ANALYTICAL METHOD FOR DETERMINATION OF MULTI-RESIDUE TRIAZOLE FUNGICIDES IN PALM OIL MATRICES

MAZNAH ZAINOL and HALIMAH MUHAMAD

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MPOB INFORMATION SERIES • ISSN 1511-7871 • JULY 2020 MPOB TS No. 188

Triazole is a class of systemic fungicides containing 1,2,4-triazole moieties, which is used to control various fungal diseases on fruit, vegetable, legume and grain crops for both pre- and post-harvest applications (Manclúset *et al*., 2008). The modes of actions of these fungicides are through xylem systemic and broad spectrum activities by blocking the ergosterol biosynthesis pathway, which leads to toxic sterol accumulation and results in fungal cell death.

Basal stem root (BSR) caused by pathogenic fungus (white-root fungus), *Ganoderma* spp. is the most serious disease of oil palm, especially in Malaysia and Indonesia. In oil palm plantation, triazole fungicides such as hexaconazole, penconazole, propiconazole and difenoconazole are effective as preventive treatment in controlling early stage of *G. boninense* infection (Idris *et al*., 2004; 2010). Recently, there is growing interest in research related to the effect of triazole fungicide efficacy through nano-delivery system, such as chitosan-base and zinc/aluminium-layered double hydroxide incorporated with hexaconazole against *G. boninense* (Mustafa *et al*., 2018; Maluin *et al*., 2019).

Therefore, higher applications of triazole fungicides are expected at the oil palm plantation for *Ganoderma* infection control. To date, there is no method available for simultaneous analysis of multi triazole residues in palm oil matrices. Hence, a simple, fast and efficient analytical method has been developed and validated for this purpose. As food safety is predominantly concern, it is important to ensure that palm oil derived from mesocarp and kernel is free from any pesticide residues.

SCOPE

The test method herein describes on the determination of multi-residue triazole analysis *i.e.* brumuconazole, difenoconazole, epoxiconazole, hexaconazole, penconazole, propiconazole, tebuconazole and tetraconazole in palm oil matrices, crude palm oil (CPO) and crude palm kernel oil (CPKO).

PRINCIPLE

Triazole residues are extracted from CPO and CPKO based on liquid-liquid extraction (LLE) using acidified acetonitrile. Extracts from multiple extractions are then combined and allowed to stand in a freezer to precipitate the lipid content. Final de-oiled extract is then subjected to clean-up by dispersive solid phase extraction (*d*-SPE) prior to analysis. The separation and quantification of triazole analytes are performed using LC-QTOF-MS/MS (*Figure 1*).

Figure 1. LC-QTOF-MS/MS.

ISSN 1511-7871
9 771511 787001

Head of Corporate Implementation and Consultancy Unit, Malaysian Palm Oil Board. 6, Persiaran Institusi, Bandar Baru Bangi, 43000 Kajang, Selangor, Malaysia.
Tel: 03-8769 4574 Fax: 03-8926 1337 E-mail: tot@mpob.gov.my Website: www.mpob.gov.my

RESULTS

Method validation and recovery study are conducted based on the requirements set in SANTE document. The calibration curve for each analyte of interest using matrix-matched standard of both matrices (CPO and CPKO) at six concentration levels ranging from 10.0 to 100.0 ng g^{-1} are constructed. All calibration curves plotted are linear with co-efficient of determination (R^2) of more than 0.990 in all matrices (CPO, CPKO and solvent). *Figure 2* shows the matrix effect found in CPO and CPKO matrices for tetraconazole analytes. The LOD and LOQ in CPO were in the range of 0.2 to 4.8 ng g^{-1} and 0.7 to 14.5 ng g^{-1}, respectively. For CPKO matrix, LOD and LOQ were in the range of 1.26 to 8.86 ng g^{-1} and 3.82 to 16.86 ng g^{-1}, respectively. *Figure 3* illustrates the total ion chromatogram (TIC) for triazole analytes. The mean recoveries ranged from 73.26% to 102.94% with RSD less than 10% were observed in CPO samples. Meanwhile, most of analytes studied were recovered in the range of 73.0% to 108.0% with RSD less than 10% for CPKO samples.

SERVICE AVAILABLE

Analysis of CPO and CPKO samples for the determination of multi triazole residues (brumuconazole, difenoconazole, epoxiconazole, hexaconazole, penconazole, propiconazole, tebuconazole and tetraconazole).

ADVANTANGES

- Simultaneous determination of triazole multi-residues comprising of 8 compounds in a single injection;
- Shorter analytical time; and
- Quantification using QTOF MS/MS can provide accurate mass data for both precursor (MS) and product ion (MS/MS) confirmation.

