TRACE ELEMENTS IN THE HAIRS OF WINTERING MEMBERS OF THE 13TH JAPANESE ANTARCTIC RESEARCH EXPEDITION

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Abstract: The concentrations of six trace elements, Hg, Au, Cu, Zn, Sb and Br, in the hairs collected from 10 members of the wintering party of the 13th Japanese Antarctic Research Expedition (1971-1973) during their stay in Antarctica, were measured by neutron activation analysis.

The mercury concentration in the hair decreased and its distribution range became narrower during one year-long stay in Antarctica. And its concentration increased and scattered over a wide range again after the party members returned to Japan.

The extremely high concentration of antimony suggests that the hair was contaminated by enviromental pollution on board the icebreaker FUJI.

No obvious trend was found in the concentrations of other elements during the stay in Antarctica.

1. Introduction

Neutron activation analysis is the most useful method for the determination of trace elements in biological samples, because of its sensitivity, specificity and nondestructive nature.

This method has revealed the accumulation of poisonous elements such as mercury and arsenic into the hair by metabolic processes. A representative work in this field was the analysis of arsenic in Napoleon Bonaparte's hair performed by FORSHUFVUD *et al.* (1961, 1964). Their results indicated that he was probably poisoned by arsenic.

Also, the mercury content in the hair is an important indication of its intake by the human body. A great many investigations of the mercury content in the hair have been performed, especially by Japanese researchers, in view of the increasing national concern for the environmental pollution by mercury.

The environmental research in Antarctica was planned by the Japanese Antarctic Research Expedition since 1973. The measurement of trace elements in the hair samples collected from the members of the wintering party was adopted in this new project, and the authors were entrusted with the task of measurement.

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2. Experimental

2.1. Sampling of hair and washing of the samples

The hair samples, obtained by usual hair-cut, of 10 members of the 13th Japanese Antarctic Research Expedition (1971–1973) were collected once before the departure, three times during the stay in Antarctica, and one after the return.

The hair was washed to remove most of the adhering dust and oily substance by the following procedures: One gram of the hair was taken into a 200 ml separating funnel, and 100 ml of 2%(v/v) nonionic detergent solution (polyethylene sorbitan mono-oleate) was added. After shaking for 5 minutes mechanically, the detergent solution was removed and then hair was washed three times with 100 ml of deionized water. Finally, the hair was washed with ethanol-acetone (1+1) mixture solution and dried at room tempetature.

2.2. Standard solution

The standard solutions of Hg, Au, Cu, Zn, Sb and Br were prepared by dissolving $HgCl_2$, $HAuCl_4 \cdot 4H_2O$, $CuSO_4 \cdot 5H_2O$, $ZnCO_3$, $C_2H_4(OH)_2(COOK)COOSb \cdot 1/2H_2O$ and KBr into deionized water or acid solution, respectively. The concentration of all these standard solutions was 1 mg/ml.

2.3. Sample preparation and irradiation

The hair sample of 500 mg was put into a small polyethylene bag, which was then heat-sealed. Each standard solution was prepared by pipetting an aliquot of its standard solution on a filter paper (1×1.5 cm) with a microsyringe and drying it carefully under an infrared lamp. Their contents were as follows: Hg: 5 μg, Au: 1 μg, Cu: 10 μg, Zn: 200 μg, Sb and Br: 10 μg. Each standard sample was packaged into a small polyethylene bag. The hair samples and the standard samples were packed together and irradiated in the HTR reactor (Tokyo Atomic Industrial Research Co., Ltd.) for 5 hours at a flux of 2.1×10^{12}n/cm^2·sec, or in the TRIGA II reactor (Institute for Atomic Energy, Rikkyo University) for 5 days (6 hours/day) at a flux of 5×10^{11}n/cm^2·sec.

