

National Institute of Advanced Industrial Science and Technology

## National Metrology Institute of Japan



## Reference Material Certificate

NMIJ CRM 7504-a  
No. +++

## Pesticides in Unpolished Rice

This certified reference material (CRM) is produced in accordance with the NMIJ's management system and is in compliance with ISO 17034 and ISO/IEC 17025. This CRM is intended for use in controlling the precision of analysis and for validating analytical methods and instruments during analysis of pesticides (Fenitrothion and Etofenprox) in unpolished rice and similar materials.

**Certified Values**

The certified values for this CRM (on a dry-mass basis) are given in the table below. The uncertainty of the certified value is the half-width of the expanded uncertainty interval calculated using a coverage factor ( $k$ ) of 2, which gives a level of confidence of approximately 95 %.

## Certified values of pesticides

Pesticide	CAS No.	Certified value, Mass fraction (mg/kg)	Expanded uncertainty, Mass fraction (mg/kg)
Fenitrothion ( <i>O</i> , <i>O</i> -dimethyl- <i>O</i> -4-nitro- <i>m</i> -tolyl phosphorothioate)	122-14-5	0.109	0.017
Etofenprox (2-(4-ethoxyphenyl)-2-methylpropyl 3-phenoxybenzyl ether)	80844-07-1	0.19	0.05

**Analysis**

The certified values were calculated from pesticide concentrations determined by the following analytical methods.

## Analytical methods:

- Pressurized liquid extraction and gas chromatography/mass spectrometry (GC/MS)  
(Isotope dilution mass spectrometry (IDMS) was employed)  
[Extraction] Solvent, acetonitrile; temperature, 130 °C (10 MPa); extraction time, 10 min × 2 cycles  
[Clean-up] Solid-phase extraction (graphite carbon/aminopropylsilanized silica gel)  
[GC/MS] Column, DB-5MS (Agilent Technologies); on-column injection; electron impact ionization (EI); selected ion monitoring (SIM)
- Pressurized liquid extraction and ID-GC/MS  
[Extraction] Solvent, acetonitrile; temperature, 130 °C (10 MPa); extraction time, 10 min × 2 cycles  
[Clean-up] Solid-phase extraction (graphite carbon/aminopropylsilanized silica gel)  
[GC/MS] Column, DB-35MS (Agilent Technologies); splitless injection; EI; SIM
- Homogenization extraction and ID-GC/MS  
[Extraction] Solvent, acetonitrile; extraction time, 2 min × 2 cycles  
[Clean-up] Solid-phase extraction (octadecylsilanized silica gel and graphite carbon/aminopropylsilanized silica gel)  
[GC/MS] Column, DB-35MS (Agilent Technologies); splitless injection; EI; SIM
- Homogenization extraction and liquid chromatography/mass spectrometry (LC/MS; IDMS was applied)  
[Extraction] Solvent, acetonitrile; extraction time, 2 min × 2 cycles

[Clean-up] Solid-phase extraction (octadecylsilylated silica gel and graphite carbon/aminopropylsilylated silica gel)  
[LC/MS] Column, Acquity BEH C18 (Waters Corporation); Atmospheric Pressure Photo Ionization (APPI, dopant: acetone); selected ion recording (SIR)

#### 5. Shaking extraction and ID-GC/MS

[Extraction] Solvent, acetone; extraction time, 30 min

[Clean-up] Solid-phase extraction (florisil)

[GC/MS] Column, DB-5MS (Agilent Technologies); on-column injection; EI; SIM

### **Metrological Traceability**

The certified values were determined by IDMS as a primary method of measurement. The purities of the crystalline pesticides were evaluated by NMIJ, and the calibration solutions used in the determination were prepared from these crystalline pesticides. The certified values are traceable to the International System of Units (SI).

### **Mutual Recognition Arrangement under Meter Convention**

This certificate is consistent with the calibration and measurement capabilities (CMCs) that are included in Appendix C of the Mutual Recognition Arrangement (MRA) drawn up by the International Committee for Weights and Measures (CIPM). Under the MRA, all participating institutes recognize the validity of each other's calibration and measurement certificates for the quantities, ranges and measurement uncertainties specified in Appendix C (as for Appendix C of MRA, see <http://kcdb.bipm.org/AppendixC/default.asp>).

