Supplementary Information (SI) for Journal of Analytical Atomic Spectrometry.

Supplementary Material for Journal of Analytical Atomic Spectrometry

SI-traceable quantification of ^{135}Cs in ^{137}Cs solution for ^{135}Cs standardization

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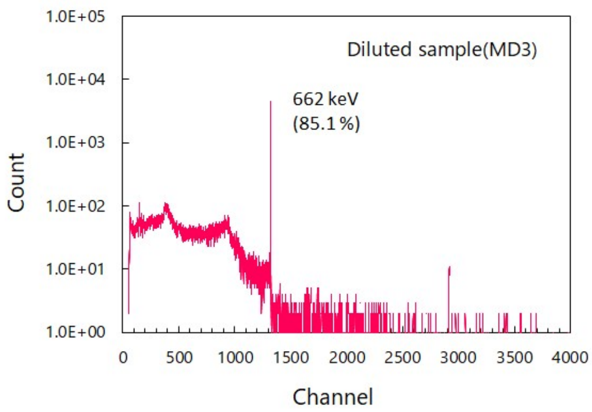

Fig. S1 Gamma spectrum of ^{137}Cs liquid sample (MD3).

Table S1 Operational settings for ICP-MS (Agilent 8800s)

RF Power	1500 [W]
Sample uptake rate	0.1 mL/min
Flow rate of Ar gas	
Carrier gas	0.68 L/min
Makeup gas	0.36 L/min
Flow rate of 4th gas (N_2O)	70% (1.05 mL/min)
Integration time	
m/z 133, 135, 137 (on-mass)	3 s
m/z 138 (on-mass)	0.1 s
Q2 peak point	1
No. of sweeps	100
No. of repetition	5

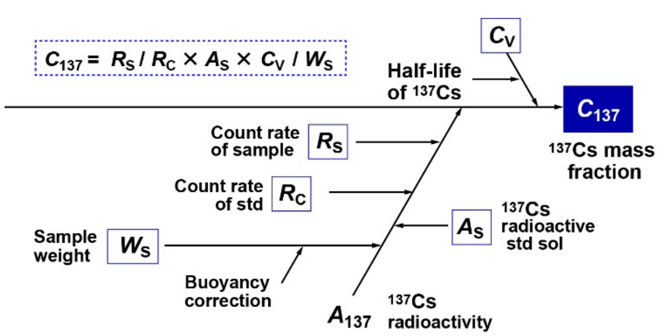

Fig. S2 Cause-and-effect diagram of ^{137}Cs mass fraction.

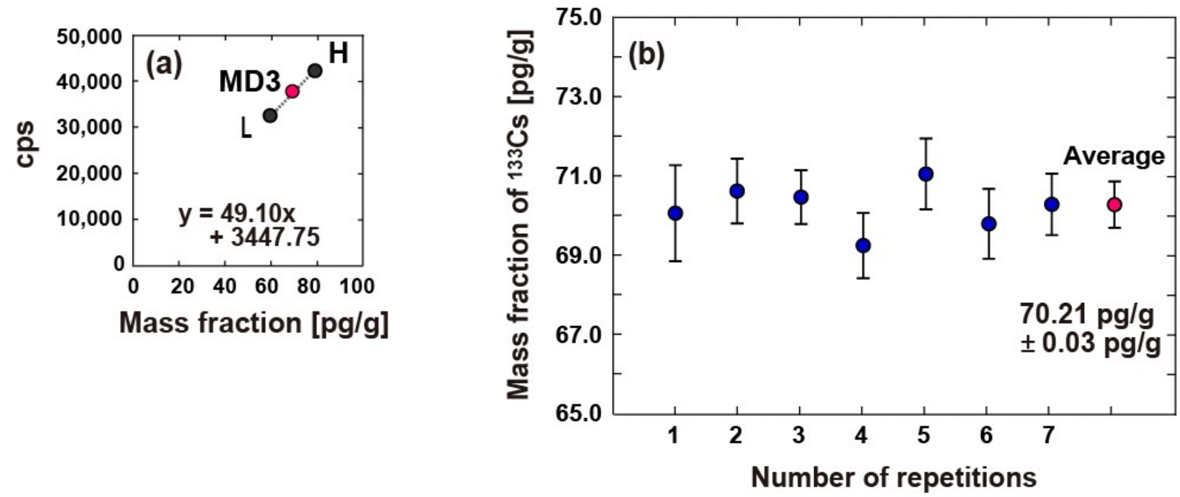

Fig. S3 Measured results of ^{133}Cs mass fraction of MD3: (a) cps vs ^{133}Cs mass fraction, (b) seven repeated measurements and average.