2.4. Chemical procedure and counting

The irradiated hair was transferred into a 100 ml conical beaker, and 5 ml of concentrated nitric acid was added. The hair was decomposed on the hot-plate. The solution obtained by decomposing the hair was diluted with deionized water to about 6 N nitric acid solution and the solution was then

passed through a HAP column (hydrated antimony pentoxide, 0.5 g, 0.8 cmϕ $\times$10 cm). The effluent was put into a polyethylene bottle and its γ-ray spectrum was measured. By passing the sample solution through a HAP column, ^{24}Na, which is a prevailing isotope in the irradiated hair and interferes the measurement of γ-ray spectra of other isotopes, was completely removed (GIRARDI, 1968). Therefore, the contents of six elements were determined simultaneously by γ-ray spectrometry without further chemical separation.

The γ-ray spectrum of sample was measured with a 48 cm^3 Ge(Li) detector (FWHM : 4.0 keV at 1332 keV) equipped with 4096 channel pulse height analyzer. The amount of each element was determined from the ratio of the

Table 1. Properties of nuclides observable in irradiated hair with Ge (Li) detector.

Element	Nuclide	Half time (hr)	Photopeak for determination (keV)
Cu	^{64}Cu	12.8	511.0
Zn	^{69m}Zn	13.8	438.7
Br	^{82}Br	35.6	776.6
Sb	^{122}Sb	65.8	564.0
Au	^{198}Au	64.8	411.8
Hg	^{197}Hg	65.0	68.8

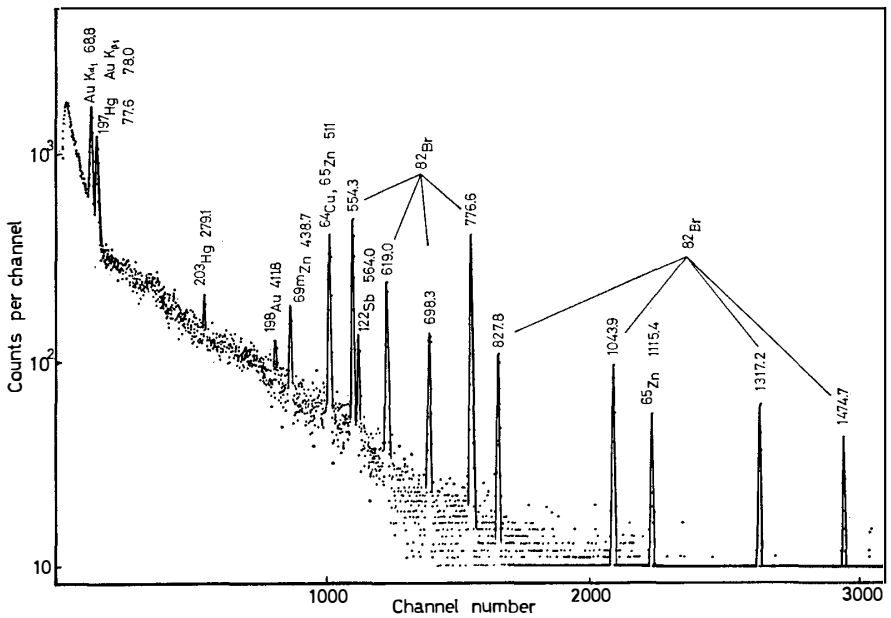

Fig. 1. Gamma-ray spectrum of an irradiated hair sample taken with 48 cm^3 Ge (Li) detector.

peak area of the sample spectrum to that of the corresponding peak in the simultaneously irradiated standard sample.

The properties of nuclides used for determination in this work are shown in Table 1. Fig. 1 shows a representative γ-ray spectrum of the irradiated hair sample.