### **Expiration of Certification**

This certificate is valid for three months from the date of shipment, provided the material is stored in accordance with the instructions given in this certificate.

### **Sample Form**

This CRM was prepared from unpolished rice, which was cultivated and prepared to contain the four pesticides. This CRM of ca. 25 g in net volume is kept in a glass bottle.

### **Homogeneity**

The homogeneity of the CRM was determined by analyzing 10 bottles randomly sampled from 330 bottles. Fenitrothion and Etofenprox were determined by pressurized liquid extraction and ID-GC/MS. The inhomogeneity of the analytes, which was evaluated by ANOVA, is not significant and is reflected in the uncertainty of the certified values.

### **Instructions for Storage**

This CRM should be stored at about  $-30\text{ }^{\circ}\text{C}$  under dark conditions.

### **Instructions for Use**

#### (1) Sample size

Considering the homogeneity, more than 3 g of the material should be used for analysis.

#### (2) Determination of water (dry mass)

The certified values of this CRM are given on a dry-mass basis. Analytical results must be calculated on a dry-mass basis. The moisture content (loss on drying) should be assessed by taking a portion (about 1 g) of the material and drying it in an oven at  $95\text{ }^{\circ}\text{C}$  for 12 h. The weighing should be performed after cooling down the CRM to room temperature in a desiccator. The approximate moisture content was found to be 13%. The samples that was used for the determination of water should not be used for the determination of pesticides.

#### (3) The CRM should be equilibrated to room temperature before weighing.

### **Precautions for Handling**

Wear a protective mask, gloves, and other protective equipment during handling the CRM. Refer to the safety data sheet (SDS) on this CRM before use.

**Preparation**

The raw material for this CRM was cultivated to contain the target pesticides in Japan. The unpolished rice used for preparing the CRM was freeze-pulverized, homogenized, and bottled into 25-g portions. The bottled samples were sterilized by  $\gamma$ -ray irradiation from  $^{60}\text{Co}$  and stored at about  $-30\text{ }^{\circ}\text{C}$  until required. The preparation of this CRM was carried out by the Environmental Technology Service Co., Ltd., Funtai-Giken Co., Ltd., and Radiation Application Development Association.

**Technical Information**

The concentrations of fthalide (4,5,6,7-tetrachlorophthalide) and isoprothiolane (di-isopropyl 1,3-dithiolan-2-ylidenemalonate) in this CRM were 0.09 and 1.3 mg/kg, respectively. Isoprothiolane was gradually degraded during the stability test. The concentration of cadmium was 5.2  $\mu\text{g}/\text{kg}$ . These concentrations are reported on a dry-mass basis.

**NMIJ Analysts**

For this CRM, the technical and production managers are YARITA T. and OTAKE T., respectively. Analytical measurements for the certification of this CRM were performed at NMIJ by OTAKE T., YARITA T., ITOH N., AOYAGI Y., MATSUO M., HANARI N., OTSUKA S., and INAGAKI K.

**Information**

If substantive technical changes occur that affect the certification before the expiration of this certificate, NMIJ will notify the registered customer. Customer registration on the NMIJ Website (given below) will facilitate notification. Technical reports regarding this CRM can be obtained from the contact details given below.

**Reproduction of Certificate**

In reproducing this certificate, it should be clearly indicated that the document is a copy.

April 1, 2020

ISHIMURA Kazuhiko  
President

National Institute of Advanced Industrial Science and Technology

If you have any questions about this CRM, please contact:  
National Institute of Advanced Industrial Science and Technology,  
National Metrology Institute of Japan,  
Center for Quality Management of Metrology, Reference Materials Office,  
1-1-1 Umezono, Tsukuba, Ibaraki 305-8563, Japan  
Phone: +81-29-861-4059; Fax: +81-29-861-4009, <https://unit.aist.go.jp/nmij/english/refmate/>

**Revision history**

February 1, 2012: Expiration of Certification was changed to “3 months after the date of shipment” on the basis of the stability test results.

The description on “Mutual Recognition Arrangement under Meter Convention” was added.

April 1, 2015: “Metrology Management Center” was renamed to “Center for Quality Management of Metrology.”