Talanta 132 (2015) 269–277

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Proficiency testing for determination of pesticide residues in soybean: Comparison of assigned values from participants' results and isotope-dilution mass spectrometric determination

Takashi Yarita *, Takamitsu Otake, Yoshie Aoyagi, Takayoshi Kuroiwa, Masahiko Numata, Akiko Takatsu

National Metrology Institute of Japan (NMIJ), National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 3, Umezono, Tsukuba, Ibaraki 305-8563, Japan

ARTICLE INFO

Article history:
Received 1 August 2014
Received in revised form
30 August 2014
Accepted 2 September 2014
Available online 16 September 2014

Keywords:
Proficiency testing (PT)
Candidate reference material
Certified reference material (CRM)
Organophosphorus pesticide
Pyrethroid pesticide
Assigned value
z-Score
Primary method of measurement

ABSTRACT

Proficiency testing (PT) for the determination of pesticide residues in soybean samples was organized by the National Metrology Institute of Japan (NMIJ). The candidate certified reference material, NMIJ CRM 7509-a, that was prepared from the raw soybeans containing target pesticides (diazinon, fenitrothion, chlorpyrifos, and permethrin) was used as the test sample. Forty participants submitted two sets of analytical results along with the details of the analytical method and conditions they applied. Two types of assigned values were established for each target pesticide: one was derived from the analytical results of the participants, and the other was provided from the analytical results by isotope-dilution mass spectrometry (IDMS). The latter values were 7.4–16% higher than the former values, plausibly because the analytical values from the IDMS measurements were not affected by the recovery ratio of the target pesticides during the analytical process. Thus, two kinds of *z*-scores were calculated for individual participants using the corresponding assigned values: one (z_1-score) showed the relative performance score for the present PT and the other (z_2-score) could be used for evaluation of the trueness of their analytical methods.

1. Introduction

Various pesticides are used worldwide to protect foods against pests and diseases [1]. However, high levels of residual pesticides in foods may result in adverse effects on human health. In Japan, the Positive List System for Agricultural Chemicals Remaining in Foods was introduced in 2006 to prohibit the distribution of foods that contain agricultural chemicals above a certain level, even if the maximum residue limits (MRLs) have not been established [2]. Under this system, analysis of a wide variety of residual pesticides in foods that are under quarantine or in the market is routinely performed.

Analytical protocols for determining the presence of pesticide residues in food samples usually involve complex extraction of the target pesticides, multi-step clean-up of the obtained extracts, and sensitive and selective quantification via a chromatographic technique [3–5]. Ensuring the reliability of the results is crucial to control the risk associated with pesticide residues. Proficiency testing (PT) is one of the key elements in the implementation of an appropriate quality assurance program and performance monitoring procedure for chemical analysis laboratories [6,7]. Consequently, a number of PT programs for the determination of pesticide residues in food samples have already been organized [8–15].

The National Metrology Institute of Japan (NMIJ) has recently undertaken the development of crop certified reference materials (CRMs) for the validation/verification and quality assurance of pesticide residue analysis. The candidate materials used for development of the CRMs were prepared from raw crops containing the target pesticides. Characterization of the target pesticides was carried out by isotope-dilution mass spectrometry (IDMS), which has the potential to be a primary method of measurement [16–19]. To date, we have issued five kinds of CRMs in this field [20–23].

Another recent undertaking of the NMIJ is the organization of PTs for inorganic-constituent analysis of food samples to support skill upgrading of food analysis laboratories [24,25]. In 2012, the NMIJ initiated another PT program for pesticide-residue analysis of food samples. The first round PT was carried out using the candidate soybean powder material, NMIJ CRM 7509-a [23], as a test sample. In this PT, two kinds of assigned values were

* Corresponding author. Tel.: +81 29 861 9416; fax: +81 29 861 6866.
E-mail address: t-yarita@aist.go.jp (T. Yarita).

http://dx.doi.org/10.1016/j.talanta.2014.09.001
0039-9140/

established: one was derived from the analytical results of the participants, and the other was provided from the analytical result used in the certification of CRM 7509-a. In this article, the process and the results of the PT are reported and the difference between the two assigned values is discussed.

2. Experimental

2.1. Test samples

An outline of the preparation of the test samples is presented as follows: the raw soybeans (*Glycine max*, cv. Enrei) were cultivated so as to contain *O*,*O*-diethyl-*O*-2-isopropyl-6-methyl-pyrimidin-4-yl phosphorothioate (diazinon), *O*,*O*-dimethyl-*O*-4-nitro-*m*-tolyl phosphorothioate (fenitrothion), *O*,*O*-diethyl-*O*-3,5,6-trichloro-2-pyridyl phosphorothioate (chlorpyrifos), and 3-phenoxybenzyl (1*RS*, 3*RS*, 1*RS*, 3*RS*)-3-(2, 2-dichlorovinyl)-2, 2-dimethylcyclopropanecarboxylate (permethrin). The soybeans were air-dried, freeze pulverized, mixed, bottled into amber glass bottles (10 g each), sterilized by γ-irradiation (15 kGy), and then the prepared samples were stored at ca. −80 °C until use. The homogeneity of the prepared samples was evaluated by the Japan Food Research Laboratories (Tokyo, Japan) by quantifying the target pesticides. The relative standard uncertainties related to the inhomogeneity were evaluated according to ISO Guide 35 [26] with values of 1.89% for diazinon, 4.00% for fenitrothion, 3.10% for chlorpyrifos, and 3.16% for permethrin. The details of the preparation and the homogeneity evaluation of the test samples have been described elsewhere [23].