3. Results and Discussion

It has been considered that the trace elements are introduced into the hair by metabolic processes and adsorbed on the hair by external contamina-

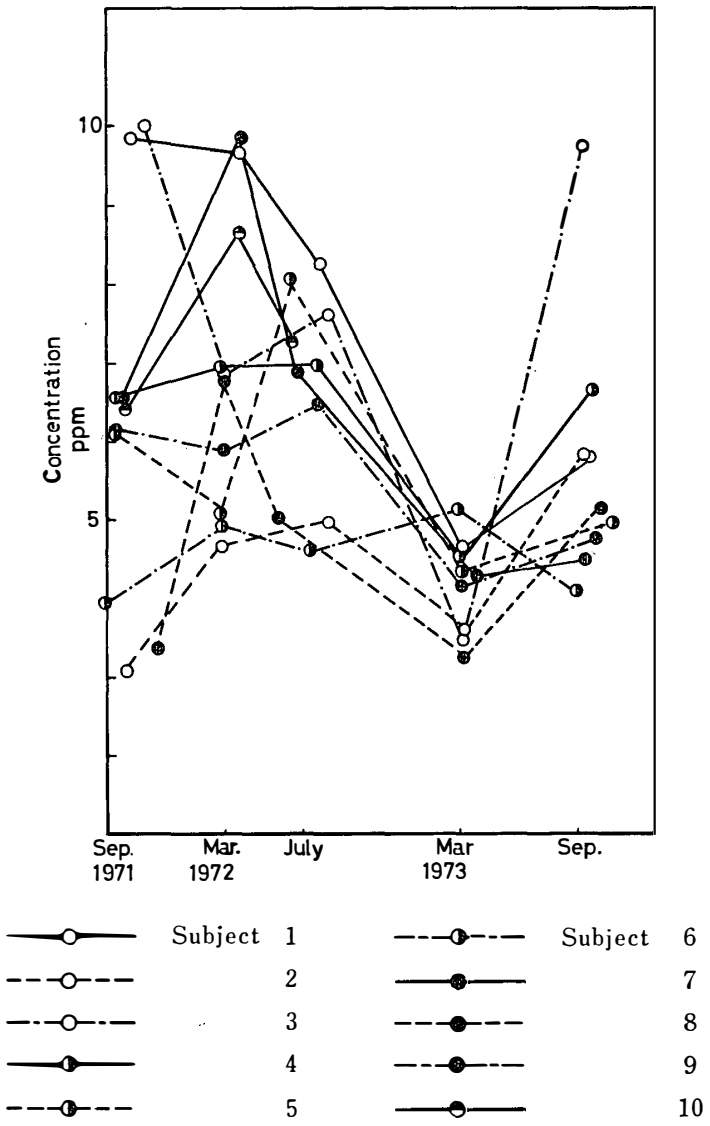

Fig. 2. Variation of mercury content in hair during the stay in Antarctica.

Table 2. Content of mercury in hair of the wintering members of the 13th Japanese Antarctic Research Expedition.

Period of collection	Range (ppm)	Mean (ppm)	Std. Dev. (ppm)
Sept. 1971	3.4—10.5	6.3	2.3
Mar. 1972	4.7— 9.9	7.0	1.8
July 1972	5.0— 8.3	6.6	1.2
Mar. 1973	3.3— 5.2	4.2	0.6
Sept. 1973	4.1— 9.8	5.8	2.1

tion. Therefore, their concentration reflects dietary, metabolic processes and environmental effects. It has been also reported that the content of trace elements varies with indivisual hairs on a single human head and with the length of the hair.

As the hair samples, analyzed by neutron activation analysis in this work, were taken from various parts of the head and from the tip of the hair (length 1 to 6 cm), we could obtain only the average pattern of trace element concentration in the hair.

The result for mercury is shown in Fig. 2. Table 2 contains the average concentration of 10 samples and its standard deviation. Mercury showed a characteristic variation during their stay in Antarctica. Namely, mercury's average concentration and its standard deviation decreased from 6.3 ppm to 4.2 ppm and from 2.3 ppm to 0.6 ppm respectively at the end of the stay in Antarctica. And its concentration increased again and scattered over a wide range after the party members returned to Japan. This trend in concentration and standard deviation of mercury appears to indicate the effect of speciality of the living conditions of the Antarctic Research Expedition party and the environment in Antarctica.

