National Institute for Environmental Studies, Japan

Date

No.

National Institute for Environmental Studies

Certified Reference Material No.13

Human Hair

This certified reference material (CRM) is prepared for use in evaluation of accuracy of methylmercury and selected heavy metals analysis of human hair and other samples with similar matrices. Each bottle contains approximately 3 g of homogenized human hair powder.

Preparation of the material

The male scalp hair of Japanese was collected in 3 barbershops located in Tokyo and Tsukuba in 1980. It was washed with non-ionic detergent, pulverized, sieved and blended. Approximately 3 g of the hair powder (<100 μm) was individually packed in acid-washed borosilicate bottles. The materials have been stored at −20 ºC in the dark immediately after bottling.

Homogeneity

The homogeneity of this CRM was evaluated by analyzing 5 subsamples from 5 randomly selected bottles for total Hg and other elements contents. Analysis of variance indicated no variability in Hg content of this CRM at 20-30 mg and in other elements (e.g., Cu and Zn) at 120 mg aliquot.

Certified values and reference values

Certified values for methylmercury, total Hg, Cd, Cu, Pb, Sb, Se and Zn are shown in Table 1. Certified values were determined by extensive collaboration analyses and were derived from at least 4 independent analytical methods specified in the table. Reference values shown in Table 2 are given for information only. Note that certified and reference values are expressed on dry weight basis. For drying instruction, see Use below.

Storage

This CRM should be stored in its original bottle at −20 ºC immediately after being received. Exposure to sunlight or UV radiation should be avoided because of possible methylmercury decomposition. Storage in a dark-colored polyethylene bag or container is recommended.

Use

1. This CRM was not sterilized because the procedure may decompose methylmercury. Handle as if it

transmits diseases.

2. The content of the bottle should be mixed well before each use to ensure homogeneity.
3. The bottle should be left at room temperature for at least 30 min before weighing samples. The minimum sample of 120 mg of the material should be used.
4. This CRM contains approximately 9 % moisture at the time of the preparation. The moisture content of the sample should be measured at the time of each use in order to correct the analytical value to dry weight basis value. Moisture content of this CRM is to be measured by the following procedure:
   1. Weigh accurately aliquot (>100 mg) of the material.
   2. Dry at 85 ºC for 4 hrs in a conventional electric oven followed by cooling for 30 min in a silica gel desiccator at room temperature.
   3. Weigh again. The difference in the two weight measurements is assigned as moisture content.
   4. In order to avoid possible loss/degradation of analytes by heating, use separate aliquot for moisture measurement from aliquots for analyte determination.
5. This CRM contains small amount of siliceous material. Addition of hydrofluoric acid to digesting acids is essential for a complete decomposition.

TABLE 1

Certified values of constituents in NIES CRM No.13 Human Hair

Constituent	Mass fraction[a]	Analytical Methods[b]
Methyl Hg	3.8±0.4	3,13,14,15
Total Hg	4.42±0.20	2,3,4,5,10
Cd	0.23±0.03	1,8,9,10
Cu	15.3±1.3	1,5,7,8
Pb	4.6±0.4	1,8,10,12
Sb	0.042±0.008	1,5,8,10
Se	1.79±0.17	1,5,6,8,9,10,11
Zn	172±11	1,5,7,8,10

a: Certified value±uncertainty expressed as μg/g dry weight. Samples should be dried at 85 ºC for 4 hrs in a conventional electric oven and then cooled in a silica gel desiccator at room temperature before weighing. For detail see text.

b: 1. atomic absorption spectrometry (AAS); 2. cold vapor AAS; 3. pyrolysis-gold amalgamation-AAS; 4. cold vapor atomic fluorescence spectrometry (CVAFS); 5. instrumental neutron activation analysis; 6. radioactive neutron activation analysis; 7.inductively coupled plasma atomic emission spectrometry; 8. inductively coupled plasma mass spectrometry (ICP-MS); 9. nitrogen microwave induced plasma mass spectrometry (MIP-MS); 10. isotope dilution ICP-MS; 11. isotope dilution MIP-MS; 12. X-ray fluorescence spectrometry; 13. gas chromatography (GC)-electron capture detection; 14. GC-CVAFS; 15. liquid chromatography-ICP-MS

