

# Study of the extraction conditions of pesticide residues by using certified reference material (CRM)

**Related CRM:**

**NMIJ CRM 7504-a Pesticides in Unpolished Rice**

# Pesticide residue analysis and quality control

Pesticide residue analysis →



Extraction and clean-up



Instrumental measurement

The analysis includes complex operations

Strict quality control is required to obtain accurate analytical results.

- [ Internal quality control : the use of CRM, recovery test, and others
- [ External quality control : proficiency testing

**In this study, microwave-assisted extraction (MAE) parameters were optimized by using food matrix CRM for the analysis of pesticide residues.**

# Recovery test and matrix CRM

## ○Recovery test :

Recovery is typically tested by adding compounds to matrix samples ('spiking'), and this is necessary for evaluating analytical methods; however, solute–matrix interactions of the native compounds in food samples may render this approach unsuitable.

## ○Matrix CRM :

Using samples containing the target native compounds such as CRMs allows a necessary examination of the analytical method including the extraction efficiency. The raw materials used for CRM samples were grown and sprayed with various target pesticides.



Recovery yields of spiked compounds may be satisfactory, but native compounds naturally contained in the sample may have failed to be extracted adequately. Thus, matrix CRM is a useful tool for validation of analytical methods.



Cultivation of a raw material

# Application of MAE for the analysis of pesticide residues in green onion



MAE system

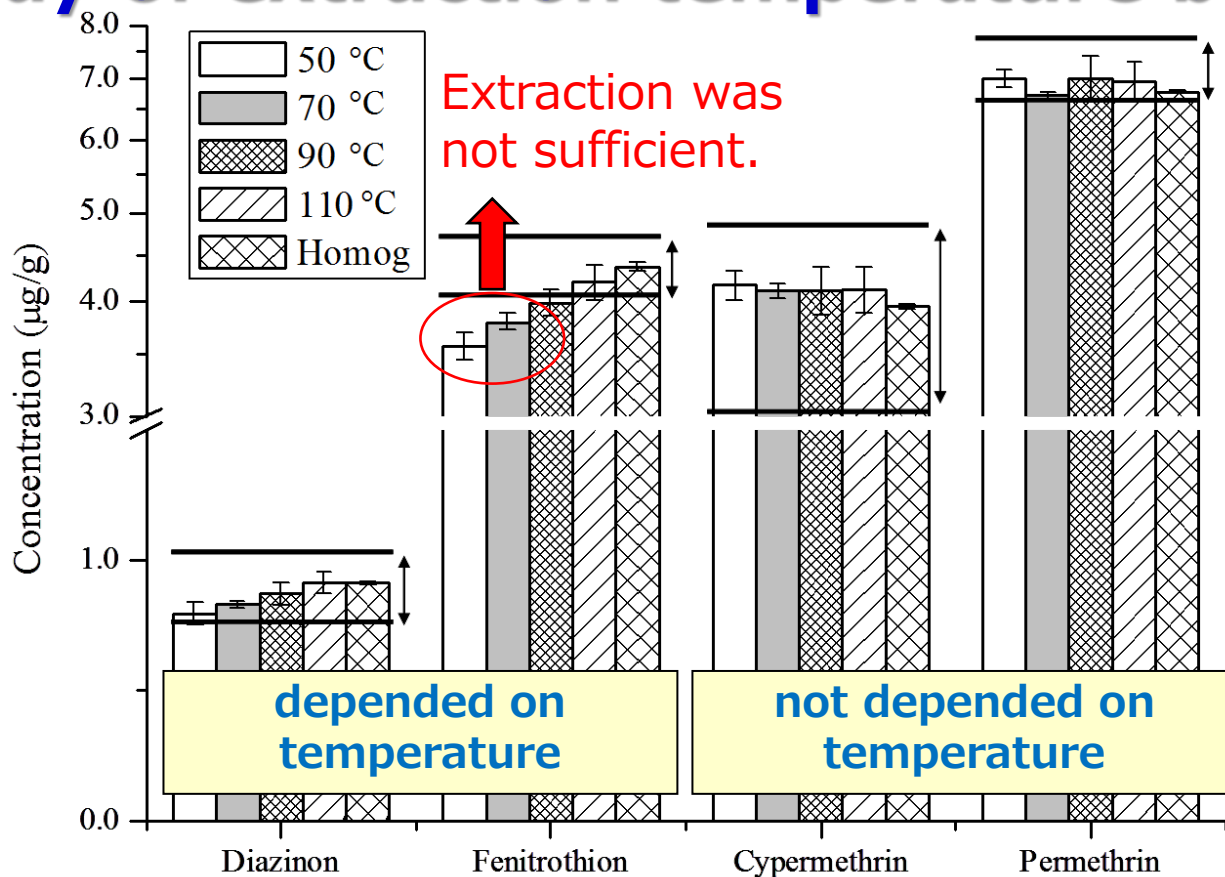
MAE enables a batch process, can be automated, and needs only a small volume of solvent.



