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# Multiresidue Analysis of 58 Pesticides in Bean Products by Disposable Pipet Extraction (DPX) Cleanup and Gas Chromatography–Mass Spectrometry Determination

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Supporting Information

**ABSTRACT:** A method based on disposable pipet extraction (DPX) sample cleanup and gas chromatography with mass spectrometric detection by selected ion monitoring (GC/MS-SIM) was established for 58 targeted pesticide residues in soybean, mung bean, adzuki bean and black bean. Samples were extracted with acetonitrile and concentrated (nitrogen gas flow) prior to being aspirated into DPX tubes. Cleanup procedure was achieved in a simple DPX-Qg tube. Matrix-matched calibrations were analyzed, and the limits of quantification (LOQ) of this method ranged from 0.01 mg $kg^{-1}$ to 0.1 mg $kg^{-1}$ for all target compounds. Coefficients of determination of the linear ranges were between 0.9919 and 0.9998. Recoveries of fortified level 0.02 mg $kg^{-1}$ on soybean, mung bean, adzuki bean and black bean were 70.2–109.6%, 69.1–119.0%, 69.1–119.8%, and 69.0–120.8%, respectively, for all studied pesticides. Moreover, pesticide risk assessment for all the detected residues in 178 market samples at Beijing market area was conducted. A maximum 0.958% of ADI (acceptable daily intake) for NESDI (national estimated daily intake) and 55.1% of ARfD (acute reference dose) for NESTI (national estimated short-term intake) indicated low diet risk of these products.

**KEYWORDS:** *multiresidue, DPX, GC/MS, beans, pesticide, analysis*

## INTRODUCTION

Bean products are one of the fundamental foods recommended by the health food pyramid. Acting as both grains and vegetables in prevention of cancer, they are rich in protein and vitamins but low in calories.[1] However, public concern over food safety, especially the potential health risk to humans cause by the high levels of pesticide residues, has increased. Measuring the trace levels of pesticide residue in beans by a simple, reliable and environmentally friendly method is becoming important. It is a particularly challenging task to test routinely and comprehensively the multiresidue pesticides in large amounts of sample matrix components that may cause false positive results. In order to clean these components up, conventional liquid–liquid extraction (LLE) is time-consuming and laborious and usually involves significant glassware usage and disposal of large volumes of hazardous organic waste.[2] Therefore, solid phase extraction (SPE) techniques are worth considering because of their selectivity, capability to preconcentrate pesticide, high efficiency of using organic solvents and variety of the adsorbent materials in the SPE column.[3,4] Furthermore, prior to chromatographic analysis, SPE cartridges have extended the application of SPE techniques for extracting and concentrating pesticides in a broad range of sample matrices.[5−7] However, SFE often requires separate optimization for different analyte types and may not extract different classes of pesticides in foods with the same efficiency.[8] Besides LLE and SPE, there are some new approaches, such as solid phase microextraction (SPME), matrix solid phase dispersion (MSPD) and stir-bar sorptive extraction (SBSE) also available to match some aspects of the requirement. But by considering their imperfections of expensiveness and fragileness,[1] large requirement of adsorbent and solvent[9,10] or commercial availability and good recoveries for polar pesticides,[1,3,11] they are probably not able to match all of our purposes.

The QuEChERS method (quick, easy, cheap, effective, rugged, and safe) has recently attracted attention for pesticide analysis.[12−14] Its main advantage is comprehensiveness, being useful for the analysis of pesticides of varying polarities, by virtue of the fact that the sorbent removes fatty acid components and pigments from acetonitrile extracts without interacting with the target analytes. Much of the literature with QuEChERS suggests that better results are obtained using the dispersive procedure, where mixing with the loose sorbent provides efficient removal of matrix compounds and provides higher recoveries of pesticides with minimal solvent.[1]

The focus of the present research is development and validation of reliable and efficient multiresidue methods for the analysis of pesticides in high oil and protein and low water and fat content matrices, such as soybeans, mung beans, black beans and adzuki beans using disposable pipet extraction (DPX)

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followed by GC/MS analysis. Meanwhile, the goal of this research is to enrich and optimize the existing DPX approaches as well.

In DPX, the solid phase sorbent is contained in a disposable pipet tip and can be thoroughly mixed with sample solutions. In dynamic mixing, components meet in a chamber and are mixed homogeneously by a "blender" (in this case the air is in the dispersive procedure, demonstrated in Figure 2). Compared to classical QuEChERS or SPE, dynamic mixing consumes less sorbent and provides faster extractions. Sample matrix interference is removed by DPX, which possesses the dispersive extractions. Thus centrifugation for the "cleanup" is unnecessary in the process . In this paper, with the principle of dispersive extraction, DPX-Qg is shown to be useful for the rapid analysis of nonpolar and polar pesticides. The DPX method is demonstrated to be efficient and reliable, taking few hours to analyze with relatively high sensitivities and recoveries.

## MATERIALS AND METHODS

**Chemicals, Reagents and Materials.** The standard pesticides were provided by Pesticide Residue and Environment Toxicology (PRET) laboratory of Ministry of Agriculture (Beijing, China). The purities of the standard pesticides were from 95% to 99%. Stock standard solutions of 20 mg $L^{-1}$ were prepared in acetonitrile and stored at −20 °C.

Working standard solutions were prepared by dilution of the corresponding stock standard solution with acetonitrile and were stored at −20 °C. The triphenyl phosphate (TPP) (Sigma, Milwaukee, WI) working solution, used as internal standard (IS), was prepared by an appropriate dilution of stock solution with acetonitrile and stored at −20 °C. Chromatographic grade acetonitrile was purchased from Fish Chemicals (Fair Lawn, NJ). Analytical reagent grade anhydrous sodium chloride (NaCl) and magnesium sulfate ($MgSO_4$) were purchased from Sinopharm Chemical Reagent (Beijing, China). DPX-Qg tips, specialized DPX tips for the removal of green pigment with a "high quality" carbon black, were purchased from Tegent Group Inc. (Shanghai, China).

51 soybean (binomial name: *Glycine max*), 45 mung bean (binomial name: *Vigna radiata*), 42 adzuki bean (binomial name: *Vigna angularis*) and 40 black bean (binomial name: *Phaseolus vulgaris*) samples used as matrices were purchased from local supermarkets in the central area of Beijing, P. R. China. The samples were stored in the freezer (−20 °C) prior to use to prevent spoilage.

**Apparatus.** An Agilent 6890N Network GC system (Agilent Technologies) with a 7683B series split−splitless autoinjector, a 7683 series autosampler and a 5975B inter XL EI/CI MSD was used for analysis of pesticides. Agilent Technologies capillary column HP-5MS analytical column (30 m × 0.250 mm i.d. × 0.25 μm film thickness) was used for GC separation, with helium (99.9999%) as carrier gas at a constant flow rate of 1.2 mL/min. The column temperature was initially at 40 °C (hold 1 min), increased to 130 °C at the rate of 20 °C/min, and then to 250 °C at the rate of 5 °C/min, and finally to 300 °C at the rate of 10 °C/min holding for 5 min. The temperature of the injector port was 260 °C, and a volume of 1 μL was injected in splitless mode. The total analysis time was 39.50 min.

The mass spectrometer was operated in electron ionization (EI) mode at 70 eV, scanning the characteristic fragment ions of each pesticide at 0.5 s per scan. The temperatures of ion source and mass spectrometer transfer line were set at 230 and 280 °C respectively. The electron multiplier voltage (EM voltage) was set at 1635 V when performing selected ion monitoring, and solvent delay was set to 6.0 min. The instrument data system also held an EI-MS library specially created for target analytes under our experimental conditions.

Centrifugation was performed in two different instruments: an Anke TDL-40B centrifuge equipped with a bucket rotor (4 × 100 mL) (Shanghai, China) and a SIGMA 3K15 microcentrifuge equipped with an angular rotor (24 × 2.0 mL) (BMH Instruments Co., Ltd., China), and a QL-901 Vortex (Kylin-bell Lab Instruments Co., Ltd., Jiangsu, China) was used for preparing the samples.

A Meiling BCD-245W refrigerator freezer (Beijing, China) was used to control the temperature of samples.

