

Suitability of PSA (Primary Secondary Amines) and Z-Sep as clean-up sorbents in AOAC official method 2007.01 for analysis of trifloxystrobin and CGA 321113 residue in dragon fruit, star fruit and watermelon

[Kesesuaian sorben pembersih PSA (Primer Sekunder Amina) dan Z-Sep dalam kaedah rasmi AOAC 2007.01 untuk analisis residu trifloxystrobin dan CGA 321113 pada buah naga, belimbing dan tembikai]

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Abstract

Two types of clean-up sorbents, namely PSA (Primary Secondary Amines) and Z-Sep were tested for reliability in AOAC official method 2007.01 for generating accurate results for analysis of trifloxystrobin and CGA 321113 (trifloxystrobin metabolite) in dragon fruit, star fruit and watermelon. A known amount of both analytes was fortified onto separate analytical portions of dragon fruit, star fruit and watermelon respectively, followed by an extraction clean-up procedure using either PSA or Z-Sep. The extracts were analysed by Liquid Chromatography Tandem Mass Spectrometry (LCMS-MS) analysis. Measured concentrations were compared with a theoretical fortified value in order to determine its recovery. Results indicated that both PSA and Z-Sep generated acceptable recovery of trifloxystrobin ranging from 76.8 – 107.7%. However, when PSA alone was used as the clean-up material, significant loss of CGA 321113 was deduced from low average recovery values in dragon fruit (47.1%), star fruit (57.4%) and watermelon (31.7%) for fortification level of 0.01 mg/kg. For higher fortification level of 0.1 mg/kg, lower average recovery values of CGA 321113 were reported in dragon fruit (23.9%), star fruit (15.4%) and watermelon (14.6%). In all the studied fruits, Z-Sep showed recoveries of CGA 321113 within the range of 80.4 – 124.2% at 0.01 and 0.1 mg/kg fortification levels indicating no significant loss during the clean-up procedure. Based on two types of residue definitions (MRL compliance and dietary risk assessment), it can be concluded that for analysis of CGA 321113, Z-Sep should be used as the clean-up sorbent in the clean-up procedure.

Keywords: quechers, clean-up procedure, primary secondary amines (PSA), Z-Sep, trifloxystrobin, CGA 321113

Introduction

Clean-up procedure is one of the common steps in most of the pesticide residue

analytical methods. The purpose of the clean-up is to eliminate or reduce co-extracted compounds other than the

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targeted analyte(s) that could interfere chromatographically with the analyte peak(s) during instrument analysis (e.g. gas chromatograph, liquid chromatograph, etc.). Such interference would render inaccurate quantitation of peak area/height and inevitably leads to inaccurate quantitative results in tested samples.

Quechers-based method is the most common method used in analysis of multi-residue of pesticides in food. Quechers or sometimes written as QuEChERS is an acronym of the method's advantageous features which are quick, effective, cheap, rugged and safe. This method was first published by Anastassiades et al. (2003), and since then variants of Quechers methods have been developed and published. Basically, the method employs analyte extraction and sample extract clean-up within one single step through the use of dispersive SPE (Solid Phase Extraction). Unlike older pesticide residue analytical methods which involve multi-steps of extraction and clean-up, Quechers-based methods are simple, fast and yet reliably giving accurate results. The adoption of this simple and yet effective method was so wide spread within few years after its introduction, that in 2007, the AOAC International (Association of Analytical Communities) had adopted the method as the AOAC official method 2007.01. Quechers-based methods were also reported in analysis of residues in environmental samples such as sediments, soils and water (Bruzzone et al. 2014).

PSA was the first dispersive SPE sorbent to be used in the first Quechers method. Further improvements to Quechers method led to the use of other sorbents such as Graphitized Carbon Black (GCB) (to remove chlorophyll and carotenoids) and C18 (to remove fatty acids). PSA is the most common clean-up sorbent used in Quechers method for food analysis as it has the ability to trap sugars and polar organic acids from co-extracted food matrix. It has also been used in combination with other types of

sorbents such as GCB or C18 for a more thorough clean-up (Chunha et al. 2007).