INDICATIVE COST

The analysis cost for each sample is RM500.00, including sample preparation and analysis. The analysis cost is subjected to change without prior notice.

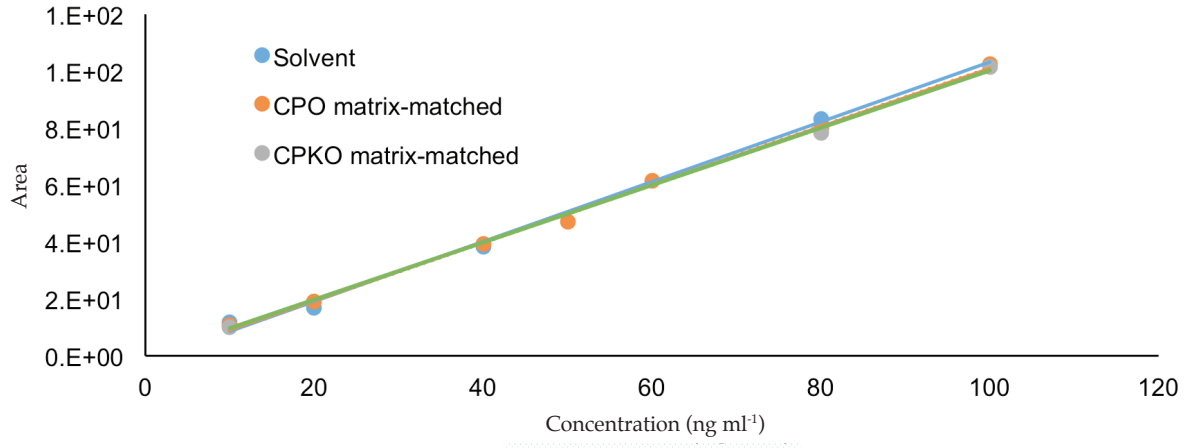

Figure 2. Matrix-matched calibration curves of tetraconazole in solvent, CPO matrix and CPKO matrix.

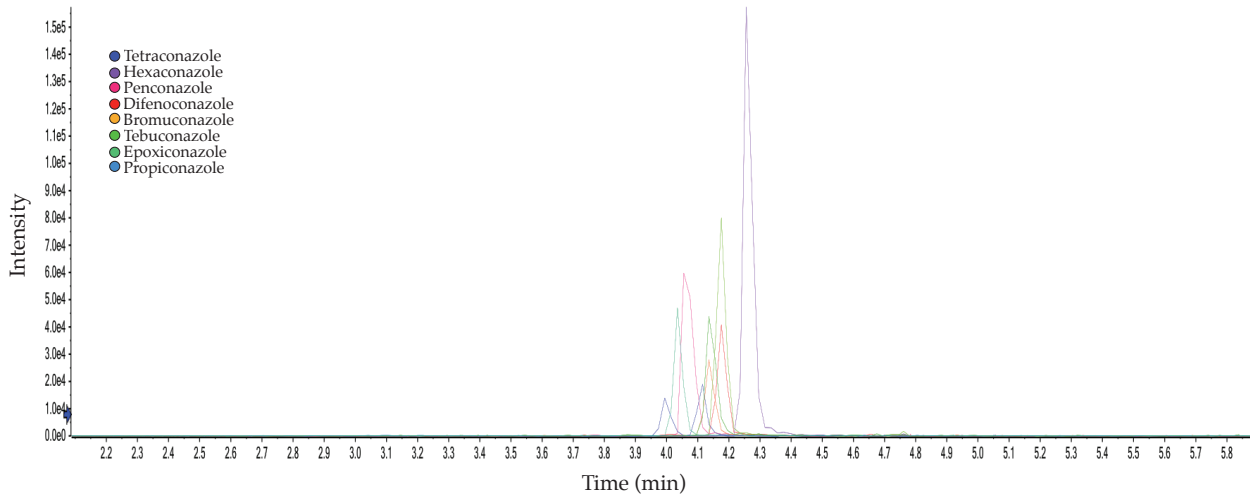

Figure 3. Total ion chromatogram of triazole analytes.

CONCLUSION

The method can be easily employed for determination of triazole multi-residues in palm oil matrices. It is important that the palm oil industry has a reference method to facilitate its quality control.

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For more information, kindly contact:

Head of Corporate Implementation
and Consultancy Unit, MPOB
6, Persiaran Institusi,
Bandar Baru Bangi,
43000 Kajang, Selangor, Malaysia
Tel: 03-8769 4574
Fax: 03-8926 1337
E-mail: tot@mpob.gov.my
www.mpob.gov.my