | | | | 17.5 | | | | | | | |
| Mean(ICP-MS) | | 1.08 | 45.7 | 65.4 | 42.7 | 1.16 | 9.19 | 0.53 | 0.16 | 0.016 | 0.112 | 0.159 | 0.075 | 0.014 | 6.39 | 0.004 | 0.069 | 0.0001 | 0.153 | 0.0014 | 0.0003 | 0.0187 |
| CV(%) | | 31.1 | 48.6 | 67.2 | 35.5 | 14.2 | 75.7 | 82.1 | 86.8 | 65.0 | 84.3 | 99.9 | 79.1 | 88.7 | 89.4 | 34.0 | 71.1 | 113 | 87.8 | 84.4 | 58.5 | 79.5 |
| Mean(INAA) | | 0.98 | 44.4 | 59.1 | 39.0 | 1.21 | | 0.68 | 0.14 | | 0.110 | | | | | | | | | | | |
| CV(%) | | 31.1 | 51.0 | 60.2 | 34.4 | 18.0 | | 63.0 | 96.9 | | 85.3 | | | | | | | | | | | |

*: ICP-MS determination, **: INAA determination -:not detected

Table 3. The concentrations(μg/g) and enrichment factors of trace elements in *Todarodes pacificus* organs as determined by ICP-MS.

| Description | | Mn | Fe | Cu | Zn | Rb | Sr | Ag | V | Cr | Co | Ni | Se | Mo | Cd | Cs | Ba | Tl | Pb | Bi | Th | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Edible part | C | 0.22 | 6.30 | 3.55 | 13.9 | 1.28 | 1.67 | 0.002 | 0.004 | 0.035 | 0.007 | 0.082 | 0.030 | 0.002 | 0.33 | 0.004 | 0.039 | 0.0001 | 0.054 | 0.0000 | 0.0001 | 0.0013 |
| | E | 6687 | 1853 | 27339 | 53593 | 12 | 0.19 | 2246 | 2 | 106735 | 4023 | 165 | 270 | 0.176 | 5914 | 14 | 3339 | 10 | 3701 | 603 | 287 | 0.404 |
| Back bone | C | 0.84 | 9.91 | 28.4 | 152 | 1.17 | 3.31 | 0.001 | 0.088 | 0.090 | 0.048 | 0.171 | 0.275 | 0.062 | 3.75 | 0.004 | 0.106 | 0.0027 | 0.291 | 0.0000 | 0.0001 | 0.0581 |
| | E | 25510 | 2915 | 218743 | 582998 | 11 | 0.38 | 1272 | 44 | 271953 | 26926 | 342 | 2502 | 6.439 | 67000 | 13 | 9021 | 222 | 20091 | 0 | 181 | 18.8 |
| Viscera* | C | 0.90 | 9.26 | 54.5 | 31.2 | 1.55 | 4.50 | 0.077 | 0.033 | 0.047 | 0.038 | 0.069 | 0.030 | 0.004 | 0.30 | 0.012 | 0.053 | 0.0002 | 0.132 | 0.0005 | 0.0002 | 0.0078 |
| | E | 27388 | 2723 | 419113 | 119852 | 15 | 0.51 | 77044 | 16 | 143132 | 20920 | 139 | 273 | 0.431 | 5326 | 38 | 4502 | 17 | 9128 | 6660 | 325 | 2.53 |
| Liver | C | 1.17 | 161 | 101 | 68.3 | 1.23 | 2.53 | 1.85 | 0.920 | 0.080 | 0.510 | 0.470 | 0.310 | 0.018 | 39.49 | 0.004 | 0.078 | 0.0006 | 2.150 | 0.0020 | 0.0004 | 0.0027 |
| | E | 35455 | 47474 | 779923 | 262692 | 12 | 0.29 | 1850000 | 460 | 242424 | 283333 | 940 | 2818 | 1.875 | 705179 | 13 | 6667 | 49 | 148276 | 27397 | 800 | 0.87 |
| Others** | C | 5.17 | 92.3 | 20.6 | 49.5 | 1.22 | 40.7 | 0.058 | 0.317 | 0.112 | 0.034 | 0.118 | 0.090 | 0.007 | 1.28 | 0.006 | 0.967 | 0.0002 | 0.152 | 0.0006 | 0.0013 | 0.0202 |
| | E | 156667 | 27159 | 158653 | 190278 | 12 | 4.62 | 58269 | 159 | 338635 | 18906 | 236 | 816 | 0.708 | 22821 | 22 | 82634 | 19 | 10490 | 7940 | 2520 | 6.51 |