In 2013, zirconia-based sorbents (Z-Sep) were introduced by Sigma-Aldrich. Z-Sep has been known as a superior alternative to PSA, with its ability to remove fatty and pigmented compounds and still retain a good recovery of analytes. Z-Sep is composed of proprietary zirconia-coated silica particles (Rajski et al. 2013) or zirconium dioxide bonded to silica (Lopez-Blanco et al. 2015). It has been used as a clean-up sorbent in validation of analytical method of post-harvest fungicides on pears and oranges (Ucles et al. 2016) and carbamate pesticides in vegetable oil (Moreno-Gonzalez et al. 2014).

Trifloxystrobin is an effective strobilurin fungicide for control of wide range of fungal pathogens on plants and trees. According to the Codex Alimentarius Commission, there are two types of residue definitions for analysis of trifloxystrobin in plant commodities, namely, residue definition for MRL (Maximum Residue Limit) compliance and residue definition for estimation of dietary intake of plant/animal commodities. Residue definition defines the compound(s) to be qualified and quantitated. The definitions for trifloxystrobin according to the Codex Alimentarius Commission are shown in *Table 1* below.

CGA 321113 or trifloxystrobin acid as it is known in some publications (Chen et al. 2014; Wang et al. 2014) is formed during plant metabolism via cleavage of the methyl ester group in the parent compound to form CGA 321113. From this text onwards, in order to avoid confusion with the residue definition of trifloxystrobin for dietary risk assessment, the parent compound is referred to as trifloxystrobin and its metabolite product is referred to as CGA 321113. Molecular structure of both compounds are shown in *Figure 1*.

For the purpose of establishing MRL, it was reported that in recent method validation and analysis of trifloxystrobin and CGA 321113 in star fruits, PSA was

Table 1. Two residue definitions for trifloxystrobin in plant commodities according to the Codex Alimentarius Commission

Residue definition	Compound
MRL compliance	Trifloxystrobin
Dietary risk assessment (for MRL development)	Sum of trifloxystrobin and [(E,E)-methoxyimino-{2-[1-(3-trifluoromethylphenyl) ethylideneaminooxymethyl] phenyl}acetic acid] (CGA 321113), expressed as trifloxystrobin

Source: *JMPR* (2004)

found to cause significant loss of CGA 321113. An alternative to PSA would be Z-Sep which could enable clean-up of sample extracts without significant loss of CGA 321113. Furthermore, analysis of the two compounds was conducted on dragon fruit and watermelon to see if the loss of CGA 321113 was also observed on other fruits with high water content. In addition, although Z-Sep is touted as a superior clean-up sorbent by the manufacturer, there is no report showing the success of Z-Sep in method validation of CGA 321113 on crops. The method validation data from this study may be the first reported study for CGA 321113 based on Z-Sep as a clean-up sorbent.

Materials and methods

Two sets of experiments were conducted using PSA and Z-Sep as clean-up sorbents. Known amounts of trifloxystrobin and CGA 321113 were fortified onto analytical portions of homogenised dragon fruit, star fruit and watermelon to derive fortified concentrations of 0.01 and 0.1 mg/kg in the analytical portions. Then the fortified analytical portions were analysed by LCMSMS (Liquid Chromatograph Mass Spectrometry Mass Spectrometry) using the AOAC official analytical method 2007.01.

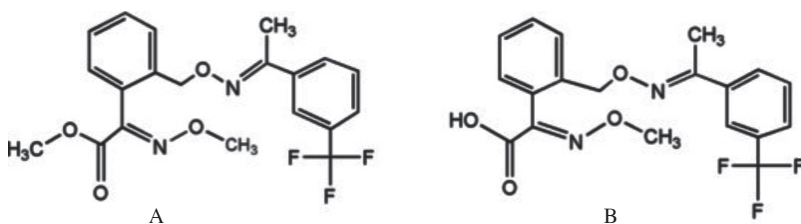


Figure 1. Molecular structure of trifloxystrobin (A) and CGA 321113 (B)

Concentrations were calculated from chromatograms and compared with fortified concentrations in order to know the percentage of recovery. A minimum of five replicates of analytical portions were made for each concentration of fortification and analyte fortified. Blank samples (no fortification) were also tested. Concentration of analytes were calculated from the following equation.

$$C_{\text{sample}} \text{ (mg/kg)} = \frac{C_{\text{calibration curve}} \text{ (\mu g/mL)} \times \text{Volume of sample extract (mL)}}{\text{Mass of analytical portion (g)}} \times F_{\text{dilution}}$$

