Rapid Analysis of Residues of 186 Pesticides in Hawk Tea Using Modified QuEChERS Coupled with Gas Chromatography Tandem Mass Spectrometry

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Abstract: In this work, the QuEChERS method was modified and evaluated for the determination of 186 pesticides from caffeine-free and fatty hawk tea prior to their gas chromatography tandem mass spectrometry analysis for the first time. The results showed that the combination of MgSO₄ + PSA + MWCNTs plus EMR-Lipid provided the lowest matrix effect and best recovery; 117 of 186 pesticides manifested weak matrix effects. Thus, for accurate quantification, it is necessary to use matrix-matched calibration curves to compensate for the matrix effect. At the spiked level of 0.1 mg/kg, the average recoveries of 184 pesticides were in the range of 70–120% and the RSDs were 0.3–14.4% by the modified method. Good linearity was shown for 186 analytes at concentration of 0.01 mg/L–0.4 mg/L, and the correlation coefficients exceeded 0.99 for 182 pesticides. The detection limits of 186 pesticides by the modified QuEChERS method were 0.001–0.02 mg/kg, and the limits of quantification (LOQ) were 0.005 mg/kg–0.05 mg/kg. The necessity of solvent exchange is also explained in this work. The successful application of the modified QuEChERS in real samples proved that this method could be one of the routine options for analysis of herbal tea.

Keywords: hawk tea; modified QuEChERS; GC-MS/MS; EMR-Lipid

1. Introduction

Hawk tea, also named eagle tea, is widely known as an “affinal drug and diet” plant which means it was used as both medicine and food with hundreds of years of history in southern China. It is a caffeine-free but fatty tea which belongs to Lauraceae family and is different from the six main categories of teas (including green tea, white tea, yellow tea, oolong tea, black tea and dark tea). Hawk tea is considered a cooling and refreshing beverage to beat the heat by the rural people in southwest China owing to it being cheap and easily available. Spicy Bampa and Szechuan cuisine restaurants provide eagle tea as a complimentary drink to relieve customers after they have consumed spicy dishes. Therefore, its nutrient value and food safety are widely accepted by consumers. Previous studies [1] mainly focused on the active components of hawk tea, including mineral elements [2], volatile oils, [3] flavonoids, [4] and polysaccharides [5]. The content of fat in hawk tea is much higher than that in green tea, and its main components are listed in Table S1 [6]. Papers have demonstrated that hawk tea has the benefits of detoxification and anti-inflammatory, antioxidation, improvement of eyesight, and reduction of blood sugar and blood lipid etc., [7–9]. With the intensive and large-scale cultivation of eagle tea, the application of pesticides cannot be avoided, which causes a potential risk to public health. Many countries and regions have stipulated the maximum residue limits of pesticides in tea to regulate the use of pesticides. Pesticide levels detected in the mainstream teas commonly exceed the MRLs prescribed by the European Union (EU) and Codex...
Alimentarius Commission (CAC) [10]. Thus, it is essential to develop reliable, robust, and sensitive analytical methods to guarantee the safe consumption of hawk tea.

The original version of the Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) method was proposed by Anastassiades et al. in 2003 [11]. Modifications were made successively in the Association of Official Agricultural Chemists method with acetate buffer (AOAC 2007.01) [12] and the European Standard method (CEN 15662) with citrate buffer [13]. In recent years, the QuEChERS method has been further modified and widely used for multi-residue preparations in complex matrices because of its inherent properties: rapidity, simplicity, low cost, high efficiency, ruggedness, and safety [14,15]. At the same time, various materials have been investigated to enhance the clean-up capacity during the QuEChERS process, such as multiwalled carbon nanotubes (MWCNTs) and enhanced matrix removal (EMR) lipid. Multiwalled carbon nanotubes (MWCNTs) were first reported in 1991 [16], and have a unique nano-hollow structure, large specific surface area, and special chemical properties. Multiwalled carbon nanotubes have become one of the excellent solid phase extraction materials for the analysis of pesticide residues due to their strong adsorption capacity, stability, durability, and low cost [17,18]. EMR-Lipid is a novel material reported by the Agilent technology company in 2015. The composition of EMR-Lipid is undisclosed. It is used for removing lipids from QuEChERS extracts of fatty food matrix products, such as avocado and animal tissues, without loss of targeted compounds [19–22]. While hawk tea contains double the fat of green tea, EMR-Lipid may selectively remove it by the QuEChERS procedure. Gas chromatography tandem mass spectrometry (GC-MS/MS) is one of the most frequently used apparatus in analyzing pesticide residues, such as organochlorines and pyrethroids [23,24]. Research has suggested that GC-MS/MS is a reliable and robust analytical method with high sensitivity and selectivity [25,26]. It provides accurate qualitative and quantitative determination of hundreds of compounds in the presence of complex matrices. Besides, in terms of the apparatus cost, use cost, and accessibility, GC-MS/MS is superior to liquid chromatography-tandem mass spectrometry (LC-MS/MS). Over the past few years, most of the previous QuEChERS methods have focused on several kinds of pesticides in tea only [27,28]. There are few reports on the simultaneous determination of more than 100 pesticides combined being detected by the modified QuEChERS method with GC-MS/MS in tea, especially in herbal tea [29,30]. Hawk tea, caffeine-free but rich in fat, is a representative herbal tea that is distinguished from the six main kinds of teas, and accompanied with its rising consumption, there is a need to pay more attention to the food safety quality controls on it. However, there are few studies reporting the analytical technologies for detecting pesticide residues in hawk tea and the potential pesticide residue risks of hawk tea.