2.2. Determination of pesticides in the test samples by NMIJ

The analytical results used in the certification of NMIJ CRM 7509-a were utilized in the present PT. These results were obtained by three analytical methods (Method 1, Method 2, and Method 3) conducted at NMIJ, the flow diagrams and the corresponding target pesticides of which are shown in Fig. 1. These methods consisted of extraction and clean-up processes that were based on the Analytical Methods for Residual Compositional Substances of Agricultural Chemicals, Feed Additives, and Veterinary Drugs in Food [3] and IDMS quantification by GC/MS measurements. Specifically, the initial analytical results (0 month) of the long-term stability assessment that were obtained by Method 1, and the analytical results of the characterization that were obtained by Method 2 or Method 3 were used to obtain the assigned values 2 (described in Section 2.4.). These analyses were performed in Nov. 2011, which was about four months prior to distribution of the samples to the participants. Additionally, the analytical results of the short-term stability monitoring that were obtained by Method 1 were used to evaluate the stability of the PT samples. These analyses were performed two weeks before distribution of the sample (April 2012) and three weeks after the deadline for submission of the participant results (August 2012).

2.3. Analysis by the participants

This PT round was announced to food manufacturers, agricultural producers, testing laboratories, public research institutes, etc., in Japan and was subscribed by 43 participants. On May 8, 2012, the test samples (2 bottles) and working instructions were sent to each participant by a delivery company using a refrigerated transport. The participants were asked to store the samples at −30 to −20 °C in the dark, and then to perform duplicate analysis of the target pesticides (the target pesticides to be determined were selectable by each participant). The participants were also asked to report the details of the analytical method and quantification conditions (such as the purity or concentration of primary calibrants, linear range of the calibration curves, the extraction and clean-up procedure, and the quantification method and its conditions) as well as the analytical results with observed chromatograms using a prescribed sheet in Excel format. The deadline was set to July 31, 2012.

2.4. Establishment of assigned values

For each target pesticide, two kinds of assigned values were established. The assigned value 1 (X_m) was obtained from the analytical results of the participants as follows: the outliers of the results were excluded by Cochran's test and Grubbs' test, and the median of the included results was then calculated. The normalized interquartile range (*NIQR*) was also calculated by multiplying the interquartile range (the difference of quartile 3 and quartile 1) of the included analytical results by 0.743. The assigned value 2 (X_{NMIJ}) was the weighted mean of the NMIJ analytical results obtained by the corresponding analytical methods (Method 1 and either Method 2 or Method 3). Simultaneously, the predicted reproducibility standard deviation ($PRSD_R$), which is the expected inter-laboratory precision for each target pesticide, was calculated using the modified Horwitz equation [27].

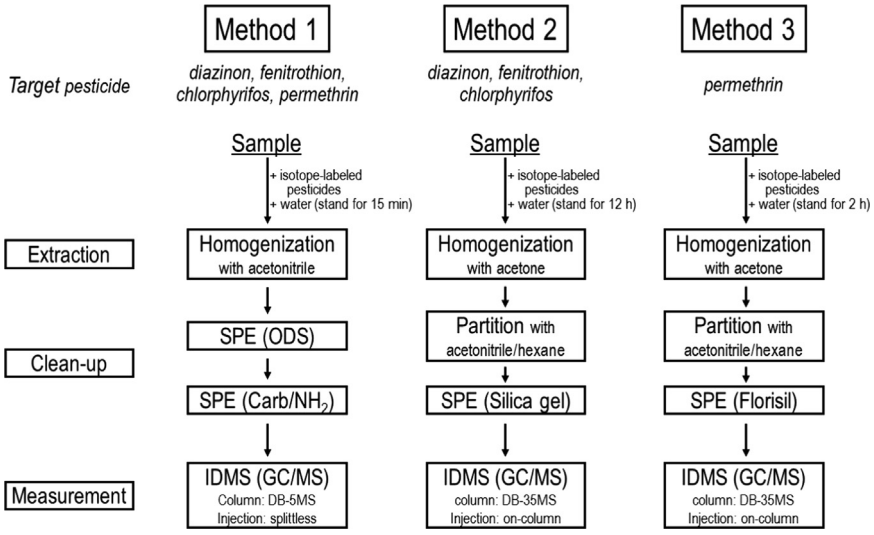

Fig. 1. Flow diagrams of the analytical methods for respective target pesticides used by NMIJ.