Journal of the Korean Nuclear Society
Volume, 8, Number 1, March, 1976

A Study on the Present Levels of Mercury and Other Trace Elements in Some Fresh-water Fish by Neutron Activation Analysis

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(Recd. Jan 27, 1976)

Abstract

A nondestructive, instrumental neutron activation analysis using a Ge(Li) detector is applied to investigate the present levels of mercury and other trace elements in some fresh-water fish. The results show large variations of mercury content which are indicative of important local sources and indicate the inter-dependence relations between two of some trace elements. Analytical results for mercury in antracites are also given with the concern for their combustion as one of major causes of the mercury pollution.

요 약

Ge(Li) 檢出機를 使用한 非破壞 放射化分析法을 利用하여 淡水魚中 水銀 및 其外 미량원소들의 現在 함량 준위를 調査하였다. 分析結果에 依하면 地域에 따라 水銀의 含量이 크게 變하였으며 이變化는 아마 地域的인 汚染源에 依한 것으로 생각된다. 그리고 分析結果로 부터 미량원소들 중 어떤 元素들 사이에는 뚜렷한 相關關係가 있음을 알았다. 水銀 汚染의 重要한 原因으로 無煙炭 燃素가 考慮될 수 있을 것으로 생각되어 數種의 無煙炭을 分析하였다.

1. Introduction

After Minamata incidents in Japan[1] and the discovery of high mercury levels in wild birds and fish in Sweden[2], it is highly desirable to assess natural baseline levels of toxic trace elements and to search elevated levels and their causes.[2] Neutron activation analysis is known as one of the ideal techniques for that purpose even though the techniqe cannot give any information on molecular states of various pollutants.[3]

In this work, an attempt has been made to apply the nondestructive, instrumental neutron activation analysis (INAA) in order to investigate the levels of mercury and other trace elements in fresh-water fish. The results showed large variations of mercury which were indicative of important local sources and indicated the interdependence

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relations between two of some trace elements. Analytical procedures for mercury content in anthracites were also described with the concern for their combustion as one of major causes of the mercury pollution.[2)]

2. Materials and Methods

2.1. Reagents

Mixed standard solution: An approximate 100-mg weight of each metal or metal oxide (specpure, Johnson and Matthey) was accurately weighed, dissolved in about 2 ml of hot concentrated nitric acid and finally diluted to 100 ml. A 10-ml aliquot of the solution was diluted to 100 ml with distilled water. The resultant solution contains 100μg of each metal per ml. Mixed standard solutions containing 0.1—10 μg of each metal per 10 ml were prepared from these solution. Neutron flux monitor: An accurately weighed piece of cobalt metal was dissolved in dilute nitric acid. After diluting to a finite volume with the distilled water, a 100 λ volume of the soluting (1 mg per ml) was pipetted onto a polyethylene sheet and dried under an infra-red lamp. After folding, the sheet was used as the monitor.

2.2. Sample preparation and irradiation.

Carp and crucian were collected directly from sampling sites with the exception of snakehead. The snakeheads were collected through the Cooperative Union of the Agricultural and Marine Products in Seoul. Fig. 1 shows the sampling sites for fish along the Han River. Species taken for the analysis along the river were crucian and carp. Fish were cut into pieces with a plastic knife. Axial muscles were taken and used for the investigation. The pieces of muscles were washed several times with distilled water, transferred into polyethylene bags and dehydrated by drying for 3 days in a thermovac freeze unit, Virtis Model 10—45 MR-TR. Anthracite samples were supplied by a related association and dryed in a desicator.

A 0.5—1 g weight of each sample and a 1-ml volume of the mixed standard solution were heat-sealed in silica vials. Silica vials were cleaned by washing with 6 N hot nitric acid and then with redistilled water before