**Sample Preparation.** Bean samples were chopped and homogenized immediately after being removed from the freezer, and the blank samples were used for validation studies and matrix-matched standard calibrations. Samples for recovery studies were spiked with a corresponding volume of the working solution and left for 1 h before the extraction.

Initial sample preparation was a modified method based on QuEChERS,[12] shown in Figure 1. An amount (10.0 ± 0.1 g) of soybean was weighed into a 50 mL centrifuge tube, and 20 mL of acetonitrile was added. The resulting suspension was shaken vigorously for 1 min with a vortex mixer followed by the addition of sodium chloride (1.0 ± 0.1 g) and anhydrous magnesium sulfate (4.0 ± 0.1 g). The centrifuge tube was shaken vigorously for 1 min to prevent salt agglomeration before centrifugation at 3800 rpm (max. RCF 2585*g*) for 10 min. The supernatant was transferred into a new 50 mL centrifuge tube and adjust to pH 4.5, in order to precipitate the proteins of soybean (p*I* 4.5). These new centrifuge tubes were stored at −20 °C 2 h before centrifugation 5 min at 12000 rpm (max. RCF 12890*g*), and the upper layer was used for further DPX cleanup.

DPX-Qg tips (5 mL) containing $MgSO_4$, PSA and graphitized carbon black (GCB) were used in the DPX cleanup procedure; a schematic diagram of DPX tips is shown in Figure 2. An aliquot of 10 mL of the upper layer was place into a 10.0 mL centrifuge tube for nitrogen gas flow concentrating to 2.0 mL. The total solution was then aspirated into the DPX-Qg tip three times from the bottom (to ensure a good mix of sorbents with sample solution) followed by an equilibration time of 30 s. The solution was dispensed into a GC vial (containing 10 μL of 10 mg $L^{-1}$ internal standard, TPP) and injected to the GC/MS.

The procedure of preparation of the matrix-matched standards was mainly the same, but the corresponding volume of multicompound working standard solution was added into the blank extract.

## RESULTS AND DISCUSSION

**Gas Chromatographic Determination.** To identify the pesticides in this GC/MS-SIM analysis, one quantitation ion and at least two identification ions were indispensable. Their relative abundances and the retention times were obtained from either the NIST's pesticide library or the GC/MS analysis of relative pesticide standard solution. Moreover, the internal standard (IS) played a role in quantification and quality control throughout the instrumental analysis due to its stability and consistency. Therefore, IS is able to improve the reliability of the method by minimizing the possible variations in retention time and peak areas. Table 1 summarizes the chosen ions along with the typical retention times.

**Validation Procedure of Method.** In order to investigate the matrix effects with this method, the blank samples were used for preparation of a blank matrix. The typical chromatograms of blank samples are shown in Figure 3. No significant matrix interference GC peaks were detected in the SIM chromatograms of the target pesticides. The 58 pesticides were divided into 40 groups according to their polarities and volatilities to increase the sensitivity. In Figure 3, the spiked samples at 0.5 mg/kg of the target analytes show that the GC program achieved good separation and met the requirements of analysis.

**Linearity.** Linearity was studied in the range between 0.02 mg $kg^{-1}$ and 0.5 mg $kg^{-1}$ with five calibration points (0.02, 0.05, 0.1, 0.2, and 0.5 mg $kg^{-1}$) by matrix-matched standard calibration which were spiked with the corresponding volume of the working solution and internal standard

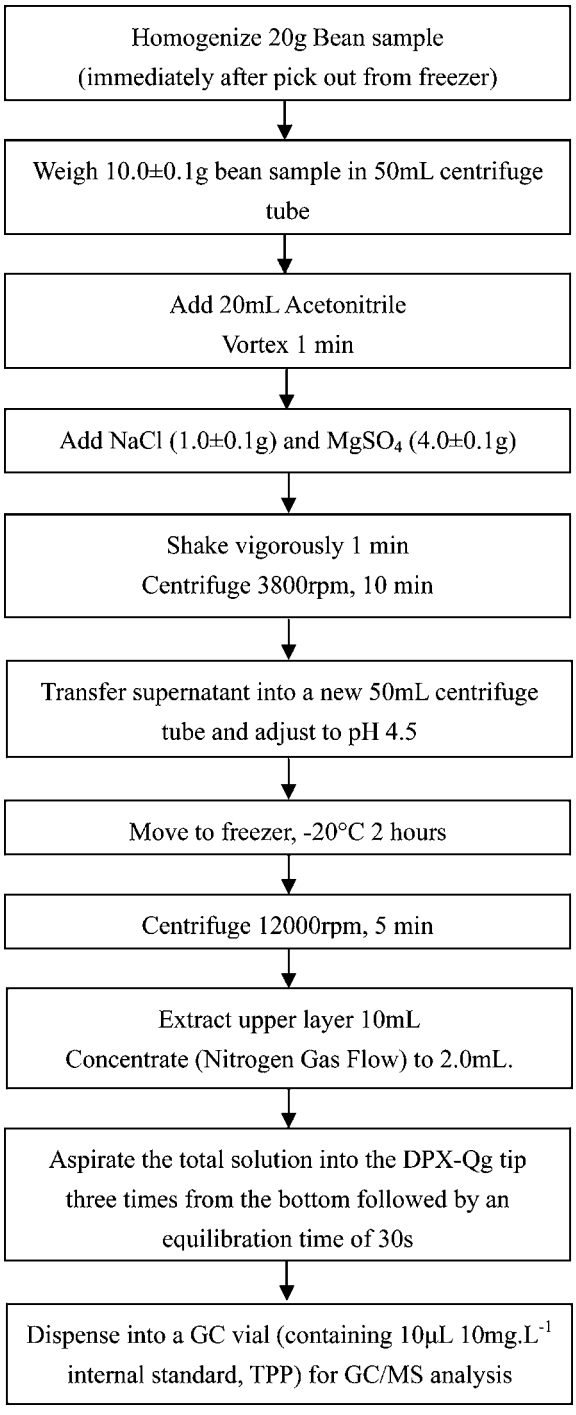


**Figure 1.** Schematic diagram of DPX multiresidue procedure.

solution. Linear calibration graphs were constructed by least-squares regression of concentration versus relative peak area (analyte/IS) of the calibration standard. Linearity values, calculated as determination coefficients ($R^2$) were in the range of 0.9919−0.9998.

**Recovery.** Accuracy was evaluated in terms of recovery (eq 1), and normally the satisfactory recoveries should lie between 70% and110%. This study was performed at three concentration levels (0.02 mg $kg^{-1}$, 0.1 mg $kg^{-1}$ and 0.5 mg $kg^{-1}$) by spiking blank soybean samples with the corresponding volume of a multipesticide working solution. Five replicates

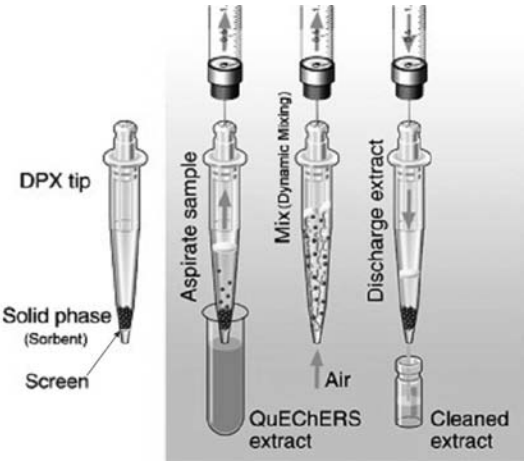


**Figure 2.** Schematic diagram of a DPX cleanup. Modified schematic diagram adapted from the online publication of GERSTEL, http://www.gerstel.de/pdf/p-gc-an-2009-01.pdf (Guan, H.; Brewer, W. E.; Morgan, S. L.; Stuff, J. R.; Whitecavage, J. A.; Foster, F. D. Automated Multi-Residue Pesticide Analysis in Fruits and Vegetables by Disposable Pipette Extraction (DPX) and Gas Chromatography/Mass Spectrometry. **2009**, AN/2009, 1−7).

at each concentration level were analyzed. The recovery data is shown in Table 2.

$$\begin{aligned}\text{recovery\%} = &[(\text{peak area of pesticide in sample})\\ &/(\text{peak area of internal standard in sample (TPP))}]\\ &/[(\text{peak area of pesticide in matrix standard})\\ &/(\text{peak area of internal standard in matrix standard (TPP))}]\end{aligned} \quad (1)$$

**Intraday Precision and Reproducibility.** Precision was studied as intraday precision and reproducibility. Intraday precision (%, RSD) was conducted by detecting five parallel samples in one day at the spike levels of 0.02 mg $kg^{-1}$, 0.1 mg $kg^{-1}$ and 0.5 mg $kg^{-1}$, and as a result, the RSD was lower than 15% at all three concentration levels. Reproducibility (%, RSD) was established by processing 3 parallel samples and each of them on 3 different days at the mentioned three concentration levels, and the RSD of reproducibility was lower than 29%, 27% and 26% for 0.02 mg $kg^{-1}$, 0.1 mg $kg^{-1}$ and 0.5 mg $kg^{-1}$, respectively.