Table S2 Results of isotope measurement for MD3 by ICP-MS

	^{137}Cs/^{133}Cs molar ratio	^{137}Cs/^{133}Cs net cps ratio	^{137}Cs/^{133}Cs net cps ratio, SD	Slope L	$K_{137/133}$	^{135}Cs/^{133}Cs net cps ratio	^{137}Cs/^{133}Cs net cps ratio, SD	^{137}Cs/^{133}Cs molar ratio	^{135}Cs mass fraction [pg/g]
1	0.3157	0.0068	0.9531	0.0117	0.9765	0.3085	0.0066	0.3005	21.559
2	0.3167	0.0037	0.9499	0.0125	0.9750	0.3086	0.0036	0.3006	21.569
3	0.3201	0.0036	0.9400	0.0150	0.9700	0.3156	0.0035	0.3074	22.056
4	0.3201	0.0036	0.9400	0.0150	0.9700	0.3144	0.0035	0.3062	21.973
5	0.3147	0.0029	0.9562	0.0110	0.9781	0.3101	0.0029	0.3021	21.675
6	0.3175	0.0054	0.9478	0.0131	0.9739	0.3137	0.0053	0.3056	21.925
7	0.3170	0.0021	0.9492	0.0127	0.9746	0.3094	0.0021	0.3014	21.624

Equations for uncertainty evaluation

1) Repeatability in the determination of the ^{133}Cs mass fraction

$C_{133,i}$ is the *i*-th measured value for the ^{133}Cs mass fraction (i = 1–7):

$$C_{133,i} = (C_H - C_L) \times \frac{(A_{133,i} - A_{L,i})}{(A_{H,i} - A_{L,i})} + C_L.$$

As defined in the manuscript,

$$C_{133} = \frac{1}{7}\sum_{i=1}^{7} C_{133,i}, \quad u_R = \frac{1}{C_{133}}\sqrt{\frac{1}{7-1}\sum_{i=1}^{7}(C_{133,i} - C_{133})}.$$

Using the expression

$$C_{133} = \frac{1}{7}\sum_{i=1}^{7} C_{133,i} = \frac{(C_H - C_L)}{7}\sum_{i=1}^{7}\frac{(A_{133,i} - A_{L,i})}{(A_{H,i} - A_{L,i})} + C_L,$$

we can find possible uncertainty sources for $A_{133,i}$, $A_{H,i}$, $A_{L,i}$ C_H, and C_L.

Although the uncertainty due to $A_{133,i}$, $A_{H,i}$, and $A_{L,i}$ is reflected in the magnitude of u_R, the relative standard deviation due to these terms is averaged over seven values as follows:

$$\frac{u_R}{\sqrt{7}}$$

We assume that the standard uncertainties of C_H, and C_L depends only on u_{CRM} as follows:

$$\frac{u^2(C_H)}{C_H^2} = u_{CRM}^2, \ \frac{u^2(C_L)}{C_L^2} = u_{CRM}^2, \ \frac{cov(C_H, C_L)}{C_H C_L} = u_{CRM}^2.$$

Thus, the variance of C_{133} due to C_H and C_L is evaluated as follows:

$$\left(\frac{\partial C_{133}}{\partial C_H}\right)^2 u^2(C_H) + \left(\frac{\partial C_{133}}{\partial C_L}\right)^2 u^2(C_L) + 2\left(\frac{\partial C_{133}}{\partial C_H}\right)\left(\frac{\partial C_{133}}{\partial C_H}\right) cov(C_H, C_L) = \left(\frac{\partial C_{133}}{\partial C_H} C_H + \frac{\partial C_{133}}{\partial C_L} C_L\right)^2 u_{CRM}^2.$$

Since

$$\frac{\partial C_{133}}{\partial C_H} = \frac{C_{133} - C_L}{C_H - C_L}, \ \frac{\partial C_{133}}{\partial C_L} = -\frac{C_{133} - C_L}{C_H - C_L} + 1,$$

the following expression holds true:

$$\left(\frac{\partial C_{133}}{\partial C_H}C_H + \frac{\partial C_{133}}{\partial C_L}C_L\right)^2 u_{CRM}^2 = \left[(C_{133} - C_L) + C_L\right]^2 u_{CRM}^2 = C_{133}^2 u_{CRM}^2.$$

Therefore, the relative standard deviation due to C_H, and C_L expressed by u_{CRM}. These two factors are considered in Eq. (6) in the manuscript.