Where

$$\begin{aligned} C_{\text{sample}} &= \text{Residue concentration in sample} \\ C_{\text{calibration curve}} &= \text{Residue concentration from calibration curve} \\ F_{\text{dilution}} &= \text{Dilution factor} \end{aligned}$$

Recovery and relative standard deviation of recovery values were derived from the following equations.

$$\text{Recovery} = \frac{\text{Concentration observed} - \text{concentration in blank sample}}{\text{Fortified concentration}} \times 100$$

$$\text{Relative standard deviation of recovery} = \frac{\text{Standard deviation of recoveries}}{\text{Mean recovery}} \times 100$$

Materials

Dragon fruits (variety Costa Rica pitaya), star fruits (B10 variety) and watermelons (Carolina cross variety) were obtained from farms with no history of insecticide products usage containing trifloxystrobin as active ingredient. These fruits were analysed prior to commencement of fortification of analytes in order to determine that trifloxystrobin and CGA 321113 were not present.

Trifloxystrobin and CGA321113 analytical standards were obtained from Bayer CropScience (M) Sdn. Bhd. The brand of PSA and Z-Sep used in the study were Sepra™ (Phenomenex) and Supel™ QuE Z-Sep Bulk (Sigma-Aldrich) respectively.

Method

Fortification of analytes

The fruits were chopped into smaller pieces. The chopped fruits were transferred into a food processor and homogenised for 2 min until a smooth sample matrix was achieved. Then 15 g of homogenised fruits (known as an analytical portion) were sub-sampled from whole homogenised matrix into a 50 ml centrifuge tube. An analytical portion was then fortified with an analyte solution and left for 15 min to let the solvent of the fortified solution to dry. Trifloxystrobin and CGA 321113 were introduced into separate analytical portions.

Analyte extraction

The analytical method adopted by the Association (AOAC) was used in this study. The analytical portion or sample size of 15 g was added to 15 ml of acetonitrile and 1.5 g of sodium acetate in a centrifuge tube. The centrifuge tube was capped and hand shaken vigorously for one min and centrifuged at 4,000 rpm for 5 min. Ten ml was decanted into a 15 ml centrifuge tube and 0.5 g PSA and 1.5 g MgSO₄ were added to it. The tube was hand shaken vigorously again for one min, followed by centrifugation at 4,000 rpm for five min. One ml of the top solution was decanted into another 10 ml graduated tube and the solution was diluted

ten times by an addition of 9 ml 0.1% formic acid in acetonitrile. The diluted extract was filtered using a syringe filter fitted with a 0.2 µm PTFE membrane. The filtered extract was then transferred into a 2 ml vial for LCMSMS analysis.

Liquid chromatograph analysis

All sample extracts were analysed using a Liquid Chromatograph Mass Spectrometry AB Sciex QTrap 5500. A Synergi 4µ Fusion-RP 80A column (50 mm long, 2 mm outer diameter and 4 µm pore size) at a setting temperature of 35 °C was used for separation of compounds and analytes prior to mass spectrometry analysis. Mobile phase and gradient flow per run are shown in *Table 2*. The flow rate of the mobile phase was set at 0.4 ml/min at constant flow mode and the injection volume was 5 µl.

Statistical analysis

One-way ANOVA was used to statistically analyse the recovery data between PSA and Z-Sep.

Results and discussion

Recovery in all replicates, recovery means and relative standard deviations are tabulated in *Tables 3* and *4*. General criteria for method validation are mean recovery within 70 – 120% range and relative standard deviation of <15% (Marin et al. 2006). Relative standard deviations observed were <15%, indicating that the method is precise.