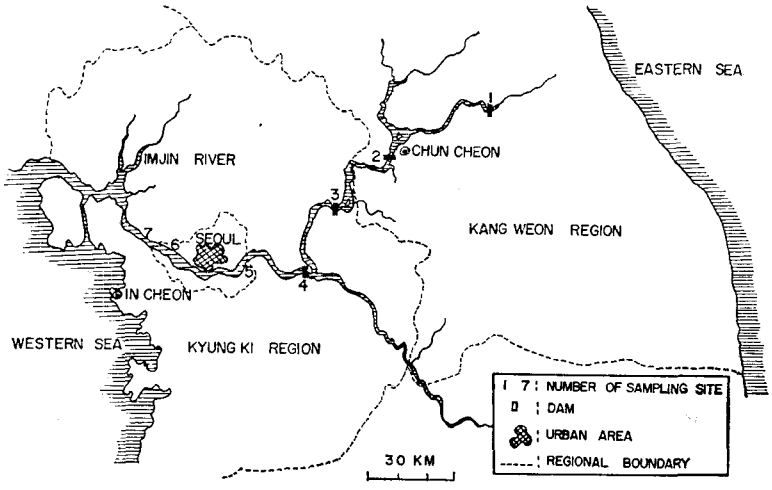

Fig. 1. The sampling sites along the Han River.

use. A cobalt monitor was attached on the outside wall of each vial. The vials were irradiated for 3 days in the thermal neutron flux of 1×10^{13}n · cm^{-2} · sec^{-1}, using the rotary specimen rack of TRIGA mark Ⅲ reactor.

2.3. Gamma-ray spectrometry

After cooling for 2 weeks, each irradiated silica ampoule was counted without opening, because the background of this ampoule was impurity free. Gamma counting was done by using a coaxial lithium-drifted germanium detector (Nuclear Diodes Model LGCC-7.0-2.3) and a 4000 channel analyzer (Nuclear Data Model 2200). The system resolution was less than 2.3ke*V* (FWHM at 1.33 meV of ^{60}Co), with a peak-to-compton ratio of 19:1.

Punch paper tape output from the multichannel analyzer was fed to CDC Cyber computer at KIST (The Korea Institute of science and Technology). The SAMPO program described by Routti and Prussin[4, 5] and developed further by Carder and Filmore[6], had been brought with an IAEA expert and used in this work. This program found the peak in a gamma-ray spectrum, determined the shape and area of each peak, and also carried out energy and efficiency calibrations. The decay-corrected peak areas were then used to determine elemental abundances in the samples as compared to the mixed standard solution.

2.4. Interference corrections

In the present work, much attention was devoted to the accurate determination of mercury and selenium, because these elements are designated as "very hazardous". When analyzing mercury content in fish, the selenium interference on mercury was found. Therefore, an attempt was made to use the SAMPO program in order to resolve the multiplet which consisted of 279.1 keV peak of ^{203}Hg and 279.6 keV peak of ^{75}Se. However, this attempt was failed because of too much similarity in the energies. As a result, the correction for the selenium interference on mercury was made by using 264.6 keV peak area of ^{75}Se, the calibrated efficiency curve of the detector and gamma-ray abundances of ^{75}Se.

When determining mercury in anthracites, it was found that not only did 279.6 keV peak of ^{75}Se interfered with 279.1 keV peak of ^{203}Hg, but also the 264.1 keV peak of ^{182}Ta interfered with 264.6 keV peak of ^{75}Se, which was used for the selenium correction on ^{203}Hg. On the other hand, 282.6 keV peak of ^{175}Yb did not interfere with 279.1 keV peak of ^{203}Hg and 262.4 keV peak of ^{169}Yb did not interfere with the 264.6keV peak of ^{75}Se, in contrast with the Sheibley's case[7]. The correction for ^{182}Ta interference on the 264.6 keV peak of ^{75}Se was made by using 1121.2 keV peak of ^{182}Ta, the calibrated efficiency curve of the detector and relative gamma-ray abundances of ^{182}Ta. The corrected 264.6 keV peak area of ^{75}Se was then used to correct the selenium interference on 279.1 keV peak of ^{203}Hg as described above for the analysis of fish.

This procedure was tested by irradiating and analyzing a known synthetic mixture. The values obtained were in agreement with those of the known sample.

