National Institute of Advanced Industrial Science and Technology

National Metrology Institute of Japan

Reference Material Certificate

NMIJ CRM 7508-a
No. +++

Pesticides in Cabbage

This certified reference material (CRM) was produced in accordance with the NMIJ’s management system, and in compliance with ISO GUIDE 34:2009 and ISO/IEC 17025:2005. This CRM is intended for use in the validation of analytical methods and instruments during analysis of pesticides (fenitrothion, chlorpyrifos and permethrin) in cabbage samples and similar materials.

Certified Values

The certified values, expressed as mass fractions, 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%.

<table>
<thead>
<tr>
<th>Pesticides</th>
<th>CAS No.</th>
<th>Certified value Mass fraction (mg/kg)</th>
<th>Expanded uncertainty Mass fraction (mg/kg)</th>
<th>Analytical Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenitrothion</td>
<td>122-14-5</td>
<td>2.41</td>
<td>0.20</td>
<td>1, 2</td>
</tr>
<tr>
<td>(O, O-dimethyl-O-4-nitro-m-tolyl phosphorothioate)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>2921-88-2</td>
<td>6.94</td>
<td>0.84</td>
<td>1, 2</td>
</tr>
<tr>
<td>(O, O-diethyl O-3, 5, 6-trichloro-2-pyridyl phosphorothioate)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Permethrin</td>
<td>52645-53-1</td>
<td>5.75</td>
<td>0.50</td>
<td>1, 3</td>
</tr>
<tr>
<td>(3-phenoxybenzyl (1RS, 3RS; 1RS, 3RS)-3-(2, 2'-dichloroviny1)-2, 2-dimethylcyclopropene-2-carboxylate)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Analysis

The certified values of this CRM were based on the analytical results of pesticides by homogenization extraction and isotope dilution-gas chromatography/mass spectrometry (ID-GC/MS) described as follows:

1. [Extraction] Solvent, acetonitrile
   [Clean-up] The extract was shaken with sodium chloride and phosphate buffer solution (pH 7.0) in a separatory funnel. The acetonitrile layer was dehydrated and dried, then, toluene/acetonitrile (1:3, v/v) was added. This was cleaned up by a solid phase extraction (graphite carbon/aminopropylsilanized silica gel).
   [GC/MS] Column, DB-5MS; splitless injection; electron impact ionization (EI); selected ion monitoring (SIM)

2. [Extraction] Solvent, acetone
   [Clean-up] The extract was shaken with ethyl acetate/hexane (1:4, v/v) and saturated sodium chloride aqueous solution in a separatory funnel. The ethyl acetate/hexane (1:4, v/v) layer was dehydrated and dried, then, hexane/acetone (1:1, v/v) was added. This was cleaned up by a solid phase extraction (silica gel).
   [GC/MS] Column, DB-17MS; on-column injection; EI; SIM

3. [Extraction] Solvent, acetone
   [Clean-up] The extract was shaken with hexane and 10 % sodium chloride aqueous solution in a separatory funnel. The hexane layer was dehydrated and dried, then, hexane was added. This was cleaned up by a solid phase extraction (Florisil).
Metrological Traceability
The certified values of this CRM were determined by IDMS. The purities of the high-purity pesticides were evaluated by NMIJ and the calibration solutions for the determination were prepared from these pesticides. The certified values are traceable to the International System of Units (SI).

Expiration of Certification
This certificate is valid for 3 months from the date of shipment, provided that the material is stored in accordance with the instructions given in this certificate.

Sample Form
This CRM was prepared from cabbage that was grown to contain the four pesticides. This CRM is in the form of a green powder and packaged in an amber glass bottle (3 g each).

Homogeneity
The homogeneity of this CRM was determined by analyzing 10 bottles selected by random sampling of 200 subdivided bottles. The inhomogeneity of the analyte was evaluated by ANOVA and was reflected in the uncertainty of the certified value.

Instructions for Storage
This CRM should be kept about -30 °C under dark condition.

Instructions for Use
The CRM should be equilibrated to room temperature before use. More than 0.2 g of the material should be used. If it’s necessary, the water that is equivalent to about ten times of sample weight can be added. When the water was added, pay attention to the degradation of target pesticides.

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

Preparation Method
This CRM was prepared to contain the target pesticides in Japan. The cabbage for the CRM was freeze-pulverized, homogenized, and bottled into 3-g portions. The bottled samples were sterilized by γ-ray irradiation with 60Co and stored about -30 °C until required.

Information
The concentration of etofenprox (2-(4-ethoxyphenyl)-2-methylpropyl 3-phenoxybenzyl ether) determined in February, 2014 was 9 mg/kg.
The moisture content assessed by drying the sample in an oven at 105 °C to 110 °C for 24 h was approximately 12 %.

NMIJ Analysts
The technical manager and production manager for this CRM is M. Numata and T. Yarita, respectively. Analysts are T. Otake, T. Yarita, Y. Aoyagi, and Y. Kuroda.

Collaborator
A part of the preparation of CRM was carried out by the General Environmental Technos Co., Ltd under a contract with NMIJ. The homogeneity study was carried out by the Japan Food Research Laboratories under a contract with NMIJ.

Technical Information
Customer registration on the NMIJ Website (given below) will facilitate notification of any revision of the information given
above. 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.

**Note**

This CRM was developed by the Research and Development Projects for Application in Promoting New Policy of the Agriculture Forestry and Fisheries of the Ministry of Agriculture, Forestry and Fisheries, Japan.

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**April 1, 2015**

Ryoji Chubachi
President
National Institute of Advanced Industrial Science and Technology

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If you have any questions about this CRM, please contact
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**Revision history**

March 30, 2012: The uncertainties for fenitrothion, chlorpyrifos and permethrin were changed.

January 7, 2015: The uncertainties for fenitrothion and permethrin, the certified value and corresponding uncertainty of chlorpyrifos, the information for etofenprox were changed. Note was added.

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