Mean recovery values of trifloxystrobin and CGA 321113 using PSA and Z-Sep are shown in *Figures 2* and *3* for interpretation of method accuracy. For trifloxystrobin, average recoveries at 0.01 mg/kg fortification based on PSA clean-up were 104.8%, 107.7% and 81.3% for dragon fruit, star fruit and watermelon respectively. At higher 0.1 mg/kg fortification, average recoveries of trifloxystrobin were 91.4% (dragon fruit), 94.6% (star fruit) and 89.1% (watermelon). Average recovery of trifloxystrobin based on Z-Sep clean-up were 100.0% (dragon fruit), 77.8% (star

Table 2. Gradient flow of mobile phases in LCMSMS analysis of trifloxystrobin and CGA 32213

Time (min)	%A (0.1% formic acid in water)	%B (0.1% formic acid in HPLC-grade acetonitrile)	Flow (ml/min)
0.00	90.0	10.0	0.3
3.00	0.0	100.0	0.3
6.00	0.0	100.0	0.3
6.10	90.0	10.0	0.3
8.00	90.0	10.0	0.3

Table 3. Recoveries of trifloxystrobin and CGA 321113 spiked at 0.01 mg/kg in star fruits, dragon fruits and watermelons from analytical method with PSA and Z-Sep clean-ups

Crop	Recovery (%)					Mean recovery (%)	Relative standard deviation of recovery (%)
	R1	R2	R3	R4	R5		
0.01 mg/kg Trifloxystrobin (PSA clean up)							
Dragon fruit	93.7	120.0	102.7	102.7	-	104.8	10.5
Star fruit	104.9	111.0	102.2	114.9	105.5	107.7	4.8
Watermelon	80.3	95.4	84.1	83.1	63.8	81.3	14.0
0.01 mg/kg Trifloxystrobin (Z-Sep clean up)							
Dragon fruit	103.6	100.9	99.1	99.1	97.3	100.0	2.4
Star fruit	81.0	80.9	72.1	72.6	82.3	77.8	6.5
Watermelon	90.7	91.6	78.1	92.6	86.0	87.8	6.8
0.01 mg/kg CGA 321113 (PSA clean up)							
Dragon fruit	44.9	50.9	49.1	45.1	45.6	47.1	5.8
Star fruit	56.1	62.9	59.9	54.7	53.5	57.4	6.8
Watermelon	33.2	35.8	32.1	29.8	27.8	31.7	9.6
0.01 mg/kg CGA 321113 (Z-Sep clean up)							
Dragon fruit	127.2	124.7	123.0	120.1	125.9	124.2	2.2
Star fruit	95.1	91.0	86.9	79.1	84.9	87.4	7.0
Watermelon	103.6	101.1	94.0	103.6	102.3	100.9	3.9

fruit) and 87.8% (watermelon) at 0.01 mg/kg fortification level. At a fortification level of 0.1 mg/kg, trifloxystrobin was averagely recovered at 93.2% (dragon fruit), 76.8% (star fruit) and 88.6% (watermelon). There was no significant difference ($p < 0.05$) in trifloxystrobin recoveries between the two clean-up sorbents in the studied fruits. Overall, for trifloxystrobin, analytical method using either PSA or Z-Sep gave recoveries within an acceptable range of 70 – 120% at concentrations of 0.01 mg/kg and 0.1 mg/kg. It can be further deduced that the analytical method can produce accurate results of trifloxystrobin within a range

of 0.01 – 0.1 mg/kg. Trifloxystrobin has been reported to be within the acceptable recovery range in honeybee samples in Quenchers-based method which used Z-Sep as the clean-up sorbent (Kiljanek et al. 2016).

As for the CGA 321113 in star fruit, mean recoveries of CGA 321113 based on PSA sorbent were 57.4% and 15.4% at fortification concentrations of 0.01 mg/kg and 0.1 mg/kg respectively. The same <70% recovery was observed in dragon fruit and watermelon. CGA 321113 was averagely recovered at 47.1% (0.01 mg/kg fortification level) and 23.9% (0.1 mg/kg fortification

Table 4. Recoveries of trifloxystrobin and CGA 321113 spiked at 0.1 mg/kg in star fruits, dragon fruits and watermelons from analytical method with PSA and Z-Sep clean-ups