**Limit of Quantification and Concentration Procedure.** According to the AOAC method validation protocol (AOAC−PVMC),the limit of quantification (LOQ) is established by using content equal to or greater than the lowest concentration point on the calibration curve (0.02 mg $kg^{-1}$), and in this paper all of these points correspond to the sample blank value plus 10 standard deviations of the blank mean (i.e., signal/noise > 10). The LOQ is shown in Table 2.

For these 58 pesticides, even though the sensitivity of the gas chromatography−mass spectrometry, which was used in this research, is between 0.005 and 0.05 mg $kg^{-1}$, the concentration of extracted solution was diluted in the sample preparation. As a result, certain LOQs and their validation procedures would probably not satisfy the requirement of relative MRLs (for instance, the LOQ of lambda-cyhalothrin-1 in soybean was 0.02 mg $kg^{-1}$, larger than its 0.01 mg $kg^{-1}$ MRL). Therefore, the following two processes are applied to the method: (1) the nitrogen gas flow was used for concentrating the extracted solution from 10 to 2 mL before DPX cleanup; (2) for these

**Table 1. Retention Time, Quantization and Identification Ions, and Validation Data[a]**

| | | | | spike level 0.02 mg kg$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | determination coeff | | recovery (%) | | RSD ($n$ = 5) (%) | |
| pesticide | $t_R$ (min) | quantization ion | identification ions | min | max | min | max | min | max |
| propoxur | 7.234 | 110 | 110; 152; 111 | 0.9900 | 0.9989 | 70.9 | 119 | 5.8 | 11.6 |
| etridiazole | 11.316 | 183 | 211; 183; 140 | 0.9924 | 0.9966 | 73.9 | 90.9 | 5.1 | 9.5 |
| chlorpropham | 14.987 | 213 | 213; 171; 153 | 0.9917 | 0.998 | 77.6 | 94.7 | 2.6 | 5.5 |
| methomyl[b] | 15.501 | 105 | 105; 58; 88 | 0.9910 | 0.9980 | 86.1 | 119 | 3.5 | 7.7 |
| dimethoate | 16.492 | 125 | 125; 143; 229 | 0.9910 | 0.9956 | 75.1 | 95.1 | 3.8 | 14.5 |
| atrazine | 16.854 | 200 | 200; 215; 58 | 0.9900 | 0.9998 | 75.4 | 98.7 | 2.9 | 5.9 |
| clomazone | 16.897 | 204 | 204; 138; 205 | 0.9900 | 0.9960 | 78.6 | 104 | 1.7 | 3.3 |
| propyzamide | 17.529 | 255 | 173; 255; 240 | 0.9930 | 0.9960 | 88.3 | 114 | 2.2 | 3.7 |
| dicamba[b] | 17.529 | 175 | 173; 175; 220 | 0.9900 | 0.9980 | 77.1 | 110 | 2.0 | 5.7 |
| metribuzin[b] | 17.721 | 198 | 198; 199; 144 | 0.9910 | 0.9990 | 79.3 | 101 | 2.3 | 4.6 |
| diazinon | 17.846 | 304 | 137; 179; 304 | 0.9900 | 0.9970 | 86.7 | 104 | 2.1 | 3.7 |
| acetochlor[b] | 19.489 | 146 | 146; 162; 223 | 0.9900 | 0.9980 | 81.1 | 113 | 0.8 | 6.6 |
| propargite | 20.076 | 135 | 135; 81; 57 | 0.9930 | 0.9943 | 85.3 | 94.2 | 2.9 | 3.7 |
| pirimiphos-methyl | 20.711 | 290 | 290; 276; 305 | 0.9900 | 0.9990 | 80.7 | 105 | 1.1 | 2.8 |
| ethofumesate | 20.745 | 207 | 207; 161; 286 | 0.9900 | 0.9990 | 84.7 | 110 | 0.6 | 3.2 |
| fenthion | 21.335 | 278 | 278; 169; 153 | 0.9910 | 0.9990 | 86.9 | 112 | 0.9 | 3.9 |
| chlorpyrifos | 21.408 | 314 | 314; 258; 286 | 0.9910 | 0.9950 | 89.1 | 108 | 0.7 | 13.3 |
| triadimefon | 21.541 | 208 | 208; 210; 181 | 0.9910 | 0.9953 | 78.1 | 111 | 2.3 | 3.2 |
| fluorochloridone | 21.933 | 187 | 187; 311; 313 | 0.9921 | 0.9992 | 93.0 | 114 | 3.5 | 11.7 |
| cyprodinil | 22.359 | 224 | 224; 225; 210 | 0.9920 | 0.9990 | 71.3 | 86.9 | 1.7 | 5.2 |
| pendimethalin | 22.600 | 252 | 252; 220; 162 | 0.9900 | 0.9970 | 76.5 | 91.2 | 1.7 | 3.1 |
| metazachlor | 22.529 | 209 | 209; 133; 211 | 0.9910 | 0.9996 | 77.9 | 95.3 | 0.2 | 3.2 |
| allethrin[b] | 22.998 | 81 | 123; 79; 81 | 0.9910 | 0.9957 | 82.0 | 113 | 3.2 | 4.0 |
| chlorfenvinphos | 22.955 | 267 | 267; 323; 269 | 0.9920 | 0.9990 | 77.9 | 116 | 2.0 | 2.5 |
| phenoxyacetic acid[b] | 22.995 | 153 | 107; 153; 94 | 0.9900 | 0.9956 | 84.5 | 110 | 1.3 | 3.5 |
| S-bioallethrin[b] | 22.998 | 136 | 123; 107; 136 | 0.9930 | 0.9955 | 81.9 | 120 | 1.3 | 2.7 |
| procymidone | 23.272 | 283 | 96; 283; 285 | 0.9940 | 0.9973 | 86.2 | 102 | 1.3 | 11.2 |
| paclobutrazol[b] | 23.741 | 236 | 236; 238; 167 | 0.9921 | 0.9960 | 117 | 119 | 1.7 | 2.9 |
| haloxyfop-R-methyl[b] | 23.736 | 288 | 288; 316; 375 | 0.9910 | 0.9990 | 84.6 | 95.5 | 0.3 | 2.9 |
| cartap hydrochloride[b] | 24.091 | 147 | 147; 104; 71 | 0.9940 | 0.9970 | 80.4 | 93.0 | 2.1 | 2.5 |
| butachlor | 24.094 | 176 | 176; 160; 188 | 0.9910 | 0.9988 | 81.3 | 99.1 | 2.1 | 6.6 |
| flutriafol | 24.196 | 164 | 219; 164; 201 | 0.9670 | 0.9973 | 90.4 | 93.3 | 3.1 | 4.7 |
| napropamide | 24.381 | 128 | 128; 271; 171 | 0.9930 | 0.9980 | 83.0 | 96.6 | 1.7 | 3.5 |
| profenofos | 24.724 | 339 | 339; 374; 297 | 0.9900 | 0.9996 | 77.2 | 97.5 | 2.1 | 9.4 |
| pretilachlor | 24.840 | 238 | 162; 238; 262 | 0.9900 | 0.9984 | 78.9 | 105 | 1.1 | 3.3 |
| uniconazole-1[b] | 24.855 | 234 | 234; 236; 131 | 0.9910 | 0.9990 | 71.5 | 101 | 2.0 | 5.7 |
| uniconazole-2[b] | 25.281 | 234 | 234; 236; 131 | 0.9920 | 0.9990 | 91.2 | 119 | 1.3 | 2.6 |
| oxadiazon | 25.052 | 175 | 175; 258; 302 | 0.9940 | 0.9990 | 83.9 | 104 | 0.3 | 4.4 |
| flusilazole | 25.276 | 233 | 233; 206; 315 | 0.9910 | 0.9992 | 97.6 | 115 | 1.6 | 7.0 |
| oxyfluorfen[b] | 25.293 | 252 | 252; 361; 300 | 0.9900 | 0.9956 | 72.9 | 87.7 | 3.2 | 7.6 |
| RH-5849[b,c] | 26.986 | 105 | 105; 240; 77 | 0.9910 | 0.9970 | 92.2 | 109 | 1.6 | 2.8 |
| propiconazole-1 | 27.565 | 173 | 173; 259; 261 | 0.9900 | 0.9930 | 71.1 | 78.4 | 1.0 | 6.2 |
| propiconazole-2 | 27.793 | 173 | 173; 259; 261 | 0.9900 | 0.9940 | 71.2 | 75.1 | 1.4 | 3.4 |
| hexazinone[b] | 28.096 | 171 | 171; 128; 252 | 0.9930 | 0.9993 | 97.4 | 118 | 3.1 | 8.7 |
| tebuconazole | 28.206 | 250 | 250; 163; 252 | 0.9910 | 0.9980 | 71.5 | 93.4 | 0.2 | 2.4 |
| diclofop-methyl | 28.341 | 253 | 253; 281; 342 | 0.9940 | 0.9990 | 84.5 | 114 | 1.6 | 4.8 |
| diflufenican | 28.476 | 266 | 266; 394; 267 | 0.9900 | 0.9970 | 76.7 | 93.9 | 0.7 | 2.7 |
| epoxiconazole | 28.813 | 192 | 192; 183; 138 | 0.9910 | 0.9995 | 72.0 | 77.6 | 2.8 | 4.7 |
| tetramethrin | 29.666 | 164 | 164; 135; 232 | 0.9941 | 0.9984 | 94.2 | 94.2 | 2.1 | 2.1 |
| tricyclazole | 30.129 | 189 | 189; 162; 161 | 0.9910 | 0.9992 | 102 | 102 | 10.5 | 10.5 |
| bifenox | 30.159 | 341 | 341; 189; 310 | 0.9910 | 0.9942 | 75.6 | 102 | 2.6 | 18.9 |
| anilofos | 30.206 | 226 | 226; 184; 334 | 0.9940 | 0.9970 | 85.2 | 106 | 2.5 | 5.1 |
| pyriproxyfen | 30.895 | 136 | 136; 78; 96 | 0.9910 | 0.9950 | 72.3 | 100 | 0.3 | 4.0 |
| cyhalofop-butyl | 31.083 | 256 | 256; 357; 229 | 0.9900 | 0.9950 | 70.7 | 73.4 | 2.6 | 6.9 |
| λ-cyhalothrin-1 | 31.111 | 181 | 181; 197; 141; 208 | 0.9910 | 0.9960 | 72.5 | 92.8 | 1.5 | 9.3 |
| λ-cyhalothrin-2 | 31.420 | 181 | 181; 197; 208; 141 | 0.9900 | 0.9940 | 76.5 | 111 | 2.2 | 3.8 |
| tralkoxydim | 31.171 | 137 | 137; 57; 109 | 0.9940 | 0.9990 | 70.0 | 97.1 | 0.6 | 6.6 |
| permethrin-1 | 32.458 | 183 | 183; 184; 255 | 0.9940 | 0.9960 | 76.2 | 110 | 1.7 | 3.1 |