3. Results and Discussion

When the irradiated fish samples were cooled for several days, the major neutron activation products were ^{24}Na and ^{82}Br but normally high enough concentration of ^{42}K,

Table 1. Analytical Results of Fresh-water Fish (ppm in wet basis)*

Sample number	Name	Sampling site	Ce x10^{-3}	Se x10^{-2}	Hg x10^{-1}	Cr x10^{-2}	Sc x10^{-4}	Fe x10^{0}	Zn x10^{0}	Ca x10^{1}	Co x10^{-3}	Sb x10^{-3}	Cs x10^{-}	Rb x10^{0}
1	Carp	Soyang, Kangweon	1.1	9.0	0.31	22	3.2	6.3	7.2	8.1	4.3	3.1	4	1.4
2	//	Euyam, //	4.7	11	0.41	3.6	2.9	4.5	5.8	3.1	4.3	5.0	4.9	1.4
3	Crucian	Chungpyung, //	3.2	9.2	0.32	5.8	1.8	2.9	4.0	3.2	3.1	2.3	3.2	0.95
4	Carp	Paldang, //	2.0	9.0	1.4	4.9	0.97	6.8	13	7.2	3.4	2.5	4.3	1.4
5	//	Kwangnaru, Seoul	2.5	12	1.5	4.0	3.6	2.7	5.0	3.4	3.1	4.3	2.9	1.5
6	//	2nd Bridge, //	4.0	8.8	4.9	70	2.3	9.5	5.0	8.6	5.0	11	14	2.2
7	Crucian	Kimpo, //	40	8.1	5.2	7.4	4.5	9.0	17	4.5	7.2	9.0	8.8	2.2
8	Snakehead	Suweon Kyungki	4.3	11	1.8	4.7	3.8	4.5	3.1	5.4	12	16	14	4.9
9	//	Kwangchun, Chungnam	9.2	9.7	6.3	3.1	2.3	2.3	4.0	1.8	7.9	7.6	14	2.3
10	//	Onyang, //	2.9	9.0	2.9	4.0	4.9	5.4	5.4	6.5	7.0	6.7	5.2	2.9
11	//	Buan, Chunbuk	3.4	11	1.6	9.5	2.9	6.5	4.3	8.3	8.8	10	14	3.2
12	//	Iri, Chunbuk	4.1	17	3.1	5.6	4.5	7.6	4.5	8.6	12	11	16	5.0
13	//	Suchun, Cungnam	2.0	9.5	0.65	5.0	5.2	6.7	2.5	9.0	12	9.7	10	2.2

* The samples had been collected for the duration of 1973~1975.

Table 2. Analytical Results of the Standard Kale Powder (ppm)

	Ce x^{0} ^{1}	Se x10^{-1}	Hg x10^{-1}	Cr x10^{-1}	Sc x10^{-3}	Fe x10^{2}	Zn x10^{1}	Ca x10^{4}	Co x10^{-2}	Sb x10^{-2}	Cs x10^{-2}	Rb x10^{1}
Values reported by Bowen	3.0	1.20	1.663	3.274	8.24	1.201	3.274	4.0841	5.85	6.9	7.42	5.201
Result of this work	3.2±0.6	1.1±0.4	1.6±0.5	3.2±0.2	8.9±0.9	0.96±0.04	3.1±0.1	4.3±0.1	5.9±0.1	6.5±0.7	7.3±0.4	5.2±0.2

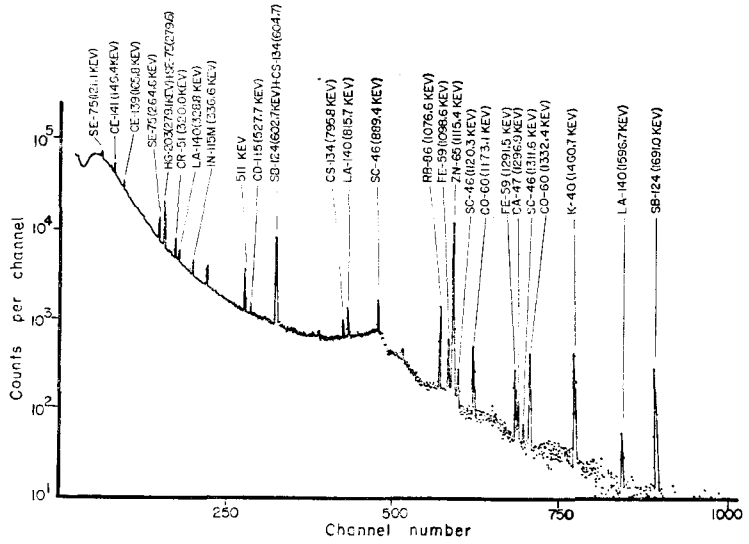

Fig. 2. Gamma-ray spectrum of neutron activated fresh-water fish. Irr. time: 3 days; count time: 1000 sec; decay interval: 15 days.

