Application of instrumental neutron activation analysis for the analysis of six fish species.

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1. Introduction

Fish is consumed by humans because of its high protein content, low saturated fat and other nutritional benefits. According to the meeting report of the Food and Agriculture Organization (FAO) [1], annual food fish supply per capita has increased from an average of 9.9 kg in the 1960s to 18.4 kg in 2009, and fish consumption was lowest in Africans (9.1 kg per capita), while Asians consumed 20.7 kg per capita. From the viewpoint of food safety, fish accumulates environmental contaminants and an analysis of hazardous chemical species including toxic heavy metals is important for human health. The aims of this study were to determine the inorganic elemental content in six popular fish species of Korea by NAA and to aid in the evaluation of dietary intake levels in terms of toxic and essential elements.

2. Experiments

2.1 Sampling and Sample Preparation

Six kinds of fish species, i.e., hairtail, mackerel, pacific saury, frozen pollack, squid and yellow croaker, were chosen and purchased from a commercial market. The preparation of analytical samples was as follows ; i) cut the edible part (e.g. flesh) of fish, ii) clean the fish samples of edible parts with de-ionized water, iii) grind the cleaned fish samples using a high speed blender made of titanium blade, iv) freeze-dry at –60 ^{o}C for 72 hours, v) homogenize the freeze-dried samples using an agate motar or variable speed rotor mill and make a fine powder. The weights of the fish samples before and after freeze-drying were measured and recorded.

2.2 Instrumental Neutron Activation Analysis

Approximately 50 mg of fish sample for short-lived nuclides and 800 mg for long-lived nuclides were put into polyethylene vials and irradiated by neutrons for 60 s and 4 hrs, respectively. The irradiation hole used was NAA#2 at the HANARO research reactor. For the measurement of the gamma-rays emitted from the irradiated samples, an HPGe detector (EG&G Ortec, 40% relative efficiency, FWHM 1.85 keV at 1332 keV of ^{60}Co) coupled to DSPEC^{PLUS} was used. The elemental contents in the samples were calculated using a software program, POWER NAA, which was developed for a fast and comfortable calculation of the INAA. The analytical conditions are shown in Table 1. For the analytical quality control, NIST SRM 1566b-Oyster Tissue and 1577b-Bovine Liver were analyzed under the same conditions as the fish samples.

Table 1. Analytical conditions of INAA for fish samples

Division	Irradiation time	Decay time	Counting time	Nuclides detected
Short	60s	5, 40 min	500, 1200 sec	^{49}Ca , ^{38}Cl, ^{27}Mg, ^{56}Mn,
Long-1st Detection	4hrs	6~7 days	10000 sec	^{76}As, ^{82}Br, ^{42}K, ^{24}Na
Long-2nd Detection	4hrs	More than 20 days	40000 sec	^{60}Co, ^{51}Cr, ^{134}Cs, ^{59}Fe, ^{203}Hg, ^{86}Rb, ^{75}Se, ^{65}Zn

3. Results and Discussion

3.1 Analytical Quality Control

Fourteen elements from NIST SRM 1566b-Oyster Tissue and 1577b-Bovine Liver were determined using the INAA method. The results are shown in Fig. 1. The relative errors for most of the elements determined are within 15% excluding a few elements that have refernce values.

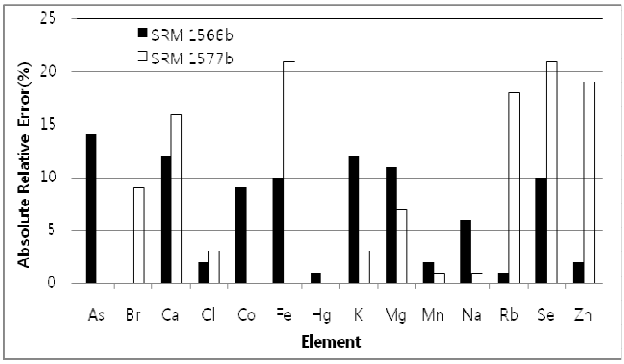

Fig.1. Relative error of 14 elements in NIST SRMs by INAA

3.2 Analytical Results of Fish Samples

Sixteen elements from six fish species were determined and are summarized in Table 2. Heavy metals are generally categorized as toxic and probably toxic and essential elements. For instance, As and Hg are toxic elements, even in trace levels and Cr, Se, and Zn are essential elements, but excessive intake causes adverse health effects [2]. If the moisture content is taken into account, the level of elemental contents for heavy metals of As, Cr, Hg are 0.82 ~ 2.18 mg/kg, 0.11 ~ 0.37 mg/kg, and 0.009 ~ 0.031 mg/kg, respectively.