*: not including liver, and stomach with diets **: stomach including diets C: concentration E: enrichment factor

### 3) Distributions of trace elements in squid organ and concentration factor

Examination of tissue-specific distributions of trace elements in fish organ and concentration factor would be extremely informative in estimating the environmental contamination as well as artificial radionuclide's behavior in marine ecosystem. *Todarodes pacificus* collected in 1996 was divided into edible part, backbone, liver, stomach including diets and other viscera, and trace elements in each organ were analyzed using ICP-MS and concentration factors for all metals were calculated from the concentrations of those in sea water(Nozaki, 1987)(table 3).

It is well known that liver is a very important organ in living organisms and have lots of metallo-enzymes. The concentrations and concentration factors of Fe(161 μg/g, 4.8 x $10^4$) Cu(101 μg/g, 7.8 x $10^5$), Zn(68.3 μg/g, 2.6 x $10^5$), V(0.92 μg/g, 460), Co(0.51 μg/g, 2.8 x $10^5$) and Se(0.31 μg/g, 2.8 x $10^3$) being very essential for enzyme functions in liver were higher than in other organs, which were consistent with the report of Ueda *et al.*(1979). In addition, the concentration of Cd(39.5 μg/g, 7.0 x $10^5$), Ag(1.85 μg/g, 1.85 x $10^6$), Pb(2.15 μg/g, 1.4 x $10^5$) and Bi(2 ng/g, 2.7 x $10^4$) in liver were highly accumulated and thus, very high concentration factors were calculated. On the other hand, the concentrations and concentration factors of Mn(stomach and diets: 2.15 ug/g, 1.4 x $10^5$), Cr(0.112 ug/g, 3.4 x $10^5$) and Ba(0.97 ug/g, 8.3 x $10^4$) in the viscera not including liver also were rather high. Therefore, it is suggested that the characteristic distribution patterns of trace elements in squid organs offer the possibility of its application to study of marine environments and squid viscera can be a good indicator organ in estimating the marine environment.

### 4) $^{60}$Co, $^{108m/110m}$Ag, and $^{137}$Cs determination in squids

Since the artifical radionuclides $^{60}$Co, $^{108m/110m}$Ag and $^{137}$Cs are important indicators of radioactive pollution in marine ecosystem(Folsom and Young, 1965; Folsom *et al.*, 1970; Fukatsu *et al.*, 1982; Fukatsu and Higuchi, 1985 and 1987; Umezu ,1992), the concentrations of $^{60}$Co, $^{108m/110m}$Ag and $^{137}$Cs in three varieties of squids were measured. As shown in table 4, 5, 6 and 7, radioactivities of $^{60}$Co, $^{108m/110m}$Ag and $^{137}$Cs depending on species and sampling location were different. Interestingly, the level of $^{108m}$Ag activities in squids collected after

