

National Institute for Environmental Studies
Certified Reference Material No.12
“ Marine Sediment”

The National Institute for Environmental Studies (NIES) announces the availability of NIES Certified Reference Material No.12, Marine Sediment.*

This Certified Reference Material (CRM) is intended for use in the quality assurance of the analysis of organotin and elements.

Preparation of NIES CRM No.12 Marine Sediment

The starting material for NIES CRM No.12 Marine Sediment was sampled in 1989 at the center of Bay of Tokyo. Approximately 200Kg (wet weight) of surface sediment was sampled by an Eckman-Burge sampler. It was transported to NIES and seawater was removed by filtration. The material was further air-dried for 2 weeks. After removing visible external materials (e.g., shell), it was pulverized in a 7-L high-purity alumina ball-mill to pass 100 μ m nylon sieve. The < 100 μ m fraction was homogenized in one lot using a V-blender for 3 h. Then, 30g aliquot of the homogenized material was doubly vacuum-packaged into a polyethylene laminate bag with oxygen absorbent to prepare 700 packages. It should be mentioned that NIES CRM No.12 Marine Sediment has not been sterilized to prevent possible decomposition of the organotin compounds by Co irradiation, a standard procedure for sterilization. Instead, they have been vacuum-packaged and stored at -20°C in a freezer to reduce any bacterial activities.

Homogeneity assessment

The homogeneity of the prepared material was assessed by analyzing the major and trace element concentrations. Three 300 mg-subsamples were taken from each of 3 randomly selected packages, and were decomposed with $\text{HNO}_3/\text{HClO}_4/\text{HF}$. The major and trace element concentrations (Na, Mg, Al, K, Ca, V, Cr, Fe, Mn, Cu, Zn, and Sr) were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The within- and between-package variation was calculated by a one-way analysis of variance (ANOVA). ANOVA did not find any statistically significant between-package variation in the element concentrations in this material. These results indicate that prepared material has a homogeneous element composition.

Moisture content

Since the certified and reference values are expressed on a dry-weight basis, the moisture content of this CRM has to be corrected to relate the analytical values to the certified/reference values. A moisture content of 6% was obtained from repetitive

measurements at NIES each time the new package was opened. Therefore, it is essential to measure the moisture content prior to measuring any analytes of this CRM if the package had been opened. The stability of the analytes in this CRM was not intensively examined once the package seal had been broken.

Certified Values

The certified values for tributyltin and total tin are based on results of determinations by at least three independent analytical techniques from collaborative laboratories. The uncertainties of the certified values were estimated based on consideration of 2 times the standard deviation of the mean of the acceptable values and of the 95% confidence intervals for the mean of individual methods.

Reference Values

Seven laboratories provided analytical results of TPT for this material. However, the reported mean values ranged from 0.006 to 0.010 mg TPT/kg dry wt., making it difficult to determine a certified value. So a simple mean of the reported values is designated as the reference value.

And the reference values for major and trace elements contents of this CRM were determined by intensive analysis at NIES. These are based on results of determinations by at least two independent analytical techniques.

Storage

The material should be stored in a freezer at -20°C. Exposure to light should be avoided.

Use

1. The package should be left at room temperature for at least 30 min before weighing samples. The minimum sample of 300 mg of the material should be used.
2. This CRM contains 6% 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 (1 g) of the material.
 2. Dry at 110°C for 4 hrs in a conventional electric oven followed by cooling for 30 min in a silicagel dessicator at room temperature.
 3. Weigh again.
 4. The difference in two weight measurements is assigned as moisture content.

In order to avoid possible loss/degradation of analytes by heating, use separate aliquot for moisture measurement from aliquots for analyte determination.

3. Certified values and Reference values are based on complete decomposition. We recommend to use an acid mixture (HNO₃, HF, HClO₄) to decompose completely. When acids do not work (for example Cr, Sn), alkali fusion¹ will be recommended.

* NIES CRM No.12 Marine Sediment is not available overseas.

Table 1 Certified and reference values of NIES CRM No.12

	Unit	Certified value	Analytical method
Tributyltin	mg TBT/kg	0.19 ± 0.03	a,b,c,d
Total tin	mg/kg	10.7 ± 1.4	e,f,g,h,i
		Reference value	
Triphenyltin	mg TPT/kg	0.008	

1. Certified values and reference value are on dry weight basis.
2. a: Gas chromatography electron capture detection, b: Gas chromatography-flame photometric detection, c: Gas chromatography-mass spectrometry, d: High performance liquid chromatography-ICP-MS detection, e: instrumental neutron activation analysis, f: Electrothermal atomic absorption spectrometry, g: Hydride generation atomic absorption spectrometry, h: Inductively coupled plasma mass spectrometry, i: Isotope dilution inductively coupled plasma mass spectrometry

Table 2 Reference values of element composition of NIES CRM No.12

Element	Reference value	Element	Reference value
Na,%	3.25	Co,ppm	16.6
Mg,%	1.46	Ni,ppm	57.6
Al,%	7.22	Cu,ppm	104
Si,%	24.2	Zn,ppm	738
K,%	1.56	Rb,ppm	69
Ca,%	1.06	Sr,ppm	126
Ti,%	0.34	Cd,ppm	3.0
V,ppm	134	Ba,ppm	254
Cr,ppm	201	Hg,ppm	1.16
Mn,ppm	837	Pb,ppm	101
Fe,%	4.31		

May 1998

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