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Tungsten-185 and -181 in Atmospheric Precipitations at Niigata in 1968—69

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For the past five years we have made measurements of the fresh debris resulting from air[1,2] and underground[3-5] nuclear test explosions, and we have had some geochemical discussions of the results obtained. We have recently found unexpected fallout activities with a unique and marked 57.5-keV photon in 16 precipitation samples between December 21, 1968, and May 20, 1969, at Niigata, while a precipitation sample from December 10—20 (86 *l*) as well as earlier ones showed no such radioactivities. All the precipitation samples were γ-spectrometrically analysed by using a 3 in$\times$3 in NaI(Tl) scintillation detector equipped with a 800-channel pulse-height analyser. Figure 1 shows a γ-spectrum typical of the 16 precipitation samples in question. The γ-spectra of the samples collected in early January, 1969, had some short-lived fission products, such as ^{131}I, ^{132}Te–^{132}I, and ^{140}Ba–^{140}La, which resulted from the 8th Chinese nuclear test on December 27, 1968, but other samples showed only long-lived fission products, ^{95}Zr–^{95}Nb, ^{137}Cs, and ^{144}Ce–^{144}Pr, originating from other earlier nuclear tests as well as the 8th Chinese test.

In order to identify these unknown radioactivities, we applied a systematic chemical-separation procedure to a precipitation sample (64 *l*) collected on December 25, 1968. The present procedure involves a preliminary 6 M hydrochloric acid leaching in order to prepare a sample solu-

1) T. Sotobayashi, T. Suzuki and S. Koyama, This Bulletin, **42**, 716 (1969).

2) T. Sotobayashi, T. Suzuki and A. Furusawa, *Nature*, **224**, 1096 (1969).

3) S. Koyama, T. Sotobayashi and T. Suzuki, *ibid.*, **209**, 239 (1966).

4) T. Sotobayashi and S. Koyama, *Science*, **152**, 1059 (1966).

5) T. Sotobayashi, T. Suzuki and S. Koyama, This Bulletin, **40**, 1260 (1967).

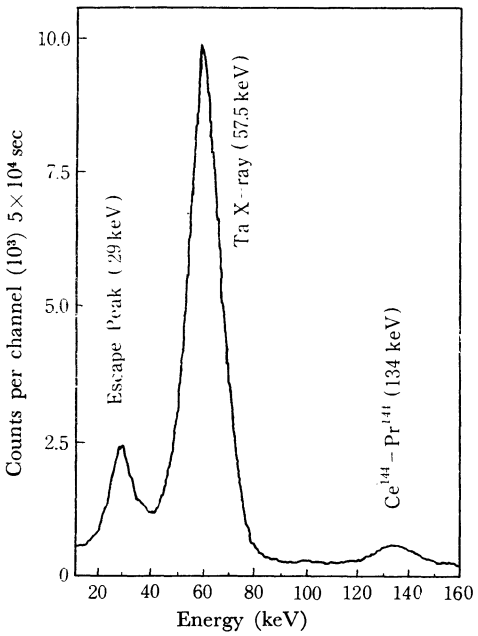

Fig. 1. A γ-ray spectrum of a precipitation sample on December 25, 1968 (64 *l*).

tion for further chemical analysis; it was followed by 3 successive liquid-liquid extractions using mineral acid-xylene solutions of TOA system consisting of 1N sulfuric, 4 N hydrochloric, and 10 N nitric acids, and of 5, 10, and 5% xylene solutions of TOA, respectively. According to the present procedure, one group of elements, V, Mo, Re, Ru, Os, W, and Sb, is expected to remain in the final aqueous phase; the γ-spectrum of the aqueous phase proved to have only a photopeak at 57.5 keV with a half-life of 140 d. As a result, a radionuclide of ^{181}W among the finally-separated 7 elements was expected to correspond to the one emitting such a photon.

For the purpose of reinforcing the present conclusion chemically, the following experiment was made on the residue fraction obtained in the above test. A sample solution for chemical analysis was prepared by the alkali fusion of the residue, followed by hot-water extraction. In this case, sodium tungstate was added to the sample solution as a carrier, and a purified tungsten trioxide was obtained by the usual cinchonine-hydrochloric acid method for tungsten analysis. A nuclide with a 57.5-keV photon was recovered nearly quantitatively, as was found by comparing the photopeak area at 57.5 keV between the residue and the trioxide.

The tungsten trioxide obtained was further submitted to 70-channel β-ray spectrometer equipment, because ^{185}W, a pure β emitter, was expected to be produced by a (n,γ) reaction of ^{184}W with a natural abundance of 30.6%. The trioxide sample proved to have a half-life of 75 d and maximum energy of 0.42 MeV (Fig. 2); these results agreed well with those of ^{185}W listed in the "Table of Isotopes."[6] Thus, it may be concluded that the 57.5-keV photon is a Ta X-ray emitted in the ^{181}W decay process (EC) and that the unknown activities in question originate from radiotungsten isotopes,^{181,185}W.