KOZUKA (1972) and KOZUKA *et al.* (1972) have investigated the concentration of trace elements in 230 hair samples, which were collected from a variety of Japanese, representing different occupations and environments. The concentration of mercury in the hair ranged from 1 to 13 ppm, averaging 5.4 ppm for male, 4.6 ppm for female, and 5.0 ppm for total. HOSHINO *et al.* (1966a, b) have reported the average of mercury to be 6.0 ppm. On the basis of these data, it seems reasonable to consider that the concentration of mercury in Japanese hair is 5～6 ppm. On the other hand, the value of 1～2 ppm has been reported for foreigners and also for Japanese students staying in foreign countries. These facts suggest that the concentration of mercury in the hair reflects dietary and environmental effects. Though the environment in Ant-

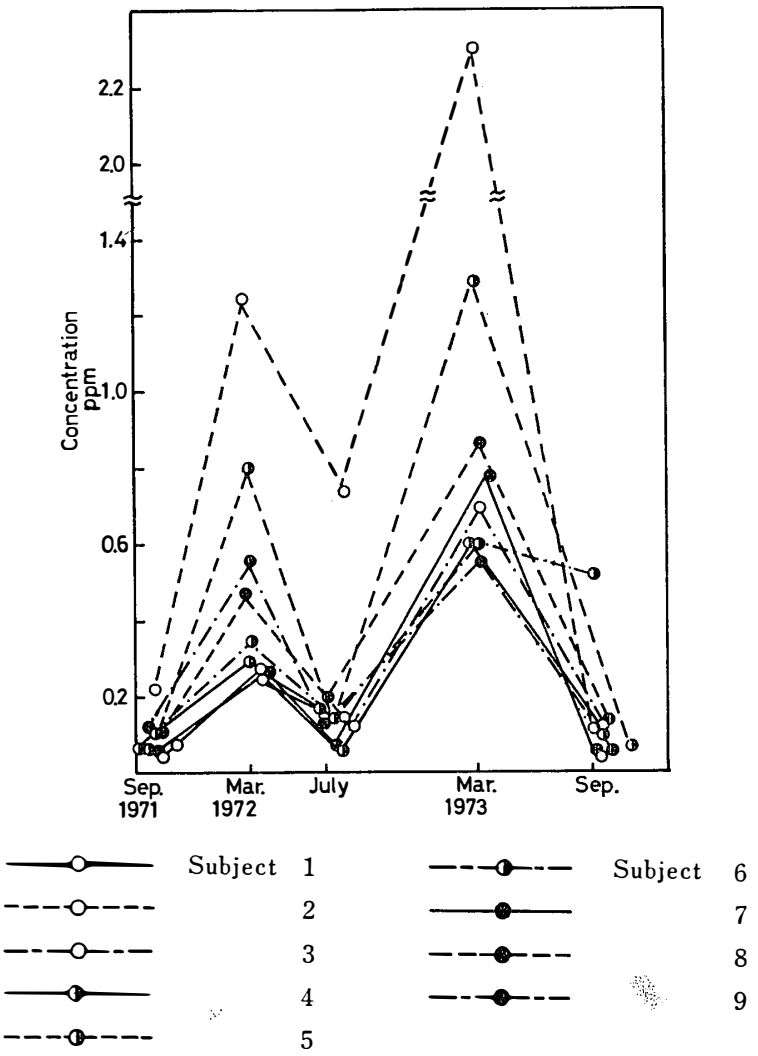

Fig. 3. Variation of antimony content in hair during the stay in Antarctica.

arctica seems to be little polluted, the concentration of mercury decreased to only 4.2 ppm which was considerably high compared with that of foreigners. Considering the fact that the food taken in Antarctica was produced in Japan, the above-mentioned value of mercury concentration may be ascribed to the intake of food.

Fig. 3 shows the variation in concentration of antimony during the stay in Antarctica. Two distinct peaks are noticed in Fig. 3. These peaks appeared in the hairs collected on board the icebreaker FUJI or not very long after leaving the ship. This fact seems to indicate that some enviromental pollution occurred on the icebreaker FUJI and the surface of the hair was contaminated with it, although the source of pollution is not clear at present. For other

elements, no obvious result suggesting the effect of their living in Antarctica was obtained.

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