National Institute for Environmental Studies, Japan

Date

No.

National Institute for Environmental Studies

Reference Material Information Sheet

NIES RM No. 1002 Pine Needles II

SAMPLE

This environmental reference material is a reference material (RM) using pine needles (*Pinus thunbergii*) collected in Ibaraki Prefecture, Japan. It was developed by the National Institute for Environmental Studies (NIES) for use in controlling the accuracy and improving the precision of the analysis of total mercury in pine needles and related plants. Analyses for trace elements and mercury isotopes were also performed to obtain informative values.

Reference Value

Element	Mass fraction			Analytical method *
	Unit	Reference value	Uncertainty	
Total Mercury (THg)	ng/g	22	2	TD-CV-AAS

The reference value was determined based on dry mass.

* TD-CV-AAS, thermal decomposition-gold amalgamation-cold vapor atomic absorption spectrometry

Characterization

The reference value of the RM was determined statistically based on the results of five analyses carried out at NIES over a one-year period. The uncertainty associated with the reference value is the expanded uncertainty using a coverage factor $k = 2$, corresponding to the half-width of a confidence interval of approximately 95 %. This reference value is used as a reference value since it does not meet the NIES certification criteria. The reference value is provided with associated uncertainties that may not include all sources of uncertainty.

Description of the Material

The RM is supplied as fine green powder in a glass bottle.

Preparation of the RM

The raw material for this RM is the second-year leaves of pine needles (*Pinus thunbergii*) collected in Nara Prefecture, Japan. The surface of the pine needles was wiped clean, dried at 70 °C for 18 hours, crushed in a rotor mill with a 200 µm-sieving ring and homogenized. The powdered samples were packed 3 g each in 68 glass bottles and sterilized by ^{60}Co irradiation (25 kGy). All procedures complied with ISO Guide 34.

Homogeneity

Homogeneity tests were carried out on 7 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 1 %. 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 total mercury, in the material were insignificant.

Instructions for Use

1. This RM should be kept tightly closed in its original bottle and stored in a desiccator at room temperature (≤30 °C).
2. Prior to weighing portions for analysis, the contents of the bottle should be shaken gently.
3. The mass fraction of the reference value in this RM is reported on a dry mass basis. The moisture content of this RM is approximately 4 % (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 50 mg is recommended.
5. 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

The expiry date for the reference value of this RM is June 2034, assuming that above mentioned storage conditions are adhered to. NIES will announce via its website if any changes in the contents are noticed within the term of validity.

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
Hiroshi Yamamoto
Director
Health and Environmental Risk Division,
National Institute for Environmental Studies

Health and Environmental Risk Division,
National Institute for Environmental Studies,
16-2 Onogawa, Tsukuba, Ibaraki 305-8506 Japan
FAX: +81-29-850-2900, Email: nies.crm@nies.go.jp

Issue date: June 3, 2024

SAMPLE

Appendix

Information values may be useful for handling this material, though the values are not certified.

A.1 Isotopic composition of Hg

The isotopic composition of Hg in plants is a useful tool for estimating atmospheric mercury dynamics. The isotopic composition of Hg in NIES RM No. 1002 Pine Needles II was measured using a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS; Nu Plasma II, Nu Instruments, UK) at NIES. A double-stage furnace and microwave (speedwave 2, BERGHOF products + Instruments GmbH, Germany) were employed as pretreatment methods for isotope analysis. For homogeneity evaluation, the Hg isotopic compositions were analyzed for within- and between-bottles and confirmed to be homogeneous within analytical precision (Table A1).

Table A1 Hg isotopic compositions of NIES RM No. 1002 Pine Needles II

	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=12)	‰	‰	‰	‰	‰	‰	‰	‰	‰
Mean	−0.92	−0.82	−1.75	−1.64	−2.42	−0.51	0.00	−0.52	0.02
2SD	0.15	0.16	0.17	0.23	0.27	0.10	0.06	0.13	0.18

＜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)).

＜Reference＞

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

A.2 Trace elements

The trace element contents in NIES RM No. 1002 Pine Needles II were measured by inductively coupled plasma mass spectrometer (ICP-MS; Agilent 8800, Agilent Technologies) and inductively coupled plasma atomic emission spectrometer (ICP-AES; ICPE-9820, Shimadzu, Japan) (Table A2). Acid digestion using a microwave sample digestion system (speedwave 2, BERGHOF products + Instruments GmbH, Germany) was employed as a pretreatment method.

SAMPLE

Table A2 Trace element contents in NIES RM No. 1002 Pine Needles II

Element	Mass fraction		Analytical method *
	Unit	Content	
Aluminium (Al)	%	0.073	ICP-OES
Calcium (Ca)	%	0.79	ICP-OES
Phosphorus (P)	%	0.081	ICP-OES
Potassium (K)	%	0.56	ICP-OES
Barium (Ba)	mg/kg	16	ICP-OES
Cadmium (Cd)	mg/kg	0.080	ICP-MS
Copper (Cu)	mg/kg	2.2	ICP-MS
Iron (Fe)	mg/kg	68	ICP-OES
Rubidium (Rb)	mg/kg	4.6	ICP-MS
Zinc (Zn)	mg/kg	27	ICP-OES

All values were determined based on dry mass.

* ICP-MS, inductively coupled plasma-mass spectrometry

ICP-OES, inductively coupled plasma-optical emission spectrometry

SAMPLE