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**Table 1. continued**

| | | | | spike level 0.02 mg kg$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | determination coeff | | recovery (%) | | RSD ($n$ = 5) (%) | |
| pesticide | $t_R$ (min) | quantization ion | identification ions | min | max | min | max | min | max |
| permethrin-2 | 32.644 | 183 | 183; 184; 255 | 0.9910 | 0.9970 | 73.0 | 102 | 1.1 | 4.2 |
| bifenthrin-1[b] | 32.457 | 181 | 181; 166; 141 | 0.9930 | 0.9990 | 77.7 | 104 | 1.0 | 10.5 |
| bifenthrin-2[b] | 32.639 | 181 | 181; 166; 141 | 0.9910 | 0.9930 | 69.2 | 102 | 1.6 | 4.0 |
| pyridaben | 32.620 | 147 | 147; 117; 364 | 0.9900 | 0.9930 | 69.0 | 89.7 | 1.1 | 1.1 |
| quizalofop-P | 33.903 | 372 | 299; 372; 163 | 0.9940 | 0.9960 | 78.1 | 102 | 1.2 | 4.0 |
| tpp | 28.437 | 326 | 326; 325 | 0.9900 | 0.9989 | 70.9 | 119 | 6.0 | 12.0 |

[a]Method validation by mung bean, adzuki bean and black bean; other spike levels are available in the Supporting Information. [b]Quantization and identification ions obtained from actual GC/MS test of standard solutions. [c]CAS of RH-5849 is 112225-87-3.

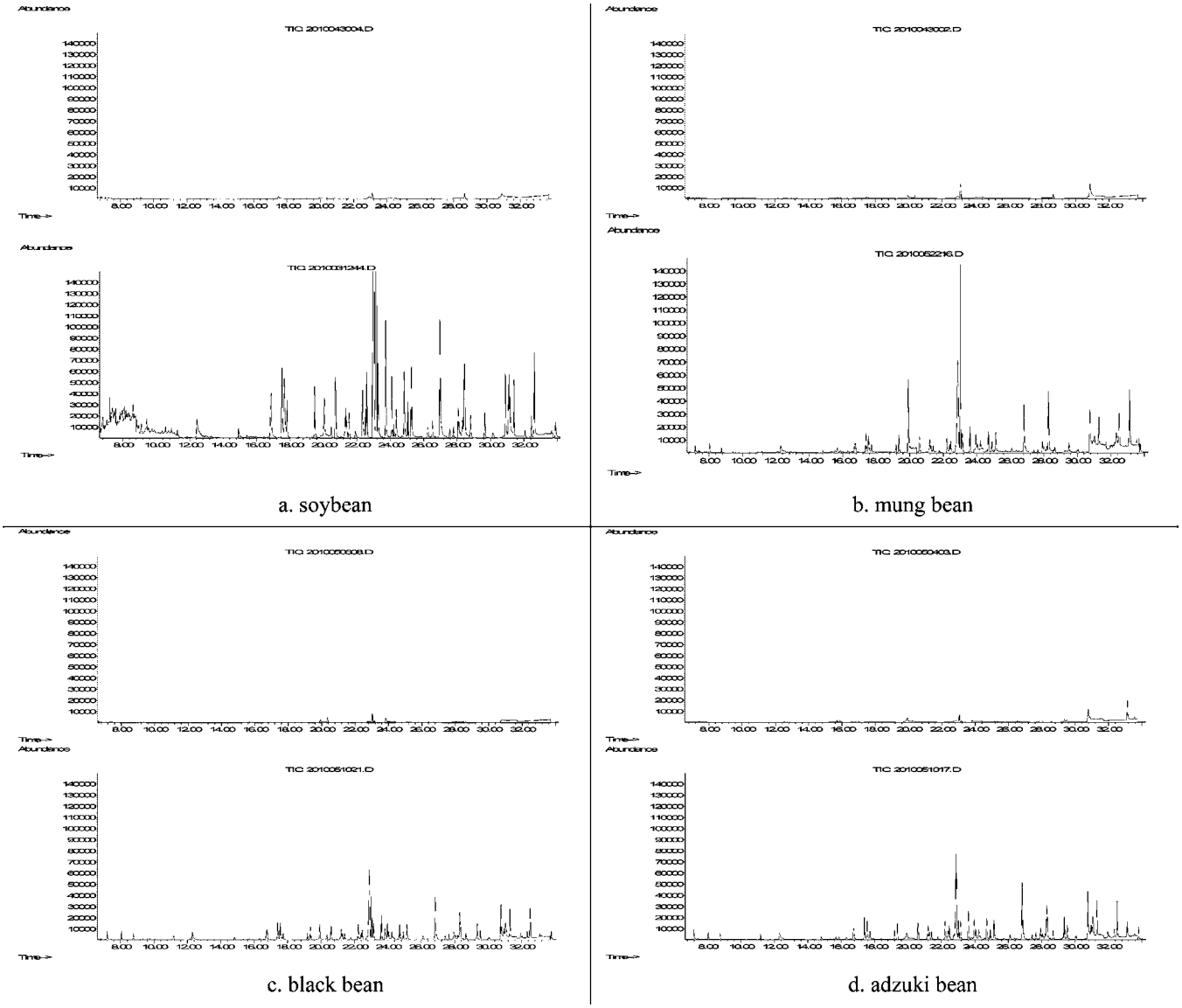


**Figure 3.** SIM chromatogram for typical blank samples and matrix-matched standards spiked with 0.5 mg kg$^{-1}$ of the target analytes.

