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Residue levels of five grain-storage-use insecticides during the production process of sorghum distilled spirits

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A B S T R A C T

Residue levels of dichlorvos, fenitrothion, pirimiphos-methyl, malathion and deltamethrin during sorghum distilled spirits production were examined. The analytical method for these pesticides in sorghum, fermented sorghum, rice hull and distilled spirits was validated through linearity, matrix effect, accuracy and precision, limit of quantification (LOQ) and limit of detection (LOD) parameters. The pesticide residue levels before/after each process of soaking, steaming, fermentation, and distillation were determined by gas chromatography coupled with tandem mass spectrometry (GC–MS/MS). Results showed that soaking process could obviously reduce dichlorvos residue with 87% decrease as its high vapor pressure. The steaming process reduced pesticide residues by 42–83% mainly due to evaporation or thermal degradation. Also, the fermentation could remove pesticide residues by 40–63% in favor of biological degradation. Moreover, the distillation process was proved to be effective for decreasing the pesticide residues in distilled spirits with the processing factors lower than other processes for each pesticide.

1. Introduction

Distilled spirits is one of the most well-known alcohol rich liquor in the world (Wang, Gao, Fan, & Xu, 2011), which plays a significant role in Chinese culture and people's daily life (Xiao-Wei et al., 2012). The annual production of distilled spirits in China has steadily increased in recent years and currently exceeds ten million metric tons (Song, 2014). The distilled spirits is typically made from grains, mainly sorghum, through soaking, steaming, fermentation and distillation (Zheng et al., 2015). However, the grains are usually stored long term at ambient temperature in barn where insecticides (such as malathion and pirimiphos-methyl) are increasingly used post-harvest to reduce the losses from storage pests (Holland, Hamilton, Ohlin, & Skidmore, 1994). Consequently, sorghum based foods have the potential to be a main source of residues in diet for these pesticides. Hence, monitoring the residue levels of these insecticides in sorghum and its processed products (such as sorghum distilled spirits) is important for human health.

A multitude of agricultural commodities are not only consumed fresh, but also consumed after multifarious culinary or commercial processing (Keikotlhaile, Spanoghe, & Steurbaut, 2010). Food processing techniques regarding pesticide residues have been extensively studied (Huan, Xu, Jiang, Chen, & Luo, 2015; Iizuka & Shimizu, 2014). Generally, most of the food processing technology would contribute to pesticide dissipation, such as washing, baking, cooking, fermentation and distillation et al. (Kaushik, Satya, & Naik, 2009). On the contrary, it might give rise to the increase of residues in processed product in some cases, e.g. fruit drying (Peng et al., 2014) or crude rapeseed oil production (Jiang, Shibamoto, Li, & Pan, 2013) et al. The unit operations of liquor-making have been continuously studied in regard to fermentation (Dordevic & Durovic-Pejcev, 2015; Dordevic, Siler-Marinkovic, Durovic-Pejcev, Dimitrijevic-Brankovic, & Umiljendic, 2013a) or distillation (Inoue, Nagatomi, Kinami, Uyama, & Mochizuki, 2010; Nagatomi, Inoue, Uyama, & Mochizuki, 2012). However, there are very few data concerning the behavior of pesticide residues during the production of sorghum distilled spirits. Accordingly, good knowledge of the fate of insecticides in liquor-making process is necessary to properly assess the human exposure from these insecticides.

The processing factor (PF) is calculated by the ratio of residue levels in processed commodities and the raw agriculture commodities. PFs aid in the risk assessment regarding the intake of related pesticides in processed products (Christensen, Granby, &

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Rabølle, 2003). In addition, when the processing techniques trigger an increase of the residue magnitudes, the PFs will play an important role in recommending MRLs for processed products (González-Rodríguez, Rial-Otero, Cancho-Grande, Gonzalez-Barreiro, & Simal-Gándara, 2011). To our knowledge, no research has been carried out to study the PFs of dichlorvos, fenitrothion, pirimiphos-methyl, malathion and deltamethrin during the production of sorghum distilled spirits. So it is of great significance to expound the PFs on the five insecticides during the production of sorghum distilled spirits.

This study was aimed to evaluate the residue levels of the five insecticides during the production of sorghum distilled spirits, and throw light on the PFs of soaking, steaming, fermentation and distillation process of sorghum distilled spirits making.

2. Materials and methods

2.1. Standards, reagents and materials

The pesticide standards dichlorvos (purity ⩾98.0%), fenitrothion (purity ⩾95.0%), pirimiphos-methyl (purity ⩾96.2%), malathion (purity ⩾95.0%), deltamethrin (purity ⩾99.0%) were provided by the Institute of the Control of Agrochemicals, Ministry of Agriculture, Peoples' Republic of China (Beijing, China). 100 mg L^{-1} standard stock solutions for mixture pesticides were prepared in acetonitrile and stored at −20 °C. The working solutions were prepared daily. HPLC-grade acetonitrile was obtained from Honeywell International Inc. (New Jersey, USA). Analytical reagent toluene, grade anhydrous magnesium sulfate ($MgSO_4$) and sodium chloride (NaCl) were obtained from Beijing Chemical and Reagent (Beijing, China). Ultra-pure water was obtained from a Milli-Q system (Bedford, MA, USA). Multi-walled carbon nanotubes (MWCNTs) with average external diameters of 5–10 nm, octadecylsilane (C_{18}, 40 μm), primary secondary amine (PSA, 40 μm) were purchased from Agela Technologies (Tianjin, China).