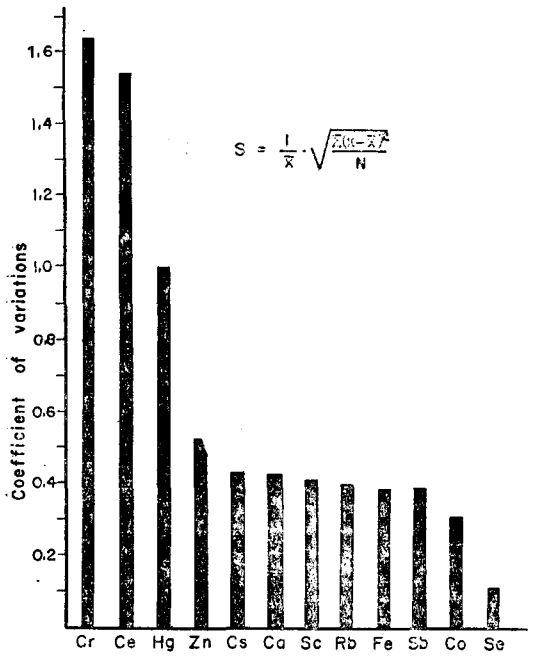

Fig. 3. Coefficient of variaton of the elements in the fresh-water fish of the Han River.

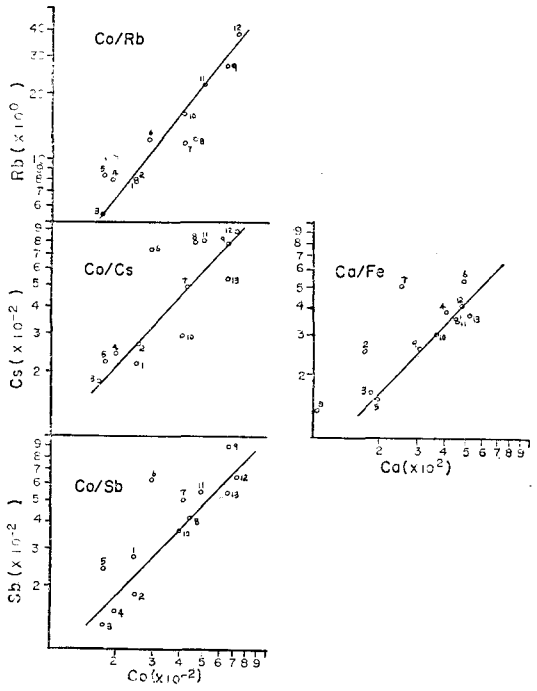

Fig. 4. Relationships between Co, Sb, Cs, Rb, Ca and Fe in fresh-water fish (g/g)

^{76}As and ^{64}Cu were also found for accurate measurements. In this work, however, only long-lived neutron activation products were measured with an attention to the determination of mercury. In Fig. 2, a typical gamma-ray spectra obtained from the irradiated fresh-water fish is shown. Analytical results are tabulated in Table 1 for fresh-water fish. The results for the mercury content of fish in Table 1, which were ob-

Table 3. Analytical Results of Anthracite (ppm)

Sample number	Name of mine	Ce	Th	Cr	Hf	Cd	Sc	Fe	Ta	Co	Eu	Sb	Hg
1	Dongwon	100	64	29	10	220	770	12000	3.0	3.8	0.93	1.1	1.1
2	Jamiwon	130	110	58	16	160	1160	13000	6.4	3.2	1.4	1.8	1.1
3	Hwangji	150	66	39	11	230	780	25000	3.2	4.4	1.2	1.4	0.84
4	Ujin	72	40	38	5.9	140	580	19000	2.0	5.2	0.86	0.70	1.3
5	Dangmok	120	64	29	9.1	190	690	15000	3.4	3.0	1.1	0.66	1.0
6	Hambaik	140	72	34	14	200	750	19000	4.0	3.4	1.0	0.65	1.3