"special" pesticides, a new 5-point calibration curve was drawn with the lowest concentration of 0.01 mg kg$^{-1}$ (other points are 0.02, 0.05, 0.1, and 0.2 mg kg-$^{1}$), by replacing the original one. As it is demonstrated in Table 2, five times concentration and the new calibration curve show their effectiveness to provide sufficient sensitivity and acceptable uncertainty to the determination.

**Method Validation on Other Matrices.** The present determination method was established by soybean matrix; therefore, it is necessary to use other similar matrices, mung bean, adzuki bean and black bean, to further validate and optmize the method in case of different matrix effects. Calibration data were generated from five parallel samples at 0.02, 0.05, 0.1, 0.2, and 0.5 mg kg$^{-1}$ respectively, and recoveries


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**Table 2. Calibration Data (Equation, Determination Coefficient), MRLs and Mean Percent Recovery ± RSD[a] of 58 Pesticides in Soybean**

| | | | | | spike level 0.02 mg kg$^{-1}$ | | reproducibility ($n$ = 9) (RSD, %) | | |
|---|---|---|---|---|---|---|---|---|---|
| pesticide | eq | determination coeff | MRLs[b] (mg kg$^{-1}$) soybean | LOQ (mg kg$^{-1}$) | recovery (%) | intraday precision ($n$ = 5) (RSD, %) | 0.02 mg kg$^{-1}$ | 0.10 mg kg$^{-1}$ | 0.50 mg kg$^{-1}$ |
| propoxur | $Y = 1.44 \times 10^3X - 2.34 \times 10$ | 0.9992 | 0.05 | 0.05 | ND | ND | ND | 24.9 | 9.2 |
| etridiazole | $Y = 7.55 \times 10^4X - 3.13 \times 10^2$ | 0.9996 | 0.05 | 0.02 | 105 | 10.8 | 9.7 | 14.7 | 19.8 |
| chlorpropham | $Y = 2.14 \times 10^3X - 1.95 \times 10$ | 0.9944 | 0.1 | 0.02 | 101 | 8.5 | 21.9 | 9.5 | 15.3 |
| methomyl | $Y = 3.77 \times 10^2X + 1.11$ | 0.9978 | 0.2 | 0.05 | ND | ND | ND | 14.2 | 19.5 |
| dimethoate | $Y = 3.04 \times 10^3X - 3.44 \times 10$ | 0.9937 | 2.0 | 0.02 | 74.0 | 3.1 | ND | 3.4 | 6.9 |
| atrazine | $Y = 5.25 \times 10^3X + 1.15 \times 10$ | 0.9988 | 0.2 | 0.02 | 80.1 | 19.3 | 24.5 | 22.2 | 6.2 |
| clomazone | $Y = 9.14 \times 10^3X + 9.07 \times 10$ | 0.9975 | 0.05 | 0.02 | 92.0 | 4.3 | 10.5 | 3.1 | 5.9 |
| propyzamide | $Y = 2.67 \times 10^3X + 1.10 \times 10$ | 0.9984 | 0.05 | 0.01 | 90.4 | 8.2 | 12.3 | 7.4 | 7.2 |
| dicamba | $Y = 8.25 \times 10^3X + 7.00 \times 10$ | 0.9990 | 0.1 | 0.01 | 94.0 | 8.2 | 14.1 | 6.9 | 6.5 |
| metribuzin | $Y = 1.59 \times 10^4X - 1.20 \times 10^2$ | 0.9988 | 0.3 | 0.02 | 107 | 8.7 | 25.7 | 13.6 | 9.7 |
| diazinon | $Y = 1.22 \times 10^3X - 2.48 \times 10$ | 0.9997 | 0.5 | 0.02 | 71.5 | 5.8 | 10.1 | 2.7 | 9.2 |
| acetochlor | $Y = 3.95 \times 10^3X + 2.47 \times 10$ | 0.9978 | 1.0 | 0.02 | 85.2 | 7.4 | 7.8 | 3.0 | 6.0 |
| propargite | $Y = 1.42 \times 10^3X + 2.41 \times 10^2$ | 0.9982 | 0.2 | 0.02 | 101 | 7.2 | 13.3 | 9.0 | 11.9 |
| pirimiphos-methyl | $Y = 4.34 \times 10^3X + 7.26$ | 0.9993 | 8.0 | 0.02 | 78.8 | 6.2 | 19.9 | 6.6 | 5.4 |
| ethofumesate | $Y = 7.20 \times 10^3X + 7.92 \times 10$ | 0.9962 | 0.1 | 0.02 | 96.1 | 8.7 | 11.6 | 7.4 | 10.4 |
| fenthion | $Y = 6.31 \times 10^3X - 7.82 \times 10$ | 0.9989 | 0.1 | 0.02 | 83.8 | 6.7 | 14.5 | 6.8 | 10.9 |
| chlorpyrifos | $Y = 1.83 \times 10^3X - 3.35$ | 0.9994 | 0.05 | 0.02 | 104 | 4.9 | 10.2 | 5.8 | 13.3 |
| triadimefon | $Y = 3.54 \times 10^3X + 3.69 \times 10$ | 0.9960 | 0.2 | 0.02 | 110 | 4.3 | 14.2 | 8.4 | 10.1 |
| fluorochloridone | $Y = 1.06 \times 10^3X - 2.75$ | 0.9995 | 0.1 | 0.02 | 86.7 | 11.6 | 20.6 | 14.8 | 13.6 |
| cyprodinil | $Y = 1.17 \times 10^4X - 5.27 \times 10$ | 0.9986 | 0.6 | 0.02 | 75.7 | 8.5 | 18.0 | 3.4 | 10.2 |
| pendimethalin | $Y = 1.32 \times 10^3X - 8.67 \times 10$ | 0.9980 | 0.1 | 0.02 | 87.5 | 7.5 | 16.2 | 4.4 | 7.5 |
| metazachlor | $Y = 2.75 \times 10^3X + 1.70 \times 10^2$ | 0.9923 | 0.1 | 0.02 | 88 | 7.7 | 19.5 | 5.7 | 5.9 |
| allethrin | $Y = 9.10 \times 10^3X + 1.06 \times 10^2$ | 0.9928 | | 0.02 | 98.5 | 12.8 | 10.2 | 4.8 | 6.4 |
| chlorfenvinphos | $Y = 5.71 \times 10^3X + 3.38$ | 0.9983 | 0.02 | 0.01 | 93.8 | 11.5 | 13.4 | 11.3 | 8.6 |
| phenoxyacetic acid | $Y = 1.31 \times 10^3X + 2.26 \times 10$ | 0.9985 | | 0.02 | 76.8 | 13.5 | 14.9 | 10.2 | 15.0 |
| S-bioallethrin | $Y = 9.24 \times 10^3X + 1.28 \times 10$ | 0.9998 | | 0.02 | 85.4 | 12.2 | 12.4 | 8.8 | 22.3 |
| procymidone | $Y = 4.11 \times 10^3X + 5.24 \times 10$ | 0.9949 | 0.05 | 0.02 | 83.6 | 7.5 | 11.3 | 9.5 | 7.8 |
| paclobutrazol | $Y = 1.88 \times 10^3X + 6.97 \times 10$ | 0.9976 | 0.02 | 0.02 | 83.6 | 4.7 | 5.2 | 6.0 | 12.1 |
| haloxyfop-R-methyl | $Y = 1.09 \times 10^4X + 1.55 \times 10^2$ | 0.9970 | 0.5 | 0.02 | 76.6 | 12.4 | 15.6 | 9.4 | 11.4 |
| cartap hydrochloride | $Y = 1.15 \times 10^3X + 9.33$ | 0.9962 | | 0.02 | 73.8 | 12.6 | 19.3 | 10.7 | 12.8 |
| butachlor | $Y = 7.25 \times 10^3X + 8.10 \times 10$ | 0.9978 | | 0.02 | 75.9 | 12.1 | 16.7 | 5.7 | 10.1 |
| flutriafol | $Y = 4.57 \times 10^3X - 4.09 \times 10$ | 0.9945 | 0.35 | 0.02 | 108 | 3.4 | 25.1 | 8.1 | 7.0 |
| napropamide | $Y = 5.30 \times 10^3X + 2.69 \times 10$ | 0.9974 | 0.05 | 0.02 | 76.7 | 9.5 | 15.4 | 8.4 | 10.1 |