**Table 4. Stable Co concentration, $^{60}$Co activity and Co specific activity in squids taken from Japan near-seas.**

| Location | Collection date | Variety | $^{60}$Co (mBq/kg wet) | | Stable Co (mg/kg wet) | Specific activity (Bq/g Ag) |
|---|---|---|---|---|---|---|
| | | | A* | B** | | |
| Hokkaido | Nov. 10, 86 | *Todarodes pacificus* | 18.9 | 5.67 | 0.141 | 40 |
| Hokkaido | Nov. 11. 88 | *Todarodes pacificus* | 12.6 | 4.94 | 0.097 | 51 |
| Miyagi | Sept. 19, 88 | *Todarodes pacificus* | 11.8 | 4.54 | 0.200 | 23 |
| Chiba | June 30, 86 | *Todarodes pacificus* | 24.4 | 7.00 | 0.065 | 108 |
| Chiba | July 3, 88 | *Todarodes pacificus* | 29.2 | 10.9 | 0.105 | 104 |
| Niigata | July 13, 81 | *Todarodes pacificus* | 51.1 | 7.62 | 0.065 | 117 |
| Niigata | June 29, 88 | *Todarodes pacificus* | 25.2 | 7.21 | 0.108 | 67 |
| Niigata | June 27, 88 | *Todarodes pacificus* | 13.0 | 4.82 | 0.087 | 56 |
| Fukui | Oct. 9, 86 | *Loligo edulis* | 7.4 | 2.20 | 0.018 | 121 |
| Okinawa | July 4, 86 | *Sepia officinalis* | 40.7 | 11.7 | 0.346 | 34 |
| Okinawa | July 19, 88 | *Sepia officinalis* | 47.0 | 17.6 | 0.239 | 74 |

*: Activity at sampling date
**: Activity decay-corrected to Jan. 1. 1996

**Table 5. Stable Ag concentration, $^{110}$mAg activity and Ag specific activity in squids taken from Japan near-seas.**

| Location | Collection date | Variety | $^{110m}$Ag (mBq/kg wet) | | Stable Ag (mg/kg wet) | Specific activity (Bq/g Ag) |
|---|---|---|---|---|---|---|
| | | | A* | B** | | |
| Hokkaido | Nov. 10, 86 | *Todarodes pacificus* | 10,730 | 1.101 | 0.91 | 1.21 |
| Hokkaido | Nov. 11. 88 | *Todarodes pacificus* | 70.3 | 0.056 | 0.67 | 0.08 |
| Miyagi | Sept. 19, 88 | *Todarodes pacificus* | 181 | 0.120 | 1.24 | 0.10 |
| Chiba | June 30, 86 | *Todarodes pacificus* | 4,070 | 0.290 | 0.64 | 0.45 |
| Chiba | July 3, 88 | *Todarodes pacificus* | 218 | 0.117 | 1.10 | 0.11 |
| Niigata | July 13, 81 | *Todarodes pacificus* | 185 | 8.990 | 0.88 | 0.00 |
| Niigata | June 29, 88 | *Todarodes pacificus* | 9,620 | 0.683 | 1.41 | 0.49 |
| Niigata | June 27, 88 | *Todarodes pacificus* | 185 | 0.098 | 1.39 | 0.07 |
| Kagoshima | June 22, 86 | *Loligo edulis* | 229 | 0.016 | 0.22 | 0.07 |
| Fukui | Oct. 9, 86 | *Loligo edulis* | 1,147 | 0.108 | 0.24 | 0.46 |
| Nagasaki | June 18, 88 | *Loligo edulis* | 340 | 0.023 | 0.17 | 0.14 |
| Okinawa | July 4, 86 | *Sepia officinalis* | 1,295 | 0.093 | 0.58 | 0.16 |