Crop	Recovery (%)					Mean recovery (%)	Relative standard deviation of recovery (%)
	R1	R2	R3	R4	R5		
0.1 mg/kg Trifloxystrobin (PSA clean up)							
Dragon fruit	81.4	90.4	89.1	95.8	100.4	91.4	7.8
Star fruit	93.0	98.5	86.4	97.4	97.7	94.6	5.4
Watermelon	96.1	99.8	96.1	86.2	67.4	89.1	14.8
0.1 mg/kg Trifloxystrobin (Z-Sep clean up)							
Dragon fruit	95.8	98.6	94.9	96.8	79.9	93.2	8.1
Star fruit	73.2	75.6	82.3	75.6	77.5	76.8	4.4
Watermelon	91.5	91.4	81.8	86.4	91.8	88.6	5.0
0.1 mg/kg CGA 321113 (PSA clean up)							
Dragon fruit	21.7	23.1	22.2	24.3	28.1	23.9	10.8
Star fruit	18.2	13.3	15.1	15.7	14.8	15.4	11.5
Watermelon	15.6	16.1	14.0	15.5	11.9	14.6	11.7
0.1 mg/kg CGA 321113 (Z-Sep clean up)							
Dragon fruit	102.8	110.7	104.9	103.2	85.7	101.4	9.2
Star fruit	78.5	76.1	85.9	85.5	76.1	80.4	6.1
Watermelon	95.8	90.0	83.4	87.5	92.1	89.7	5.2

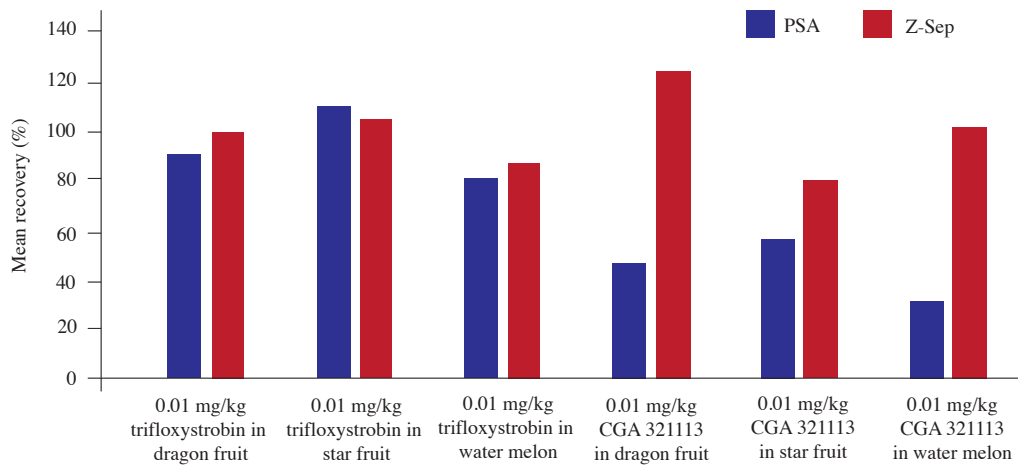


Figure 2. Mean recoveries of trifloxystrobin and CGA 321113 fortified at 0.01 mg/kg in star fruit, dragon fruit and watermelon from analytical method with PSA and Z-Sep as clean-up sorbents

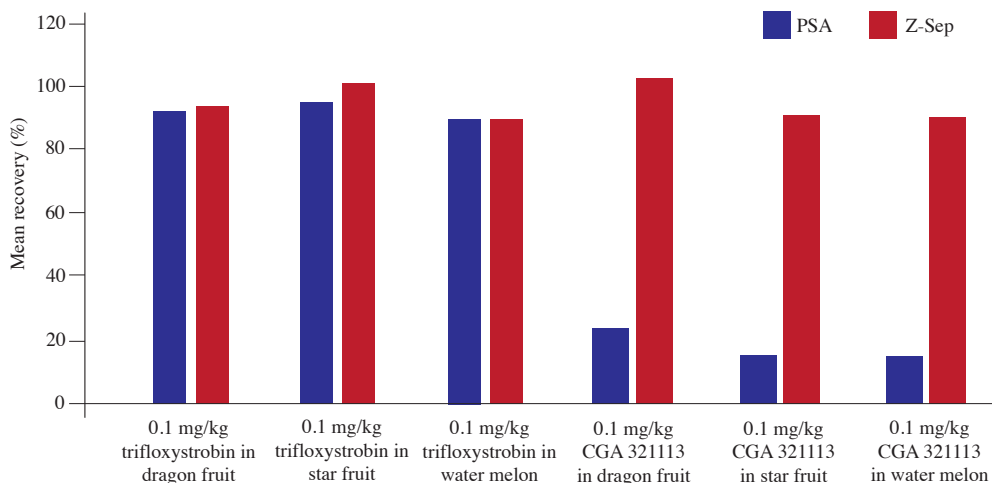


Figure 3. Mean recoveries of trifloxystrobin and CGA 321113 fortified at 0.1 mg/kg in star fruit, dragon fruit and watermelon from analytical method with PSA and Z-Sep as clean-up sorbents