tained by INAA, were in agreement with the previous values determined by using the Sjöstrand method[8]. The standard sample of Bowen's dried kale powder was further analyzed in order to provide a running check of the method. The analytical results of the kale are in agreement with the values reported by Bowen[9], as shown in Table 2. Among the sampling sites along the Han River shown in Fig. 1, the Soyang Lake(site No. 1) is the farthest spot from industrialized areas and is one of the least polluted areas in this investigation. The five fish from the lake had a mean of 0.031ppm(wet basis) mercury with a range of 0.021-0.060, which are near the lower limit (—0.04 ppm) of mercury concentration naturally occurring in fish[10]. The four fish from Kimpo (site No. 7) had mean of 0.52 ppm(wet basis mercury with a range of 0.36-0.55 ppm. This value is higher than those from Soyang by a factor of about 17.

It was reported[8] that mercury content increases from crucian and carp to snakehead by an approximate factor of 6. Ecologists suggested that the high mercury content of snakehead arises from its habit of feeding on fish. The analysis of snakeheads here by INAA were in agreement within 15% with the values obtained previously by the Sjöstrand method which included chemical procedures[8].

Fig. 3 shows the coefficient of variation, S, over the whole sampling areas along the Han River for each element. It may be calculated as follows,

$$S=\frac{1}{\bar{X}}\cdot\sqrt{\frac{\sum_{1}^{N}(X-\bar{X})^2}{N}}$$

where N, x_i and $\bar{x}$ are respectively the number of sites, the concentration at a partic ular site i, and the arithmatic mean concentration. It can be seen from Fig. 3 that elements Cr, Ce and Hg show large variation indicative of important local sources, while the concentrations of the element selenium vary only to a comparatively small content over the areas. Fig. 4 shows the existing interdependence of the concentrations (g/g) of some trace element(Co/Rb, Co/Cs, Co/Sb and Ca/Fe) in the freshwater fish.

Among the various mercury sources, combustion of anthracites could be considered as one of major causes of pollution, especially near urban areas like Kimpo(site No. 7). In Fig. 5 a typical gamma-ray spectra obtained from the irradiated anthracites is shown. Analytical results are tabulated in Table 3 for anthracites. The accuracies of these data were checked by analyzing the known synthetic mixture which was similar

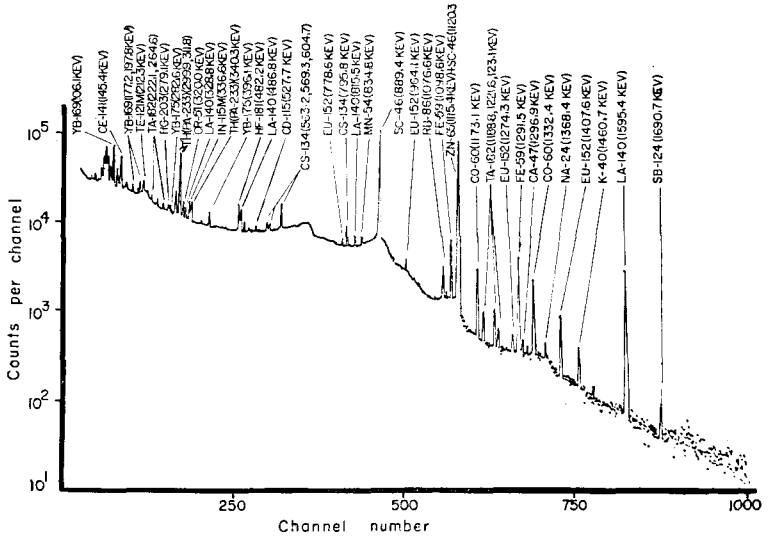

Fig. 5. Gamma-ray spectrum of neutron activated anthracite. Irr. time:3 days; count time: 1000 sec; decay interval: 15 days.

to anthracites in compositions. It was reported that the mercury from fly ash and/or flue gas was continuously input to streams and converted to the more toxic form by microorganisms[10]. The anthracite comsumption in Seoul was 6.43×10^6 tons in 1974[11]. Assuming 1 ppm mercury content in anthracite from Table 3 and 50% mercury loss in exhaust gas from the stacks of houses, 6.43×10^6 tons of anthracite consumed annually in Seoul corresponds to a release of such large amounts as 3.22 tons of mercury. It is highly desirable to know in detail the fate of potentially harzardous trace substances like mercury.

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