2.2. Sample preparation and processing

The sorghum, rice hull and Daqu without the target compounds residue were obtained from market. The 3.0 kg sorghum were sprayed with 300 mL standard stock solutions for mixture pesticides (100 mg L^{-1}) wholly. Then the sorghum was made to stand for 24 h at room temperature in a fume hood to achieve a residue level of approximate 10 mg/kg.

Generally speaking, the production process of sorghum distilled spirits mainly includes six steps: soaking, steaming, primary fermentation, primary distillation, secondary fermentation, and secondary distillation, as shown in Fig. 1. The samples in the main processing steps were collected to monitor the residue levels of selected pesticides during the liquor making processes. The detailed processing procedures are as follows:

Soaking: the coarse crushed sorghum was soaked with boiled water for 22 h.

Steaming: the soaked sorghum was steamed in a small steaming bucket for 1 h.

Primary fermentation: the steamed sorghum was cooled down with cold water, and mixed with Daqu (9–10%). Then the mixture was fermented at 26–30 °C for 28 days in an airtight glass jar (10 L).

Primary distillation: the primary fermented sorghum was mixed with rice hull (15–20%) homogeneously, then distilled in the steaming bucket to produce primary distilled spirits.

Secondary fermentation: the primary distilled sorghum was cooled down with cold water again, and mixed with Daqu. Following, the mixture was fermented at 26–30 °C for 21 days in an airtight glass jar (10 L).

Secondary distillation: the secondary fermented sorghum was mixed with rice hull homogeneously, and distilled in the steaming bucket to produce secondary distilled spirits.

Finally, the primary distilled spirits and the secondary distilled spirits were blended to produce commercial distilled spirits.

2.3. GC–MS/MS analytical conditions

The determination was performed using the Thermo Scientific TSQ Quantum XLS GC triple quadrupole mass spectrometer with a Trace GC Ultra gas chromatograph and a TriPlus AI 1310 autosampler (Thermo Fisher Scientific, San Jose, CA). Chromatographic separation was carried out using a HP-5MS capillary column (30 m × 0.25 mm, 0.25 μm film thickness) (J&W Scientific, USA), with the following temperature program: 80 °C hold for 1 min, 80–120 °C at 20 °C/min, 120–160 °C at 10 °C/min, 160–190 °C at 30 °C/min, then 190–290 °C at 40 °C/min, hold for 9 min. The total run time was 19.5 min. The inlet temperature was set at 270 °C. Helium gas (99.999% purity) was used as carrier gas with a constant flow of 1.2 mL/min. The splitless mode was used with a splitless time of 1.0 min and a split flow of 50 mL/min. The transfer line to tandem MS was maintained at 290 °C. The triple quadrupole MS was operated in the selected reaction monitoring (SRM) mode with electron energy of 70 eV and an emission current of 25 μA. Argon gas (Ar) was chosen as collision gas with the pressure of 1.5 mTorr. The ion source temperature was set at 250 °C. The injection volume was 1 μL. The product ion and collision energy (CE) were optimized for individual analytes in Table 1. Xcalibur software together with LCQuan software incorporated in TSQ Quantum was used to process quantitative data obtained from the calibration standards and samples.

2.4. Extraction and purification procedure

2.4.1. Sorghum, fermented grain and rice hull

A total of 5.0 g homogenized sorghum, fermented grain samples (rice hull was 2.0 g) was weighed into a 50 mL PTFE centrifuge tube. 5.0 mL of purified water were added into the centrifuge tube and the centrifuge tube was shaken for a few seconds to hydrate the sample. Then 5.0 mL acetonitrile was added and the mixture was shaken on a VX-III Multi-Tube Vortexer (Beijing Targin Technology, China) for 2 min at 1200 strokes min^{-1}. After that, 3.0 g of NaCl was added and shaken 1 min again. Following, the tubes were centrifuged with a TG16-WS centrifuge (Xiangyi Centrifuge Machines, China) for 5 min at 3800 rpm. Then, an aliquot of 1 mL supernatant was transferred to a single-use centrifuge tube containing 5 mg MWCNTs, 15 mg PSA, 15 mg C_{18} sorbents plus 150 mg anhydrous $MgSO_4$, and agitated for 1 min and centrifuged using a SIGMA 3K15 micro-centrifuge (BMH Instruments Co., Ltd., China) for 1 min at 10,000 rpm. After that, 1 mL of upper layer was filtered with 0.22 μm Nylon syringe filters (Agela Technologies, China) for analysis.

2.4.2. Distilled spirits

A total of 5.0 g distilled spirits sample was weighed into a 50 mL spin steaming bottle. The ethanol was removed under vacuum distillation for 5 min before extraction. Then 5.0 mL acetonitrile was used to wash the spin steaming bottle (twice) and transferred to a 50 mL PTFE centrifuge tube. The mixture was shaken on a VX-III Multi-Tube Vortexer (Beijing Targin Technology, China) for 2 min at 1200 strokes min^{-1}. After that, 3.0 g of NaCl was added and shaken 1 min again. Following, the tubes were centrifuged with a TG16-WS centrifuge (Xiangyi Centrifuge Machines, China) for 5 min at 3800 rpm. Then, an aliquot of 1 mL supernatant was