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Notes

Pretreatment conditions for detecting ^{134}Cs -Eight years after the Fukushima Daiichi nuclear accident-

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^{134}Cs is an activation product with a short half-life (2.06 years) that was released during the Fukushima Daiichi nuclear disaster. It is an important indicator of contamination from the disaster because it has been more than 30 years since the last event when ^{134}Cs was released. The radioactivity ratio of ^{137}Cs to ^{134}Cs was approximately 1 at the time of the accident, and thus, it is possible to quantitatively evaluate the sources of ^{137}Cs from the radioactivity of ^{134}Cs in environmental samples. In particular, because the radioactivity of ^{134}Cs in foodstuffs in Japan is low due to its short half-life, pretreatment (concentration) is essential for quantification. For analyses using a 2-L Marinelli vessel and a conventional HPGe semiconductor detector (relative efficiency 25%), the detection limit for ^{134}Cs was approximately 0.05 Bq/kg without pretreatment. For the ^{137}Cs contamination source segregation in Japan in March 2020, the radioactivity in samples must be at least 0.83 Bq/kg of ^{137}Cs. This study provided guideline requirements for sample volume and pretreatment.

1. Introduction

Since the Fukushima Daiichi nuclear disaster, significant amounts of radioactive nuclides have been released to the environment, mainly in the North Pacific Ocean and eastern Japan.[1] Japan has devoted substantial financial and technical resources to measuring radioactive nuclides in foodstuffs,[2,3] and regulated radioactive nuclides include radioactive cesium (^{134}Cs and ^{137}Cs). Since April 2012, the regulated radioactivity level for total radioactive cesium has been set to 100 Bq/kg for general foods and 570 Bq/kg-dry for dried shiitake mushrooms (*Lentinula edodes*) under the Japanese domestic law.[4-6] As of 2019, very few foods in markets exceeded the regulatory level. The detection of ^{134}Cs ($T_{1/2}$ = 2.06 y) is crucial for quantitative evaluation of the contamination sources (Fukushima Daiichi nuclear disaster or pre-Fukushima, such as earlier nuclear bomb incidents and tests or the Chernobyl disaster).[7] ^{134}Cs is a gamma-emitted neutron activation product from stable ^{133}Cs and representative of nuclides released to the environment by the Fukushima Daiichi nuclear disaster.

Many crops in Japan are harvested annually, and there are two major implications for high-accuracy gamma ray analysis of annual crops. First, at supermarkets, there can be many crops from all over Japan without any environmental sampling. Second, the ability to detect small amounts of ^{134}Cs in a crop can more clearly identify the areas affected by the Fukushima nuclear accident in Japan. In 2019, 8 years after the Fukushima Daiichi nuclear disaster, the radioactivity of ^{134}Cs had decreased to less than 1/16 of the radioactivity at the time of the accident, and thus, high-accuracy gamma ray measurement is needed with increased measurement time.

In this study, we present specific measurement and pretreatment methods for improving the detection limits of ^{134}Cs using a conventional Ge semiconductor detector.

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2. Methods

A conventional HPGe semiconductor detector (GC2518-7500 SL-2002CSL) manufactured by Mirion Technologies, Canberra, was used to analyze gamma rays with a relative efficiency of 25% (actual catalog spec 27.7%). The absolute detection efficiencies at 0.6 and 1.4 MeV using a 2L Marinelli vessel were 0.81% and 0.4%, respectively. To determine ^{137}Cs, the 662 keV photopeak was used, whereas the peaks at 604 and 795 keV were used for calculating ^{134}Cs; the detection limit was set to 3 sigma.[8]

Studied food samples were purchased from markets and treated following the official methods in Japan.[9]

3. Results and discussion

3.1. Relationship between the detection limit and live time. Generally, the detection limit decreased with increasing measurement time. Table 1 presents the limit of quantification (LOQ) for ^{137}Cs in a 2-L Marinelli vessel using the HPGe detector with a relative efficiency of 15%.[10] The regulatory limit for milk in Japan since April 2012 has been 50 Bq/kg. The LOQ for ^{137}Cs was 0.8 Bq/L when measuring gamma rays in a 2-L Marinelli vessel for one hour. Since the specific gravity of milk is approximately 1.03, a radioactivity of 0.8 Bq/L is

TABLE 1: The limits of quantification (LOQ) for different food samples at measurement times (live times) of 1 and 10 h

Sample	Sample amount	LOQ (live time)		Unit
		(1 hour)	(10 hours)	
Milk	2 L	0.8	0.3	Bq/L
Green Vegetable	1 kg	1.6	0.5	Bq/kg-raw
Seaweed/Fish	2 kg	0.8	0.3	Bq/kg-raw
Grain/Meat/Egg	2 kg	0.8	0.3	Bq/kg-raw

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considered equivalent to 0.8 Bq/kg. Even one hour was too long to determine the ^{137}Cs activity concentration in milk if it exceeded the regulatory level.

