National Institute for Environmental Studies, Japan

Date

No.

National Institute for Environmental Studies

Certificate of Analysis

NIES CRM No. 13-a Human Hair

This environmental certified reference material (CRM) was developed and certified by the National Institute for Environmental Studies (NIES) for the determination of methylmercury and selected heavy metals analysis of human hair and other samples with similar matrices. This CRM is the successor to NIES CRM No. 13 Human Hair, which was produced at NIES in 1996. Analyses for mercury isotopes were also performed to obtain information values.

Certified Values

Element	Mass fraction			Analytical method *
	Unit	Certified value	Uncertainty	
Methyl Mercury (as Hg)	mg/kg	0.858	0.075	GC-CV-AFS, GC-ECD, ID-GC-ICP-MS, LC-ICP-MS
Total Mercury (THg)	mg/kg	1.06	0.07	CV-AAS, ICP-MS, ID-GC-ICP-MS, TD-CV-AAS
Arsenic (As)	mg/kg	0.255	0.016	HG-AAS, ICP-MS
Cadmium (Cd)	mg/kg	0.165	0.012	ICP-MS
Lead (Pb)	mg/kg	7.42	0.62	ICP-MS
Selenium (Se)	mg/kg	0.463	0.052	HG-AAS, ICP-MS
Zinc (Zn)	mg/kg	337	22	ICP-MS, ICP-OES

All certified values were determined based on dry mass.

* CV-AAS, cold vapor atomic absorption spectrometry
GC-CV-AFS, gas chromatography-cold vapor atomic fluorescence spectrometry
GC-ECD, gas chromatography-electron capture detector
HG-AAS, hydride generation-atomic absorption spectroscopy
ICP-MS, inductively coupled plasma-mass spectrometry
ICP-OES, inductively coupled plasma-optical emission spectrometry
ID-GC-ICP-MS, isotope dilution-gas chromatography-inductively coupled plasma-mass spectrometry
LC-ICP-MS, liquid chromatography-inductively coupled plasma-mass spectrometry
TD-CV-AAS, thermal decomposition-gold amalgamation-cold vapor atomic absorption spectrometry

Reference Values

Element	Mass fraction			Analytical method *
	Unit	Reference value	Uncertainty	
Calcium (Ca)	%	0.14	0.01	ICP-OES
Magnesium (Mg)	%	0.031	0.002	ICP-OES
Sodium (Na)	%	0.058	0.005	ICP-OES
Sulfur (S)	%	4.7	0.3	ICP-OES
Antimony (Sb)	mg/kg	0.062	0.005	ICP-MS
Barium (Ba)	mg/kg	11	1	ICP-MS, ICP-OES
Copper (Cu)	mg/kg	19	2	ICP-MS, ICP-OES
Iron (Fe)	mg/kg	71	8	ICP-OES
Manganese (Mn)	mg/kg	37	2	ICP-MS, ICP-OES

All reference values were determined based on dry mass.

* ICP-MS, inductively coupled plasma-mass spectrometry
ICP-OES, inductively coupled plasma-optical emission spectrometry

Characterization

The property values of the material were statistically determined based on chemical analyses by 14 organizations (including 20 laboratories) using a wide range of methods. A property value satisfying the following conditions was accepted as a certified value:

1) the relative standard deviation associated with the mean of the laboratory means was 10 % or less,
2) the number of laboratories contributing to the mean of the laboratory means was at least eight, and
3) the number of analytical methods contributing to the mean of the laboratory means was at least two.

The uncertainty associated with the certified values is the expanded uncertainty using a coverage factor $k = 2$, corresponding to the half-width of a confidence interval of approximately 95 %. A property value failing to satisfy one or two of the NIES criteria for certification but supplying valuable additional information about the material is given as a reference value.

Description of the Material

The CRM is supplied as fine black powder in a glass bottle.