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**Table 2. continued**

| pesticide | eq | determination coeff | MRLs[b] (mg kg$^{-1}$) soybean | LOQ (mg kg$^{-1}$) | spike level 0.02 mg kg$^{-1}$ recovery (%) | spike level 0.02 mg kg$^{-1}$ intraday precision ($n$ = 5) (RSD, %) | reproducibility ($n$ = 9) (RSD, %) 0.02 mg kg$^{-1}$ | 0.10 mg kg$^{-1}$ | 0.50 mg kg$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| profenofos | $Y = 1.07 \times 10^3X - 1.41$ | 0.9968 | 0.05 | 0.02 | 104 | 13.6 | 26.3 | 21.7 | 16.9 |
| pretilachlor | $Y = 3.13 \times 10^3X + 3.61 \times 10$ | 0.9938 | | 0.02 | 83.9 | 9.0 | 10.9 | 3.7 | 5.7 |
| uniconazole-1 | $Y = 6.40 \times 10^3X - 5.50 \times 10$ | 0.9989 | | 0.02 | 99.0 | 9.0 | 22.2 | 14.7 | 10.1 |
| uniconazole-2 | $Y = 2.28 \times 10^3X - 8.98$ | 0.9974 | | 0.02 | 94.5 | 4.5 | 9.6 | 26.7 | 7.9 |
| oxadiazon | $Y = 3.16 \times 10^3X + 6.81 \times 10$ | 0.9924 | 0.05 | 0.02 | 79.2 | 10.3 | 13.3 | 6.9 | 11.8 |
| flusilazole | $Y = 1.19 \times 10^4X + 5.00 \times 10$ | 0.9995 | 0.04 | 0.02 | 82.6 | 4.6 | 7.2 | 27.5 | 9.4 |
| oxyfluorfen | $Y = 2.15 \times 10^3X + 9.99$ | 0.9956 | 0.05 | 0.02 | 77.5 | 10.7 | 27.0 | 12.2 | 10.4 |
| RH-5849 | $Y = 2.69 \times 10^4X - 6.11 \times 10$ | 0.9993 | | 0.02 | 104 | 4.0 | 15.6 | 4.2 | 10.3 |
| propiconazole-1 | $Y = 1.27 \times 10^3X + 1.13 \times 10$ | 0.9964 | 2.0 | 0.02 | 95.4 | 1.1 | 17.1 | 17.1 | 15.2 |
| propiconazole-2 | $Y = 1.78 \times 10^3X + 1.35 \times 10$ | 0.9962 | 2.0 | 0.02 | 89.2 | 7.5 | 17.5 | 15.3 | 14.1 |
| hexazinone | $Y = 8.38 \times 10^3X - 8.72 \times 10$ | 0.9975 | | 0.02 | 90.0 | 6.7 | 5.3 | 10.2 | 26.1 |
| tebuconazole | $Y = 2.38 \times 10^3X + 3.35 \times 10^{-1}$ | 0.9937 | 0.08 | 0.02 | 101 | 8.2 | 13.1 | 9.0 | 7.0 |
| diclofop-methyl | $Y = 3.00 \times 10^3X + 2.49 \times 10$ | 0.9945 | 0.1 | 0.02 | 86.5 | 7.5 | 19.1 | 13.3 | 13.1 |
| diflufenican | $Y = 1.25 \times 10^4X + 6.50 \times 10$ | 0.9984 | 0.05 | 0.02 | 77.2 | 11.3 | 14.2 | 4.6 | 8.3 |
| epoxiconazole | $Y = 5.40 \times 10^3X - 1.82 \times 10$ | 0.9972 | 0.05 | 0.02 | 90.5 | 2.8 | 9.2 | 14.4 | 14.0 |
| tetramethrin | $Y = 1.10 \times 10^4X - 2.09 \times 10^2$ | 0.9993 | | 0.02 | 89.5 | 8.9 | 18.5 | 25.0 | 15.3 |
| tricyclazole | $Y = 3.63 \times 10^2X + 8.47$ | 0.9919 | 0.05 | 0.05 | ND | ND | ND | 10.1 | 11.4 |
| bifenox | $Y = 3.35 \times 10^2X - 5.76$ | 0.9993 | 0.05 | 0.02 | 102 | 10.0 | 19.3 | 13.1 | 6.4 |
| anilofos | $Y = 1.36 \times 10^2X - 4.66$ | 0.9931 | | 0.02 | 70.2 | 11.3 | 16.0 | 19.6 | 16.7 |
| pyriproxyfen | $Y = 1.53 \times 10^4X + 6.06 \times 10^2$ | 0.9936 | 0.2 | 0.02 | 105 | 5.1 | 21.4 | 6.6 | 17.0 |
| cyhalofop-butyl | $Y = 3.00 \times 10^3X + 1.65 \times 10$ | 0.9941 | 0.03 | 0.02 | 89.0 | 9.8 | 19.3 | 14.9 | 12.7 |
| $\lambda$-cyhalothrin-1 | $Y = 3.23 \times 10^3X + 6.78$ | 0.9971 | 0.01 | 0.01 | 98.6 | 5.9 | 25.3 | 14.4 | 12.0 |
| $\lambda$-cyhalothrin-2 | $Y = 5.82 \times 10^3X - 2.53 \times 10$ | 0.9986 | 0.01 | 0.01 | 94.0 | 13.6 | 28.7 | 7.1 | 16.5 |
| tralkoxydim | $Y = 9.87 \times 10^3X - 2.81 \times 10$ | 0.9980 | 0.02 | 0.02 | 86.0 | 11.7 | 29.4 | 20.3 | 16.7 |
| permethrin-1 | $Y = 4.83 \times 10^3X + 5.83 \times 10$ | 0.9956 | 0.05 | 0.02 | 86.6 | 10.4 | 19.1 | 4.1 | 5.9 |
| permethrin-2 | $Y = 5.94 \times 10^3X + 7.69 \times 10$ | 0.9949 | 0.05 | 0.02 | 72.4 | 12.7 | 21.3 | 3.7 | 6.7 |
| bifenthrin-1 | $Y = 2.30 \times 10^2X + 1.26 \times 10$ | 0.9994 | 0.3 | 0.05 | ND | ND | ND | 14.7 | 12.2 |
| bifenthrin-2 | $Y = 3.03 \times 10^2X - 3.08$ | 0.9976 | 0.3 | 0.05 | ND | ND | ND | 27.2 | 6.9 |
| pyridaben | $Y = 1.35 \times 10^4X + 6.97 \times 10$ | 0.9970 | 0.05 | 0.02 | 82.0 | 6.9 | 13.8 | 3.9 | 9.2 |
| quizalofop-P | $Y = 2.36 \times 10^3X - 3.28 \times 10$ | 0.9960 | 0.1 | 0.02 | 73.9 | 13.6 | 22.4 | 14.7 | 23.2 |

[a]Other spike levels are available in the Supporting Information. [b]MRL data from http://www.codexalimentarius.net/mrls/pestdes/jsp/pest_q-e.jsp; US Code of Federal Regulations - Title 40, Part 180; EU pesticides database, http://ec.europa.eu/sanco_pesticides/public/index.cfm.