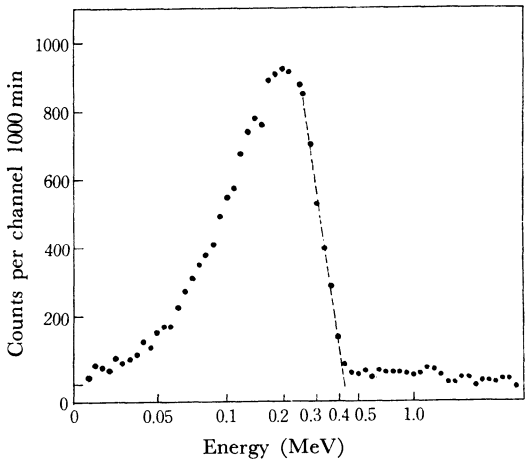

Fig. 2. A β-ray spectrum of a purified tungsten trioxide from a precipitation sample.

The radiotungsten was believed to have occurred in the chemical form of tungsten trioxide on the basis of following chemical behavior of the radiotungsten present in the precipitation samples: (1) Most of the radiotungsten (60—70%) was in the carrier-free state, extracted from precipitation samples into a sodium hydroxide solution (6 M), and when sodium tungstate was added as a carrier the extraction coefficient amounted to more than 95%. (2) No radiotungsten was leached from precipitation samples by distilled water, even in the presence of sodium tungstate as a carrier. (3) Though about 50% of the radiotungsten was leached with hydrochloric acid (6 M) from a precipitation sample in the carrier-free state, the leached radiotungsten was completely precipitated, together with the dehydrated silica produced, when the leachate solution was evaporated to dryness; the solid cake thus obtained was then dissolved in dilute hydrochloric acid.

Table 1 shows the day-to-day variation in the activity concentration of radiotungsten for the precipitation samples from between December 21—30, 1968, together with the averaged values for intervals from 7 to 20 days from December 21, 1968, to May 20, 1969. All the activity values in Table 1 are corrected for decay to the mid-col-

6) C. M. Lederer, T. M. Hollander and I. Perlman, "Table of Isotopes," John Wiley & Sons, N. Y. (1967), p. 108.

Table 1. Radiotungsten in precipitations between December 21, 1968—May 20, 1969

Date of collection	Sample volume (l)	Relative activity (cps)	Relative activity concentration (10^{-3} cps/l)
12/21 1978	64	5.2	81
12/22	64	5.3	83
12/23	64	3.2	50
12/24	64	4.1	64
12/25	64	30.4	457
12/28	60	4.0	67
12/30	43	3.3	77
12/21—28, 1968	75.5	12.4	164
12/29—1/3, 1969	116	0.98	8.4
1/4—16	81	0.77	9.6
1/20—2/1	83	0.60	7.2
2/2—20	52	0.56	10.8
2/21—3/31	160	1.21	7.6
4/1—20	79	0.26	3.3
4/21—30	59.3	—	—
2/1—20	64	0.18	2.8

Relative activity; Photopeak area at 57.5 keV.

lection date. As may be seen, the levels of the radiotungsten concentration in precipitations were kept relatively high for the first 10-day period; then they dropped rapidly to about one-twentieth of the initial levels and remained unchanged until mid-February. Thereafter, the levels continued to decrease gradually. From this decrease rate, the half-time of the removal process for airborne radiotungsten from the atmosphere was roughly estimated to be 33 d. Such atmospheric behavior of airborne radiotungsten seems like that observed in 1965 at Niigata for airborne radiostrontium released by a Soviet underground nuclear test on January 15, 1965.[5]

The radiotungsten fallout was reported to be detected in Italy[7] and Finland.[8] The first arrival at Pisa, Italy (10°E, 44°N), of radioactive clouds with radiotungsten was on December 17, 1968, while it was on December 21 at Niigata (139°E, 38°N). Further, taking into consideration the atmospheric conditions (Niigata had several rain or snow storms, with strong convective activities, for a week before and after the day in question (Dec. 21)), it can possibly be assumed that 4 days were required for the radiotungsten to travel the 10000 km from Italy to Japan and that the radiotungsten travelled at a speed of about 100 km/hr from west to east along the 40th Parallel. This assumed speed was found comparable with that, 110—80 km/hr, observed at Niigata in connection with the recent, fresh Chinese nuclear debris.[9,10] This radiotungsten fraction which at first reached Niigata was probably carried in the jet stream in the tropopause levels. On the other hand, the highest activity concentration of radiotungsten was observed at Niigata on December 25, a week after the appearance of the highest one at Pisa (Dec. 18). This finding suggests that the cloud with the highest concentration of radiotungsten came here at a slower speed of 50 km/hr through relatively lower levels—perhaps about 5 km high—in the atmosphere. Though we found no volatilely-behaving, short-lived fission products in the precipitation samples in question, we may finally make the assumption, from the fallout pattern and the global circulation speed observed, that the radiotungsten in question is attributable to a US underground nuclear test at Nevada on December 8, 1968, which was reported to release radiotungsten-rich radioactivities into the atmosphere by a US Public Health Service report.[11]

7) L. de Franceschi, A. Gentili, G. Gremigni and D. Guidi, *Nature*, **224**, 571 (1969).

8) L. Blomqzist and M. Asikainen, *ibid.*, **225**, 58 (1970).

9) T. Sotobayashi, T. Suzuki and S. Koyama, *ibid.*, **215**, 728 (1967).

10) T. Sotobayashi, T. Suzuki and S. Koyama, This Bulletin, **41**, 2796 (1968).

11) *US Public Health Service, Radiological Health Data and Reports*, **10**, 171 (1969).