*: Activity at sampling date

**: Activity decay-corrected to Jan. 1, 1996

**Table 6. Stable Ag concentration, $^{108}$mAg activity and Ag specific activity in squids taken from Japan near-seas.**

| Location | Collection date | Species | $^{108m}$Ag (mBq/kg wet) | | Stable Ag (mg/kg wet) | Specific activity (Bq/g Ag) |
|---|---|---|---|---|---|---|
| | | | A* | B** | | |
| Hokkaido | Nov. 11. 88 | *Todarodes pacificus* | 34.0 | 32.7 | 0.67 | 49 |
| Chiba | July 3, 88 | *Todarodes pacificus* | 74 | 71.0 | 1.10 | 65 |
| Niigata | July 13, 81 | *Todarodes pacificus* | 44.4 | 41.0 | 0.88 | 47 |
| Kagoshima | June 22, 86 | *Loligo edulis* | 229 | 217 | 0.22 | 990 |
| Nagasaki | June. 18, 88 | *Loligo edulis* | 340 | 323 | 0.17 | 1,901 |
| Okinawa | July 4, 86 | *Sepia officinalis* | 74 | 70.3 | 0.58 | 120 |

*: Activity at sampling date

**: Activity decay-corrected to Jan. 1, 1996

**Table 7. Stable Cs concentration, $^{137}$Cs activity and Cs specific activity in squids taken from Japan near-seas.**

| Location | Collection date | Variety | $^{137}$Cs (mBq/kg wet) | | Stable Cs (mg/kg wet) | Specific activity (Bq/g Ag) |
|---|---|---|---|---|---|---|
| | | | A* | B** | | |
| Hokkaido | Nov. 10, 86 | *Todarodes pacificus* | 66.6 | 54.0 | 0.004 | 13,496 |
| Hokkaido | Nov. 11. 88 | *Todarodes pacificus* | 32.2 | 27.3 | 0.003 | 9,115 |
| Miyagi | Sept. 19, 88 | *Todarodes pacificus* | 111 | 93.9 | 0.005 | 18,780 |
| Niigata | July 13, 81 | *Todarodes pacificus* | 62.9 | 45.1 | 0.003 | 15,037 |
| Okinawa | July 4, 86 | *Sepia officinalis* | 88.8 | 71.4 | 0.004 | 17,849 |

*: Activity at sampling date

**: Activity decay-corrected to Jan. 1, 1996

Chernobyl accident in April 1986 were increased. The accumulation was much more in *Todarodes pacificus*, a migratory squid than in *Loligo edulis* and *Sepia officinalis*, sedentary ones. However, $^{110m}$Ag(127.7 y) activities having longer physical half life were higher in *Loligo edulis* than other squids. It seemed to be closely related to regional level of $^{110m}$Ag in marine environment.

Unlike $^{108m/110m}$Ag, $^{60}$Co levels in squids were generally decreased year by year. *Sepia officinalis* has higher $^{60}$Co activity than *Todarodes pacificus* and *Loligo edulis*. On the other hand, $^{137}$Cs specific activities in squids were 10 - 100,000 times higher than those of $^{60}$Co or $^{108m/110m}$Ag.

## 4. CONCLUSION

This study shows that the inductively coupled plasma-mass spectrometry (ICP-MS) can be used for the simultaneous determination of 21 trace elements in squid. In the practical ICP-MS measurement of squid ash samples, corrections for spectral interferences caused by polyatomic ions of $Cl(^{35}Cl^{16}O^{+}$ on $^{51}V$ and $^{40}Ar^{37}Cl^{+}$ on $^{77}Se$) were not required. Since there was a good relation between ICP-MS and INAA in the determination of V, Mn, Fe, Co, Cu, Zn, Rb, Ag and Cd, ICP-MS is thought to be a reliable technique for the trace element analysis of squids.

The different chemical composition between two varieties was observed; high concentrations of Fe, Cu, Zn, Ni, Mo, Cd, Pb and U in *Todarodes pacificus*, a migratory squid and of Sr, V, Co, and Se in *Sepia officinalis*, a sedentary one. The change of Cd values in squid samples from different sampling sites might be caused due to the possible contamination of their environment.

The analytical data for the stable isotopes measured by ICP-MS were closely correlated with the results of radioactive counting of $^{60}$Co, $^{110m}$Ag and $^{137}$Cs by gamma spectrometry.

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