As described previously, although a measurement guideline is available, quantitative evaluation of the measurement time and the LOQ or detection limit remains sparse for gamma ray analysis. Here a general solution is examined using results from actual measurements.

Figure 1 presents the radioactivity of ^{134}Cs, ^{137}Cs, and ^{40}K with respect to measurement time (live time) and detection limits for dried shiitake mushrooms that were manufactured and sold in Yugawara City, Kanagawa Prefecture, in January 2014. The dried mushroom sample had a density of 0.422 g/cm^3 and weight of 0.844 kg and was crushed and measured in a 2-L Marinelli vessel without pretreatment.

The radioactivities of ^{134}Cs, ^{137}Cs, and ^{40}K at a measurement time of 67,500 s (live time) were 26.3 ± 0.2, 120 ± 0.6, and 578 ± 5 Bq/kg, respectively. The radioactivity of radioactive cesium (sum of ^{134}Cs and ^{137}Cs) in the dried mushroom sample was 147 ± 0.6 Bq/kg at the time of measurement. This value was below the regulatory limit of 570 Bq/kg for dried *shiitake* mushrooms and thus suitable for distribution in Japan.

^{40}K was first determined to be 774 ± 200 Bq/kg at a live time of 75 s. Since the detection limit was 420 Bq/kg 75 s after measurement started, it was determined in excess of 3σ. However, the coefficient of variation (c.v.), which is an indicator of accuracy, fell below 10% after the measurement time exceeded 1000 s.

Although the sum of the radioactivities of ^{134}Cs and ^{137}Cs was lower than the ^{40}K activity concentration, the measurement time was not required to determine accuracy. The c.v. for the radioactivity of ^{134}Cs and ^{137}Cs were below 10% at 496 and 257 s, respectively. This was mainly because the detection efficiency near 0.6 MeV was approximately two times higher than that near 1.4 MeV.

The detection limit could be approximated as a function of the live time under ideal conditions, such that the gamma ray analysis ignored Compton scattering, summing peaks from the photopeaks of higher energy than targeted peaks. For foodstuffs, this approximation was applied because natural nuclides, except ^{40}K, were often absent.

The detection limit for ^{137}Cs was related to the live time by an exponent based on values for the 11 data points in Fig. 1. This relationship yielded a detection limit of 0.054 Bq/kg for measurements from 14 consecutive days.

Measurements of the radioactivity of cesium in approximately 259 food samples[7] using 2L Marinelli vessels and the HPGe detector revealed that the detection limit for ^{134}Cs or ^{137}Cs was 0.05 Bq/kg for a reasonable live time (up to 2 weeks) regardless of the radioactivity or density. Thus, increasing the measurement time was an inefficient method for lowering the detection limit.

Conversely, sample concentration before counting gamma rays was very effective in lowering the detection limit. Removing water from samples by heating was a suitable method for concentrating radiocesium. According to our previous study,[11] the ^{133}Cs loss rate from heating was approximately 0.4%. Therefore, if the sample was prepared, radiocesium could be determined more efficiently by concentrating samples by heating for water removal.

3.2. Pretreatment conditions for the detection of ^{134}Cs nine years after the Fukushima Daiichi nuclear disaster. On the 8th anniversary of the Fukushima Daiichi nuclear disaster (March 11, 2020), the activity ratio of ^{134}Cs to ^{137}Cs was expected to be approximately 0.06.[8] Therefore, if a conventional Ge semiconductor detector (^{134}Cs detection limit 0.05 Bq/kg) was used, the theoretical required radioactivity of ^{137}Cs would be at least 0.833 Bq/kg. This theoretical radioactivity assumed that all detectable ^{137}Cs originated from the Fukushima Daiichi nuclear disaster.