level) in dragon fruit. In watermelon, average recoveries were 31.7% (0.01 mg/kg fortification level) and 14.6% (0.1 mg/kg fortification level). The mean recoveries of CGA 321113 based on PSA sorbent in the studied fruits were low. However, clean-up with Z-Sep still yielded mean recoveries of CGA 321113 within the range of 70 – 125% for all the studied fruits at both levels of fortifications. In dragon fruit, mean recoveries were observed at 124.2% (0.01 mg/kg fortification level) and 101.4% (0.1 mg/kg fortification level). Mean recoveries of 87.4% (0.01 mg/kg fortification level) and 80.4% (0.1 mg/kg fortification level) were obtained in star fruit. In watermelon, mean recoveries of CGA 321113 were 100.9% (0.01 mg/kg fortification level) and 89.7% (0.1 mg/kg fortification level). There was a significant difference between mean recoveries of CGA 321113 obtained from PSA and Z-Sep at $p < 0.05$ for star fruit, dragon fruit and watermelon.

It seems that a low recovery of CGA 321113 could be due to its retention by PSA sorbents. CGA 321113 is structurally similar to trifloxystrobin with the exception of the methyl ester compound (-O-CH₃) in trifloxystrobin which is in the form of (-OH) in CGA 321113. It could be due to

the (-OH) being more negatively charged and attracted towards the positive charge of amines (-NH⁺) in PSA. It could also be deduced that analysis of CGA 321113 using PSA in other fruits with high water content (similar to star fruit) such as dragon fruit, watermelon and orange may not give acceptable recovery of CGA 321113. For future studies, recovery of CGA 321113 could be carried out in other crops with higher fatty or oil content such as in durian, chilli and pepper or in crops with higher starch content as in rice to see if a similar pattern is observed.

In a study by Wang et al. (2014), recovery of CGA 321113 was <70% if PSA and Graphitised Carbon Black (GCB) was used as clean up sorbents in analysis of soil and tomato matrix. Following that observation, Wang et al. (2014) decided to use only C18 sorbent as clean up sorbent and the recoveries reported (75 – 109% based on HPLC-MSMS analysis) were acceptable. It seems that the observation from Wang et al. (2014) seemed to support the findings in this study. Kang et al. (2017) used octadecylsilane-based or C18 sorbent in analysis of trifloxystrobin and CGA 321113 in watermelon and soil. The recoveries of the fungicides in watermelon, pulp and

soil were 72.3 – 99.2% for difenoconazole, 74.7 – 87.7% for trifloxystrobin and 78.6 – 92.7% for CGA 321113. Absence of PSA in this study could be assumed albeit indirectly that PSA would not be a suitable clean-up sorbent for analysis of CGA 321113.

Different conclusions on recoveries of CGA 321113 were obtained by other researchers such as Liu et al. (2011). These studies reported acceptable recoveries for CGA 321113. A recovery range of 68 – 106% was obtained for a recovery study of CGA 321113 on cucumber, tomato, chinese cabbage, apple and grape (Liu et al. 2011). The analysis was done using GC-NPD and GC-MS/MS.

Between the methods used in the current study and the quoted studies (Liu et al. 2011; Kang et al. 2017; Wang et al. 2014), the chemicals used for extraction and clean up were the same (acetonitrile and sodium chloride) although there were slight variations in the quantitative amounts used. These variations could be ruled out as a source of different conclusions of PSA as a suitable clean-up sorbent. The reason for discrepancies of conclusions of CGA 32111 recoveries between this study and quoted studies could be due to the brand of PSA used. There could be differences in composition ratio of primary amines and secondary amines between the brands used in the studies and this is speculated by the authors as the source of discrepancies. It could be either primary amines or secondary amines that is more efficient in retaining CGA 321113. The brands reported in these studies (supporting and contradicting conclusions) were not the same with the current study. Therefore, it can be suggested for analysis of CGA 321113, different brands of PSA could be tested in terms of CGA 321113 recovery.