Minerals of Ca, Fe, Se, Zn are 52 ~ 640 mg/kg, 1.5 ~ 23.6 mg/kg, 0.24 ~ 0.53 mg/kg, and 4.85 ~10.35 mg/kg, respectvely.

Table 2. Analytical results of fish species. (unit : wet mg/kg)

Element	Hairtail	Mackerel	Pacific Saury	Frozen Pollack	Squid	Yellow Croaker
As	1.32	1.25	1.53	1.47	2.18	0.82
Br	4.95	7.26	8.69	9.24	7.02	4.19
Ca	251	103	640	145	52	452
Cl	1042	3836	3460	2100	1729	823
Co	0.0013	0.0044	0.0148	0.006	0.0029	0.0081
Cr	0.11	0.16	0.3	0.37	0.17	0.11
Cs	0.0209	0.0131	0.0078	0.0317	0.0052	0.0075
Fe	1.84	6.49	23.63	11.65	1.51	3.17
Hg	0.0234	0.0197	0.0308	0.0186	0.0156	0.0094
K	3742	2724	1802	3653	2830	1708
Mg	271	342	398	212	292	146
Mn	0.11	0.13	0.28	0.12	0.091	0.072
Na	657	2536	2493	1387	937	697
Rb	0.68	0.49	0.35	0.83	1.14	0.3
Se	0.26	0.53	0.41	0.24	0.27	0.29
Zn	5.86	7.18	9.78	8.56	10.35	4.85

3.3 Application for the Assessment of Heavy Metal Intake by Fish Consumption.

The Korean National Health and Nutrition Examination Survey (KNHANES) was carried out in 2010 [3]. In accordance with the survey report, Koreans consume 4.55 g/day of hairtail, 1.42 g/day of mackerel, 1.78 g/day of pacific saury, 0.17 g/day of frozen pollack, 0.07 g/day of squid, and 0.04 g/day of yellow Croaker, respectively. In addition, an average amount of fish intake at one time are 39.7 g for hairtail, 56.3 g for Mackerel, 61.4 g for Pacific saury, 74.9 g for frozen Pollack, 44.9 g for Squid and 62.1 g for yellow Croaker. Based on these survey data, intake levels for 3 toxic heavy metals by each fish species can be evaluated for Koreans, and the results are shown in Table 3.

Table 3. Evaluation of intake levels for 3 heavy metals by 6 fish species (unit : μg)

Fish/Element	As	Cr	Hg
Hairtail	53(6.02)	4.31(0.49)	0.93(0.11)
Mackerel	70(1.77)	9.21(0.23)	1.11(0.03)
Pacific Saury	94(2.72)	18.43(0.53)	1.89(0.05)
Frozen Pollack	110(0.25)	28.01(0.06)	1.39(0.003)
Squid	98(0.15)	7.47(0.01)	0.70(0.001)
Yellow Croaker	51(0.03)	6.88(0.004)	0.58(0.0004)

*Values in parenthesis stand for an average amount of daily intake

Due to the high daily consumption rate, the level of average daily intake for heavy metals from hairtail is dominant. On the contrary, intake by yellow croaker is very low. In terms of the amount of fish intake at once, the amount of highest intake for 3 heavy metals is 110 μg of As and 28.0 μg of Cr by frozen pollack, and 1.89 μg of Hg by pacific saury. These dietary intake values for heavy metals can be used for an assessment of human health risk by a comparison with the guideline values of the U.S. Environmental Protection Agency (EPA) and of the Joint FAO/WHO Committee on Food Additives (JECFA).

4. Conclusions

An INAA for the six fish species that are popular in Korea was performed, and sixteen elemental contents were determined. Based on these analytical data and survey data in 2010, intake levels for 3 toxic heavy metals by each fish species are evaluated for Koreans. These dietary intake values for heavy metals can be used for an assessment of human health risk.

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