and RSDs had been validated at 0.02, 0.10, and 0.50 mg kg$^{-1}$ for the same target ion as soybean matrix. From the validation data, which is shown partly in Table 1, recoveries were 69.11−118.97% (mung bean), 69.09−119.81% (adzuki bean) and 69.02−120.81% (black bean), with RSDs less than 20%; they met the requirements of the validation criteria (recovery, 70−120%;


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Table 3. Pesticide Residue on Real Samples from Market (Soybean, Mung Bean, Adzuki Bean and Black Bean)[a]

| pesticide | no. of samples | concn range (mg kg$^{-1}$) min | concn range (mg kg$^{-1}$) max | MRL (mg kg$^{-1}$) | MVD (mg kg$^{-1}$) |
|---|---|---|---|---|---|
| | | Soybean (51) | | | |
| methomyl | 2 | 0.149 | 0.204 | 0.1 | 0.176 |
| propyzamide | 6 | <LOQ | 0.165* | – | 0.045 |
| dicamba | 9 | <LOQ | 0.212 | 0.1 | 0.012 |
| fluorochloridone | 11 | <LOQ | 0.069* | – | 0.025 |
| allethrin | 4 | <LOQ | 0.035* | – | 0.027 |
| chlorfenvinphos | 6 | <LOQ | 0.088* | – | 0.015 |
| phenoxyacetic acid | 2 | <LOQ* | 0.036* | – | 0.025 |
| S-bioallethrin | 5 | <LOQ | 0.028* | – | 0.017 |
| pyriproxyfen | 11 | <LOQ | 2.406 | 0.2[b] | 1.167 |
| | | Mung Bean (45) | | | |
| triadimefon | 12 | 0.105* | 0.165* | – | 0.129 |
| fluorochloridone | 12 | <LOQ* | 0.048* | – | 0.033 |
| haloxyfop-R-methyl | 8 | <LOQ | 0.029* | – | 0.014 |
| cartap hydrochloride | 12 | 0.026* | 0.041* | – | 0.034 |
| uniconazole | 6 | 0.011* | 0.018* | – | 0.015 |
| RH-5849 | 12 | 0.018* | 0.05* | – | 0.026 |
| propiconazole | 12 | <LOQ | 0.022 | 2 | 0.016 |
| pyriproxyfen | 12 | <LOQ | 0.026 | 0.2[b] | 0.021 |
| | | Adzuki Bean (42) | | | |
| etridiazole | 3 | 0.057* | 0.072* | – | 0.064 |
| pyriproxyfen | 6 | <LOQ | 0.032 | 0.2[b] | 0.019 |
| tralkoxydim | 6 | 0.017* | 0.025* | – | 0.021 |
| bifenthrin | 1 | 0.383 | 0.383 | 0.3 | 0.383 |
| | | Black Bean (40) | | | |
| etridiazole | 2 | 0.038* | 0.043* | – | 0.041 |
| methomyl | 4 | 0.082 | 0.706 | 0.1 | 0.539 |
| triadimefon | 2 | <LOQ | <LOQ | – | 0.006 |
| allethrin | 6 | <LOQ | 0.011* | – | 0.007 |
| phenoxyacetic acid | 3 | <LOQ | 0.021* | – | 0.015 |
| S-bioallethrin | 8 | <LOQ | 0.049* | – | 0.017 |
| cartap hydrochloride | 10 | 0.016* | 0.053* | – | 0.034 |
| propiconazole | 10 | 0.073* | 0.113* | – | 0.095 |
| epoxiconazole | 10 | 0.022* | 0.055* | – | 0.045 |
| tetramethrin | 4 | 0.025* | 0.043* | – | 0.035 |
| bifenthrin | 2 | 2.072 | 2.634 | 0.3 | 2.353 |

[a]Only demonstrates the samples that have pesticide residues exceeding MRLs of relative products; dash ("–") stands for "not detected in the real sample"; asterisk ("*") stands for MRL is not available for this molecule; if the value > relative LOQ, the default MRL (e.g., EU 0.01 mg kg$^{-1}$, Japan 0.01 mg kg$^{-1}$, etc.) may be applicable to the identified values. [b]The United States does not maintain a specific MRL for these pesticide/crop combinations, but does maintain an MRL of 0.02 ppm for its "vegetable, Legume Group 6" group.

RSDs ≤ 20%) proposed by US EPA[15] and EU Commission.[16] Since the soybean is the typical representative commodity of *Oil Seed and Product Thereof*,[16] it can be concluded that this method not only can be applied to beans but also possibly can be used for the products of oil seed, such as sunflower, cotton seed or peanut.

**High Protein Sample Process.** Beans, especially soybean and black bean, are products with rich protein and oil, which can dramatically increase the viscosity of extraction in the concentration step of this research. This concentrated and sticky liquid can block the screen of the tip, and make the DPX cleanup process less effective. To avoid this, the extraction was frozen in −20 °C for 2 h prior to the DPX step in order to precipitate the proteins in a relatively short time. At the sample time, freezing, for agglomerating the oil and fat, is critical for the fat-removal process in bean matrix.

**Advantages and Disadvantages of DPX-Qg.** The main advantages of DPX are its speed and ease of use, taking only seconds to mix sample solutions with the solid-phase sorbent, which makes the automation achievable. The cleanup procedure can be processed automatically before the chromatographic analysis, and the analyst will only have to perform the initial sample preparation of extracting and concentrating a corresponding solution.

The advantage of the DPX-Qg over other QuEChERS products is that the screen of the DPX tip acts as a filter removing the sorbent and salt particulate matter from the solution. This allows dispersive extractions without the need for centrifugation for the "cleanup", thereby providing a convenient means of conducting the QuEChERS extraction.

In addition, relatively high recoveries and better reproducibility, for almost all studied matrices and pesticides that have various physicochemical properties ($-0.55 < \log P < 8$, figures available in the Supporting Information), are generally observed because the dispersive sorbent and GCB were used with the

Table 4. Chronic Dietary Exposure Assessment of Pesticide Residues in Soybean, Mung Bean, Adzuki Bean and Black Bean on Chinese Food Consumption Data[a]

| pesticide | daily intake[b] (mg kg$^{-1}$ bw day$^{-1}$) soybean | mung bean | adzuki bean | black bean | ADI (mg kg$^{-1}$) | total daily intake (mg kg$^{-1}$ bw day$^{-1}$) | % of ADI |
|---|---|---|---|---|---|---|---|
| etridiazole | | | 0.0000045 | 0.0000029 | 0.025 | 0.0000074 | 0.0296 |
| methomyl | 0.0000123 | | | 0.0000377 | 0.02 | 0.0000500 | 0.250 |
| propyzamide | 0.0000032 | | | | 0.08 | 0.0000032 | 0.0094 |
| triadimefon | | 0.0000090 | | | 0.03 | 0.000009 | 0.03 |
| fluorochloridone | 0.0000018 | 0.0000023 | | | 0.039[c] | 0.0000041 | 0.0105 |
| chlorfenvinphos | 0.0000011 | | | | 0.0005 | 0.0000011 | 0.22 |
| S-bioallethrin | 0.0000012 | | | 0.0000012 | 10[c] | 0.0000024 | 0.000024 |
| haloxyfop-R-methyl | | 0.0000010 | | | 0.0003 | 0.000001 | 0.333 |
| cartap hydrochloride | | 0.0000024 | | 0.0000024 | 0.1[c] | 0.0000048 | 0.0048 |
| propiconazole | | 0.0000012 | | 0.0000066 | 0.04 | 0.0000078 | 0.0195 |
| epoxiconazole | | | | 0.0000031 | 0.003 | 0.0000031 | 0.103 |
| pyriproxyfen | 0.0003111 | 0.0000015 | 0.0000013 | | 0.1 | 0.0003139 | 0.314 |
| tralkoxydim | | | 0.0000014 | | 0.205[c] | 0.0000014 | 0.00068 |
| bifenthrin | | | 0.0000268 | 0.0001647 | 0.02 | 0.0001915 | 0.958 |

[a]Chinese food consumption data for "dry beans" is 4.2 g/day/person. [b]Based on an assumption of average body weight of Chinese adult as 60 kg. [c]ADI proposed by NOEL/100.

concept of the QuEChERS, which efficiently removes fatty acid components, pigments and other interference.