NMIJ CRM 7507-a  
Green onion powder

MAE parameters were optimized for extracting two organophosphorus (OP, diazinon and fenitrothion) and two pyrethroid (PYR, cypermethrin and permethrin) pesticides in a green onion CRM. Further, a recovery test by spiking pesticides into blank green onion sample was carried out for 16 OP and 10 PYR pesticides.

# Study of extraction temperature by using CRM



[ Otake et al. (2012) *J. AOAC Int.* **95**, 232-237 ]

Pesticide concentrations in green onion CRM obtained by MAE with changes in temperature and homogenization.

[ Homog: homogenization. Extraction was performed with ACN at 50, 70, 90, and 110°C for 10 min. Values and error bars represent means and SDs, respectively. The horizontal rule and up-down arrows denote the range of expanded uncertainty ( $k = 2$ ) for certified concentrations;  $n = 3$ . ]

# Study of extraction temperature by using CRM

- The concentrations obtained by MAE were consistent with certified concentrations, except for 50 and 70 °C with fenitrothion. Thus, 90 and 110 °C of MAE temperatures seem to be suitable for the analysis of target pesticides; 110 °C is considered to be better, since the concentration of fenitrothion obtained at 90°C was significantly lower than that obtained by homogenization.
- The observed concentrations for OP pesticides (diazinon and fenitrothion) depended on extraction temperature, but for PYR pesticides (cypermethrin and permethrin) did not. Although the reason is not clear, the difference for the affinity of pesticides to the anatomy of green onion between OP (diazinon and fenitrothion) and PYR (cypermethrin and permethrin) pesticides may be related to this result.

# Recovery yields by the spiking test

MAE_temperature (spiked concn, µg/g-sample)	MAE_50 °C (0.2)			MAE_110 °C (0.2)		
	Mean	±	SD	Mean	±	SD
	(% )			(% )		
OP pesticides						
Butamifos	92.1	±	0.5	108.3	±	1.5
Chlorpyrifos	85.0	±	1.2	94.8	±	1.7
Diazinon	83.1	±	0.8	96.6	±	2.2
EPN	86.4	±	1.5	105.3	±	1.3
Fenitrothion	89.3	±	1.4	79.7	±	2.5
Fenthion	80.6	±	1.0	85.6	±	1.9
Fosthiazate (isomer 1, 2)	87.7	±	0.7	94.7	±	1.9
Isofenphos	83.3	±	0.9	95.8	±	1.6
Isofenphos oxon	85.0	±	1.1	98.3	±	2.3
Malathion	83.2	±	0.7	76.0	±	2.0
Phenthoate	87.0	±	1.6	82.9	±	1.9
Pirimifos–methyl	84.6	±	1.5	93.0	±	2.1
Prothiofos	85.5	±	1.2	95.6	±	1.9
Quinalphos	86.0	±	1.4	101.9	±	4.7
Terbufos	76.9	±	1.9	89.6	±	2.6
Tolclophos–methyl	82.4	±	1.7	89.5	±	2.0

(MAE was performed with acetonitrile at 110°C for 10 min;  $n = 3$ .)

# Recovery yields by the spiking test

MAE_temperature (spiked concn, µg/g-sample)	MAE_50 °C (0.2)			MAE_110 °C (0.2)		
	Mean	±	SD	Mean	±	SD
	(%)			(%)		
PYR pesticides						
Acrinathrin	81.6	±	1.1	73.5	±	2.8
Bifenthrin	85.5	±	1.8	98.4	±	1.3
Cyfluthrin (isomer 1–4)	91.7	±	0.8	89.2	±	3.7
Cyhalothrin (isomer 1, 2)	86.6	±	1.2	101.1	±	1.3
Cypermethrin (isomer 1–4)	85.4	±	0.8	101.4	±	1.4
Deltamethrin	72.0	±	1.8	72.4	±	4.8
Fenvalerate (isomer 1, 2)	88.6	±	5.2	90.5	±	0.4
Flucythrinate (isomer 1, 2)	86.2	±	0.9	98.6	±	0.8
Fluvalinate	83.0	±	0.6	90.2	±	1.6
Permethrin (isomer 1, 2)	91.5	±	2.9	107.3	±	2.0

(MAE was performed with acetonitrile at 110°C for 10 min;  $n = 3$ .)



# Comparison of the results for recovery test and CRM

## ○Recovery test

- ➡ The results for both 50 °C and 110 °C were acceptable because the recoveries were in the range of 70 % to 120 %. This result may lead to the conclusion that 50 °C is suitable for the extraction temperature.

## ○CRM

- ➡ One of the target pesticides was not extracted sufficiently when the temperature was set at 50 °C.

It is necessary to evaluate the analytical methods by using matrix CRMs because recovery tests may be insufficient for the evaluation of extraction efficiency for some cases.