Preparation of the CRM

The raw material for this CRM is scalp hair of east Asian women. It was washed with non-ionic detergent, crushed using a roll press and a cold grinding pin mill, and classified (74 μm or less) by the air jet sieve method and homogenized. The powdered samples were packed 3 g each in 806 glass bottles and sterilized by ^{60}Co irradiation (20 kGy). All procedures complied with ISO Guide 34.

Homogeneity

Homogeneity tests were carried out on 10 sample bottles selected by stratified random sampling. The between-bottle variation evaluated by a one-way analysis of variance (ANOVA) showed the homogeneity standard deviations between

bottles for the analytes to be less than 2.6 % for methylmercury and 2 % for other elements. The material, therefore, is sufficiently homogeneous for its intended use as a reference material.

Stability

Stability tests demonstrated that any long-term variations in the values of methylmercury and selected heavy metals in the material were insignificant.

Instructions for Use

1. This CRM should be kept tightly closed in its original bottle and stored under 5 ºC.
2. Prior to weighing aliquots for analysis, the contents of the bottle should be shaken gently.
3. The mass fractions of all certified and reference values in this CRM are reported on a dry mass basis. The moisture content of this CRM is approximately 8 % (dried at 85 °C for 4 hours). Correction to dry mass should be made by measuring the moisture content after each analysis.
4. For convenient handling, a minimum sample intake of 20 mg for MeHg, THg, 50 mg for other elements is recommended.
5. This CRM contains small amount of siliceous material. Addition of hydrofluoric acid to digesting acids is essential for a complete decomposition.
6. Do not use for purposes other than research. When disposing of samples, adhere strictly to local laws concerning processing and disposal of waste materials.

Expiry Date of Certification

The expiry date for the certified values of this CRM is June 2034 assuming that the recommended storage conditions are adhered to. NIES will notify via its website if any changes in the contents are recognized within the term of validity.

Collaborating Laboratories in Analysis

The certified and reference values for this CRM were based on the analytical values from the following participating organizations:

National Institute for Environmental Studies; Hokkaido University; Institute of High Energy Physics, Chinese Academy of Sciences(Research Center for Eco-environmental Sciences; Institute of Geochemistry); Jozef Stefan Institute; National Institute for Minamata Disease, Ministry of the Environment; Tokyo University of Science; Université de Pau et des Pays de l'Adour / CNRS; University of Oviedo; University of Rochester School of Medicine and Dentistry; IDEA Consultants, Inc.; Murata Keisokuki Service Co.,Ltd.; NIPPON STEEL TECHNOLOGY Co.,Ltd.

Collaborating Organizations in Preparation

IDEA Consultants, Inc

Technical Information

Technical information and the latest reports regarding this material can be obtained from the website.
http://www.nies.go.jp/labo/crm-e/index.html

June 3, 2024

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Certificate date: June 3, 2024

Appendix

Isotopic composition of Hg in NIES CRM No. 13-a, 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-a, Human Hair has been determined and included in the certificate as additional information.

The isotopic composition of Hg in NIES CRM No. 13-a Human Hair was measured using a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS; Nu Plasma II, Nu Instruments, UK) at NIES (Table A1). A Hot Dry Bath (HDB-2N, AS ONE Corp., Japan) and microwave (speedwave 2, BERGHOF products + Instruments GmbH, Germany) were employed as pretreatment methods for isotope analysis. It was confirmed that there was no difference in the Hg isotopic composition of this CRM among the different types of acids used for decomposition (concentrated nitric acid + concentrated hydrochloric acid, concentrated nitric acid + concentrated hydrochloric acid + hydrogen peroxide water + bromine chloride) and heating methods. This CRM can be used to confirm analytical results and for the precision management of analytical data.

Table A1 Hg isotopic composition of NIES CRM No. 13-a, 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=30)	‰	‰	‰	‰	‰	‰	‰	‰	‰
Mean	0.64	0.55	1.00	0.98	1.38	0.39	0.05	0.26	−0.09
2SD	0.08	0.07	0.12	0.10	0.14	0.06	0.05	0.07	0.09

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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