2) Isotopic composition

$A_f(x)$: Isotopic composition of ^{x}Cs, $R(m)$: molar ratio of ^{m}Cs/^{133}Cs

$$A_f(133) = 1/(1 + R(135) + R(137))$$
$$A_f(135) = R(135)/(1 + R(135) + R(137))$$
$$A_f(137) = R(137)/(1 + R(135) + R(137))$$

$$u^2(A_f(133)) = \left(\frac{-1}{(1 + R(135) + R(137))^2}\right)^2 \cdot u^2(R(135)) + \left(\frac{-1}{(1 + R(135) + R(137))^2}\right)^2 \cdot u^2(R(137))$$

$$u^2(A_f(135)) = \left(\frac{R(137) + 1}{(1 + R(135) + R(137))^2}\right)^2 \cdot u^2(R(135)) + \left(\frac{-R(135)}{(1 + R(135) + R(137))^2}\right)^2 \cdot u^2(R(137))$$

$$u^2(A_f(137)) = \left(\frac{-R(137)}{(1 + R(135) + R(137))^2}\right)^2 \cdot u^2(R(135)) + \left(\frac{R(135) + 1}{(1 + R(135) + R(137))^2}\right)^2 \cdot u^2(R(137))$$

3) Cs molar mass

m_{Cs}:Cs molar mass, m_x: atomic mass of isotope x

$$m_{Cs} = m_{133} \times \left(\frac{1}{1 + R(135) + R(137)}\right) + m_{135} \times \left(\frac{R(135)}{1 + R(135) + R(137)}\right) + m_{137} \times \left(\frac{R(137)}{1 + R(135) + R(137)}\right)$$

$$\frac{\partial m_{Cs}}{\partial R(135)} \cong \frac{-2(R(137) - 1)}{(1 + R(135) + R(137))^2}$$

$$\frac{\partial m_{Cs}}{\partial R(137)} \cong \frac{2(2 + R(135))}{(1 + R(135) + R(137))^2}$$

$$u^2(m_{Cs}) = \left(\frac{-1}{(1 + R(135) + R(137))^2}\right)^2 \cdot u^2(m_{133}) + \left(\frac{-R(135)}{(1 + R(135) + R(137))^2}\right)^2 \cdot u^2(m_{135}) + \left(\frac{-R(137)}{(1 + R(135) + R(137))^2}\right)^2 \cdot u^2(m_{137}) + \left(\frac{-2(R(137) - 1)}{(1 + R(135) + R(137))^2}\right)^2 \cdot u^2(R(135)) + \left(\frac{2(2 + R(135))}{(1 + R(135) + R(137))^2}\right)^2 \cdot u^2(R(137))$$

4) Covariance between C_{133} and $K_{135/133}$

Since

$$C_{137} = C_{133}\frac{I_{137}}{I_{133}}K_{137/133}\frac{m_{137}}{m_{133}},$$

$$K_{137/133} = \frac{C_{137}I_{133}m_{133}}{C_{133}I_{137}m_{137}}.$$

Thus,

$$\frac{\partial K_{137/133}}{\partial C_{133}} = -\frac{K_{137/133}}{C_{133}}.$$

The covariance between C_{133} and $K_{135/133}$ is derived with using Equations (9) and (10) in the main manuscript as follows:

$$u(C_{133},K_{135/133}) = \frac{\partial K_{135/133}}{\partial C_{133}}u^2(C_{133}) = -\Delta m_{(135-133)}\frac{\partial L}{\partial C_{133}}u^2(C_{133})$$

$$= \frac{\Delta m_{(135-133)}}{\Delta m_{(137-133)}}\frac{\partial K_{137/133}}{\partial C_{133}}u^2(C_{133}) = -\frac{K_{137/133}}{C_{133}}\frac{\Delta m_{(135-133)}}{\Delta m_{(137-133)}}u^2(C_{133}).$$

We hence obtain

$$\frac{u(C_{133},K_{135/133})}{C_{133}K_{135/133}} = -\frac{K_{137/133}\Delta m_{(135-133)}u^2(C_{133})}{K_{135/133}\Delta m_{(137-133)}\ C_{133}{}^2}.$$