However, comparing to the pesticide-extracting or pesticide-isolating method, for instance the DPX-RP,[1] the disadvantage of this method is the resultant sample solutions are relatively "dirty", in which we are not able to identify or quantify some pesticide residues at low concentration level, for instance, pesticide propoxur, methomyl, dimenthoate and tricyclazole at the spike level of 0.02 mg kg$^{-1}$ (Table 2). Therefore, for the further research focus on these pesticides or pesticides more sensitive at a relatively low concentration, we suggest using the process standard (or surrogate standard) to fully minimize, calibrate and assess the matrix effect, coprecipitation and absorption phenomena in the processes of analysis, in order to achieve satisfactory results at low residue level in this "dirty" matix.

**Residue Determination and Risk Assessment of Real Samples.** 51 soybean, 40 black bean, 45 mung bean and 42 adzuki bean samples from local markets and supermarkets in the central area of Beijing were sampled and analyzed following the sample preparation method described above. The residues were detected in 21.9% of the total samples (39 out of 178 samples). They were found in 11 soybean, 10 black bean, 12 mung bean and 6 adzuki bean samples. Pesticide levels encountered in the analyzed samples are shown in Table 3.

All of the 39 detected pesticides were registered in China, EPA, EU Commission or Codex Alimentarius Commission. Among these pesticides, 18 were used as selective herbicide, insecticide and fungicide for beans, 10 were broad-spectrum pesticide, 8 were "long-residue" or "hard-to-degrade" products, and the remaining 11 were widely applied in cereals. Furthermore, the most commonly found residues were cyprodinil (controls a wide range of pathogens), haloxyfop-R-methyl (post-emergence for control of annual and perennial grasses in soya bean) and pyriproxyfen (control of public health insect pests), which were detected in each matrix and determined in 5.1%, 15.7% and 21.9% of analyzed samples, respectively.

In order to evaluate the dietary risk of these 39 pesticides, the mid-value of detected (MVD) and daily intakes were calculated (eq 2). In Table 3, the concentrations of certain residues were below the LOQ. As a general rule, where all residues are less than LOQ, the MVD value would be assumed to be at the LOQ.[17] In this case, the estimated MVD of bifenthrin in adzuki bean is 0.383 mg kg$^{-1}$; the concentrations of propyzamide residue in soybean were <0.02, <0.02, 0.011, 0.023, 0.045, 0.165, thus, the estimated MVD is 0.017 mg kg$^{-1}$; moreover, the concentration of acetochlor in soybean is <0.02, <0.02, <0.02, 0.02, 0.025, 0.029, 0.032, 0.033, therefore, the estimated MVD is 0.022 mg kg$^{-1}$.

$$\text{daily intake} = \frac{\text{MVD} \times \text{food consumption data}}{\text{body weight}} \quad (2)$$

**Exposure Assessment.** Based on Chinese food consumption data on considering the worst case scenario, chronic exposures of 39 pesticides in these 4 kinds of beans are demonstrated in Table 4. We assumed that soybean, mung bean, adzuki bean and black bean are represented by "dry beans". The consumption group data used here contains a wider range of foods than the real commodities.

During the authorization procedure of plant protection product, the MRL is set in such a way that no MRL exceedance means no significant acute exposure. Therefore, acute exposure is usually calculated for active substances that exceed MRLs. Among these 39 pesticides, 9 of them were able to be assessed for an acute exposure by ARfD; in Table 5, the estimated short-term intakes of pesticides in soybean, mung bean, Adzuki bean and black bean were calculated by using Japan's, Thailand's and France's beans (dry) large portion (LP) consumption data respectively, as considering these data were capable to reflect the quantity consumed of these two beans in China.

**Risk Characterization.** Comparing the estimated daily intakes and estimated short-term intakes with the WHO recommended ADIs and ARfDs, only 0.0000238−0.983% of ADIs, 0.000210−63.5% of ARfDs are occupied so far. This result indicates that the dietary risk of pesticides in beans is fairly low for the Chinese general population.

In conclusion, a rapid and sensitive method for the analysis of 58 nonpolar and slightly polar pesticides in soybean, mung bean, adzuki bean and black bean has been built by using DPX-Qg. For compounds with log $P$ values between −0.55 and 8, high recoveries of over 70% were achieved with relative

Table 5. Acute Dietary Exposure Assessment for Chinese General Population[a]

| | pesticide | high residue measured (mg kg$^{-1}$) | large portion (g kg$^{-1}$ bw day$^{-1}$) | estimated short-term intake (mg kg$^{-1}$ bw day$^{-1}$) | ARfD[g] (mg kg$^{-1}$) | % of ARfD |
|---|---|---|---|---|---|---|
| soybean[b] | methomyl | 0.204 | 3.03 | 0.0006181 | 0.02 | 3.0905 |
| | dicamba | 0.212 | 3.03 | 0.0006424 | 0.3[f] | 0.21413 |
| | S-bioallethrin | 0.028 | 3.03 | 0.0000848 | 0.03[e] | 0.2827 |
| | pyriproxyfen | 2.406 | 3.03 | 0.0072902 | 10[f] | 0.072902 |
| mung bean[c] | triadimefon | 0.165 | 1.50 | 0.0002475 | 0.08 | 0.30938 |
| adzuki bean[d] | tralkoxydim | 0.025 | 6.90 | 0.0001725 | 0.001[f] | 17.250 |
| | bifenthrin | 0.383 | 6.90 | 0.0002643 | 0.033[e] | 8.009 |
| black bean[d] | methomyl | 0.706 | 6.90 | 0.0048714 | 0.02 | 24.3570 |
| | S-bioallethrin | 0.049 | 6.90 | 0.0003381 | 0.03[e] | 1.1270 |
| | propiconazole | 0.113 | 6.90 | 0.0007797 | 0.3 | 0.25990 |
| | epoxiconazole | 0.055 | 6.90 | 0.0003795 | 0.005 | 7.590 |
| | bifenthrin | 2.634 | 6.90 | 0.0181746 | 0.033[e] | 55.075 |

[a]Large portion data prepared by GEMS/Food for the Codex Committee on Pesticide Residues and the Joint FAO/WHO Meetings on Pesticide Residues, updated April 2008 (http://www.who.int/foodsafety/chem/gems/en/index2.html). [b]Large portion consumption data of soybean (dry) in Japan. [c]Large portion consumption data of mung bean (dry) in Thailand. [d]Large portion consumption data of bean (dry) in France. [e]USA ARfD data. [f]EU ARfD data. [g]ARfD data prepared by JMPR.

standard deviations of less than 15%. This method was applied to real samples and detected 39 pesticide residues, indicating that the proposed method to determine various classes of pesticide residues is sensitive. Compared to QuEChERS method, these analyses were achieved with efficient cleanup procedures, desirable eliminating method for proteins and oils, and feasibility of rapid, high throughput analysis of almost all kinds of pesticides by performing DPX extractions of acetonitrile extracts of those 4 kinds of beans with no solvent exchange step. Moreover, from the pesticide risk assessment above, we conclude that intakes of various pesticides in soybean, mung bean, adzuki bean and black bean are less than the ADIs and ARfDs recommended by JMPR (Joint Meeting on Pesticide Residue, FAO and WHO) and other related pesticide legislation authorities.

## ■ ASSOCIATED CONTENT

### Supporting Information

Additional figures and tables as discussed in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

## ■ ABBREVIATIONS USED

DPX, disposable pipet extraction; GCB, graphitized carbon black; DPX-Qg, DPX tip containing GCB for the QuEChERS procedure specially; C18, octadecylsilyl; PSA, primary-secondary amine; LOQ, limits of quantification; % RSD, relative standard deviation; MVD, mid-value of detected; ADI, acceptable daily intake; ARfD, acute reference dose; NESDI, national estimated daily intake; NESTI, national estimated short-term intake

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## NOTE ADDED AFTER ASAP PUBLICATION

After ASAP publication on May 2, 2012, the recovery values in Tables 1 and 2 were made consistent in significant figures. This correction is available in the ASAP posting of May 4, 2012.