Since PSA is commonly used in most Quenchers methodology for analysis of pesticide residues, it should be noted that there is a non-issue if analysis is intended for MRL compliance, in which case, the quantitative concentrations of

trifloxystrobin from test results is sufficient for determination of MRL compliance, due to residue definition for compliance in plant commodities that only specifies trifloxystrobin. Determination of CGA 321113 can be considered as an additional test for dietary risk assessment, in addition to trifloxystrobin determination. Dietary risk assessment must be conducted before MRL is set. In other words, determination of trifloxystrobin and CGA 321113 is mainly for MRL development of trifloxystrobin in plant commodities, in which case, dietary risk assessment of both compounds is necessary.

Since Z-Sep was only introduced less than five years ago, its adoption as a clean-up sorbent would be rather slow. Currently there exists combinations of GCB, C18, PSA and Z-Sep sorbents within one clean-up kit promoted by certain manufacturers. Han et al. (2016) successfully validated 192 pesticides that included trifloxystrobin in meats and poultry using combination of C18, PSA and Z-Sep using Quenchers-based method. It would remain to be investigated whether such combinations of sorbent would affect recovery of CGA 321113.

Conclusion

At fortification levels of 0.1 and 0.01 mg/kg, average recoveries of trifloxystrobin in dragon fruit, star fruit and watermelon were within an acceptable range of 76.8 – 107.7%, indicating no significant loss of trifloxystrobin when PSA or Z-Sep was used as clean-up sorbent. Significant loss of CGA 321113 was observed as reflected in a lower average recovery range of 14.6 – 57.4% in the studied fruits at fortification levels of 0.01 and 0.1 mg/kg when PSA was used as clean-up sorbent. In a clean-up procedure using Z-Sep, no significant loss of CGA 321113 was observed as reflected in the higher average recovery range of 80.4 – 124.2% in the studied fruits at fortification levels of 0.1 and 0.01 mg/kg. In conclusion, for residue analysis of trifloxystrobin and CGA 321113 in dragon fruit, star fruit,

watermelon or other fruits of similar matrix composition (high water content) for MRL development using the Quechers method, PSA is not suitable to be used as clean-up sorbent as it will reduce significantly the concentration of CGA 321113. Replacement of PSA with Z-Sep sorbent in the AOAC official method 2007.01 was found to result in no significant loss of CGA 321113 residue.

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Abstrak

Dua jenis sorben pembersih iaitu Primer Sekunder Amina (PSA) dan Z-Sep diuji dalam kaedah AOAC untuk menghasilkan keputusan tepat dalam analisis trifloxystrobin dan CGA 321113 dalam buah naga, belimbing dan tembikai. Amaun atau kepekatan analit yang tertentu ditambah pada setiap bahagian analitikal buah naga, belimbing dan tembikai, diikuti dengan pencerakanan dan prosedur pembersihan samaada dengan PSA atau Z-Sep. Ekstrak kemudian dianalisis oleh Kromatografi Cecair Spektrometri Jisim (LCMSMS). Kepekatan yang diukur kemudian dibanding dengan kepekatan fortifikasi untuk menentukan perolehansemula. Keputusan menunjukkan perolehansemula trifloxystrobin yang memuaskan dalam julat 76.8 – 107.7%. Namun begitu, apabila PSA digunakan sebagai bahan pembersih, kehilangan ketara CGA 321113 dideduksikan daripada nilai purata perolehansemula yang rendah pada buah naga (47.1%), belimbing (57.4%) and tembikai (31.7%) dalam paras fortifikasi 0.01 mg/kg. Untuk fortifikasi yang lebih tinggi pada 0.1 mg/kg, nilai purata perolehansemula yang rendah dilaporkan pada buah naga (23.9%), belimbing (15.4%) dan tembikai (14.6%). Dalam semua buah yang dikaji, Z-Sep menunjukkan perolehansemula dalam julat 80.4 – 124.2% pada paras fortifikasi 0.01 dan 0.1 mg/kg dan ini menunjukkan tiada kehilangan ketara semasa prosedur pembersihan. Berdasarkan kepada dua definisi residu (pematuhan MRL dan penilaian risiko diet), boleh disimpulkan bahawa untuk analisis CGA 321113, Z-Sep patut digunakan sebagai sorben pembersih dalam prosedur pembersihan.