In Japan, pre-Fukushima events, such as nuclear bombs in

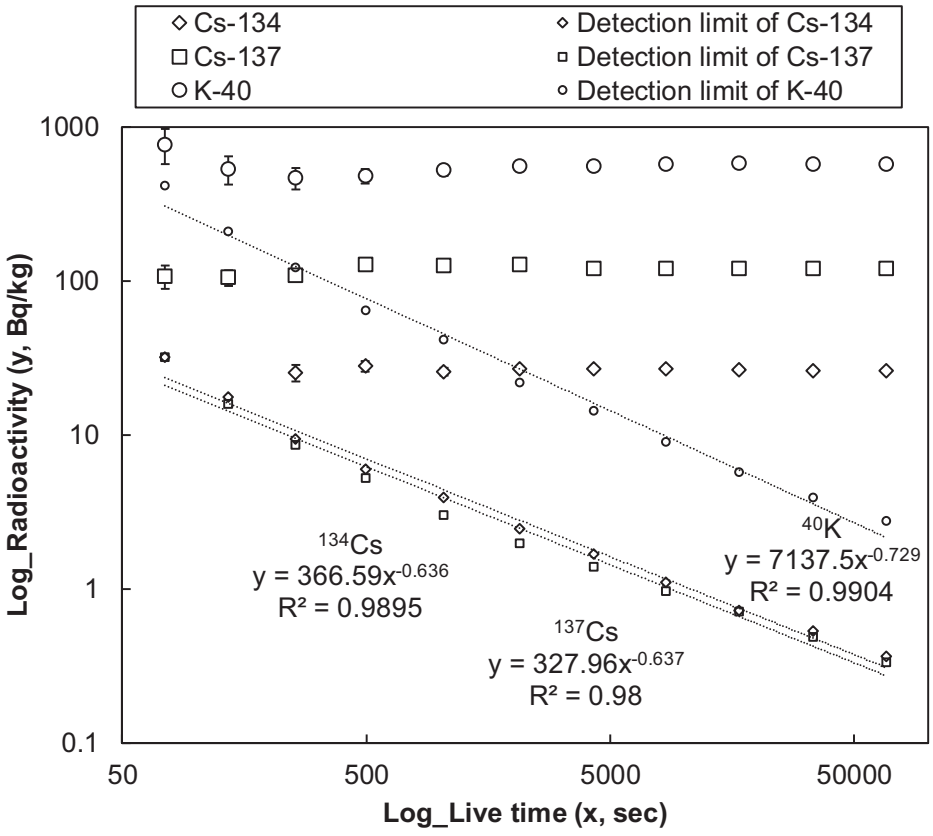

Figure 1. Radioactivity and detection limit (3 sigma) of ^{134}Cs, ^{137}Cs, and ^{40}K relative to live time (s).

1945, atmospheric nuclear weapons testing in other countries (1950s and 1960s), and the Chernobyl disaster in 1986 introduced ^{137}Cs to the environment. Therefore, ^{137}Cs detected in most samples exceeded the theoretical radioactivity calculated from the ^{134}Cs/^{137}Cs ratio based on the Fukushima Daiichi nuclear disaster.

Pretreatment methods depended on the sample type. For large fish living and caught in the North Pacific Ocean, approximately 50% of the ^{137}Cs content was attributed to the Fukushima Daiichi nuclear disaster.[7] Salmon caught in Hokkaido, Japan had ^{137}Cs yields of approximately 0.1 Bq/kg-raw level. [7]

Therefore, ^{137}Cs source discrimination for fish samples required quantification of at least 1.6 Bq/kg ^{137}Cs after concentration. That is, concentration to 16 times by weight was required prior to gamma ray counting. This is not a realistic pretreatment method.

Conventional HPGe with a detection efficiency of 25% was used in this study; however, other approaches, such as using a Ge semiconductor detector with a higher detection efficiency, a higher peak over Compton ratio, or a low-back environment, could lower the detection limit.

Although the application range was limited to Japan, to efficiently detect ^{134}Cs for investigating ^{137}Cs sources, pre-measuring ^{137}Cs radioactivity or extracting it from a database[12] and calculating the concentration ratio from the ^{134}Cs/^{137}Cs ratio backwards from the radioactivity could be effective.

4. Conclusions

Several years after the Fukushima Daiichi nuclear disaster, the quantification of ^{134}Cs over time has become difficult. The absolute detection efficiency of ^{134}Cs for the conventional HPGe using a 2L Marinelli vessel was approximately 0.1%. Under these conditions, the achievable detection limit was approximately 0.05 Bq/kg, even if samples were measured for 2 weeks. Concentrating the sample by removing water was more effective for decreasing detection limits than extending the measurement time. As of March 2019, to quantitatively distinguish the sources of ^{137}Cs from the Fukushima Daiichi nuclear disaster and previous events like the Chernobyl accident, a sample with ^{137}Cs of approximately 0.1 Bq/kg-fresh would require at least 16 times ^{137}Cs concentration on a weight ratio basis. Since such an enrichment of radioactivity levels is not feasible, a sample with higher radioactivity should be chosen, or a high-performance germanium semiconductor detector should be used.

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