TABLE 2

Reference values of constituents in NIES CRM No. 13 Human Hair

Constituent	Mass fraction[a]
Al	120
Ag	0.10
As	0.10
Ba	2.0
Ca	820
Co	0.07
Fe	140
Mg	160
Mn	3.9
Na	61
S (%)	5.0
V	0.27

Note: Reference values are not certified and given only for information.

a: µg/g dry weight unless otherwise indicated.

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Appendix

Isotopic composition of Hg in NIES CRM No.13, Human Hair

The isotopic composition of the mercury (Hg) in human hair is a useful tool for determining the routes of exposure to mercury. The isotopic composition of Hg in NIES CRM No.13, Human Hair has been determined and included in the certificate as additional information.

Within- and between-bottle variations in Hg isotopic measurements for NIES CRM No. 13 were found to be sufficiently small for the CRM to be used for its intended purpose (Table 1). The CRM can be used to confirm analytical results and for the precision management of analytical data. Further experimental details are given in A. Yamakawa et al., Accred. Qual. Assur. (2016) DOI 10.1007/s00769-016- 1196-x.

Table 1 Hg isotopic composition of NIES CRM No.13, Human Hair

	δ^{199}Hg	δ^{200}Hg	δ^{201}Hg	δ^{202}Hg	δ^{204}Hg	Δ^{199}Hg	Δ^{200}Hg	Δ^{201}Hg	Δ^{204}Hg
(n=11)	‰	‰	‰	‰	‰	‰	‰	‰	‰
Mean	2.13	0.98	2.77	1.89	2.76	1.65	0.04	1.36	-0.04
2SD	0.07	0.08	0.10	0.10	0.16	0.06	0.04	0.07	0.11

Because mass independent fractionation in human hair varies with the type and quantity of the food, particularly seafood consumed, it can be used to estimate the sources of exposure. In addition, absorption of mercury, mostly in the form of methylmercury, by the human organism was shown to induce mass dependent fractionation of +2‰ for δ^{202}Hg, implying that the isotopic composition of Hg in human hair is as expected following its ingestion and distribution in the body (e.g., Yamakawa et al., 2016).

＜Supplemental Information＞

Isotopic compositions are reported in the delta (δ) notation relative to NIST SRM 3133:

$\delta^{***}\mathrm{Hg}\ (‰) = ([(^{***}\mathrm{Hg}/^{198}\mathrm{Hg})_{\mathrm{sample}}/(^{***}\mathrm{Hg}/^{198}\mathrm{Hg})_{\mathrm{NIST\ SRM\ 3133}}] - 1) \times 1000$

(*** ：mass of the Hg isotopes: 199, 200, 201, 202, and 204)

Mass-independent fractionation (MIF) is reported in capital delta (Δ) notation as the difference between the measured and the theoretical δ^{***}Hg value:

$\Delta^{***}\mathrm{Hg}\ (‰) = \delta^{***}\mathrm{Hg} - (\beta \times \delta^{202}\mathrm{Hg})$,

(β ： the kinetic or equilibrium fractionation factor appropriate for the particular isotope: $\delta^{199}\mathrm{Hg}/\delta^{202}\mathrm{Hg}=0.252$, $\delta^{200}\mathrm{Hg}/\delta^{202}\mathrm{Hg}=0.502$, $\delta^{201}\mathrm{Hg}/\delta^{202}\mathrm{Hg}=0.752$, $\delta^{204}\mathrm{Hg}/\delta^{202}\mathrm{Hg}=1.492$ (Bergquist and Blum, 2007)).

＜References＞

B. A. Bergquist, J. D. Blum : Science, 318, 417(2007).

A. Yamakawa, A. Takeuchi, Y. Shibata, S. Berail, and O. F. X. Donard : Accred. Qual. Assur. (2016) DOI 10.1007/s00769-016-1196-x.

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