In this work, fatty hawk tea was selected as the research object. The QuEChERS method was firstly modified by MWCNTs and with EMR-Lipid to evaluate their applicability for multi-pesticide residue determination in hawk tea combined with GC-MS/MS. Our analysis describes 186 pesticide residues in hawk tea for the first time. The pre-treatment procedures and instruments conditions were optimized respectively. A series of parameters including recovery, precision, linearity, limit of detection (LOD), and limit of quantification (LOQ) were evaluated for the method validation. Finally, the proposed method was successfully applied to the determination of these pesticides in real hawk tea samples.

2. Materials and Methods

2.1. Chemicals and Reagents

We purchased 186 pesticide reference material standards with purities greater than 95% from Sigma-Aldrich (Saint Louis, MO, USA) and Dr. Ehrenstorfer GmbH (Augsburg, Germany). MS-grade solvents, such as acetonitrile and ethyl acetate, were purchased from Merck Companies (Darmstadt, Germany); analytical grade acetic acid was obtained from Chengdu Kelong Chemical Reagent Company (Sichuan, China); analytical grade salts, such as sodium chloride (NaCl) and magnesium sulfate (MgSO₄), were from Shanghai GuoYao Chemical Reagents (Shanghai, China). Graphitized Carbon Black (GCB, 40 μm), MWCNTs,
and Primary Secondary Amine (PSA, 40 µm) were purchased from ANPEL Laboratory Technologies Inc. (Shanghai, China). EMR-Lipid was obtained from Agilent Technologies, Inc. (Santa Clara, CA, USA). Ultra-pure water was obtained using a MilliQ UF-Plus system (Millipore, Darmstadt, Germany) with a resistivity of at least 18.2 MΩ cm at 25 °C.

2.2. Equipment and Experimental Conditions

Analysis was carried out using a Shimadzu GCMS-TQ8050 triple-quadrupole (QqQ) mass spectrometer with an electron ionization interface and an auto sampler AOC 20i/s. Chromatographic separation was achieved on a SH-Rxi-5Sil MS column (30 m × 0.25 mm i.d., 0.25 µm) from Shimadzu.

Other equipment included: Vortex oscillator (IKA-Werke GmbH & CO. KG Janke & Kunkel, Staufen, Germany); centrifuge (Beckman Coulter, Inc., Indianapolis, IN, USA); nitrogen evaporator (Organomation Associates, Inc., Berlin, MA, USA); analytical balance with 0.0001 accuracy. Centrifuge tubes: 15 mL, 50 mL; pipettes: 1 mL, 5 mL, 10 mL; filter membrane: 0.22 µm.

2.3. QuEChERS Extraction Procedures

Two grams of each hawk tea powder was weighed into a 50 mL centrifuge tube containing EMR-Lipid materials. Then, 10 mL distilled water was added, shaken for 30 s, and left to stand for 30 min. Next, the samples were extracted with 10 mL acetonitrile, shaken for 30 s, put in 4 g NaCl and shaken by vortex for 1 min. Then, the samples were centrifuged at 5000 rpm for 10 min immediately. Afterwards, the upper 3 mL extraction solvent was transferred to a 15 mL QuEChERS purification falcon tube (contained with 1200 mg MgSO₄, 400 mg PSA, 200 mg MWCNTs). Then, 3 mL toluene was accurately added to the tube. The tube was vortexed for 1 min and centrifuged for 10 min at 8000 rpm. The supernatant acetonitrile and toluene mixture layer (2 mL) was dried under N₂ gas and re-dissolved with 1 mL ethyl acetate. It was passed through a nylon filter (0.22 µm) before analysis.

3. Results and Discussions

3.1. Optimization of GC/MS/MS Conditions

In this research, a total of 186 pesticides listed in Table 1 were selected for investigation, then one quantitation and at least two identification ions were adopted for scanning under the multi-reaction monitoring (MRM) model to avoid false positive response. First, in each different sample matrix, the same ions have a different response intensity, so the hawk tea matrix standard solution was used to establish a parent ion scan mode, with a scanning range from 50 to 550 (m/z). Next, the precursor ions of the 186 pesticides were selected for the second collision of ions with different voltages. Then, we selected a signal value and the highest percentage collision value of the two ions and voltages. Finally, we determined the highest value for the quantitative ion, followed by the qualitative ion. On this occasion, pesticides could be successfully separated and identified via GC-MS/MS. For example, the retention times (RTs) of triadimefon and isazofos are 11.882 min and 11.886 min, respectively, and they cannot be separated and identified via gas chromatography. However, according to the differences of their quantitative ion pairs (208.10/111.00 * and 257.00/162.00 *) and qualitative ion pairs (208.10/127.00 and 257.00/119.00), under the multi-reaction monitoring (MRM) model of GC-MS/MS, these two pesticides were distinguished correspondingly. The RT of pesticides may vary slightly in different sample matrices. In order to avoid this, we added pesticides to the hawk tea matrix, and then changed the GC-MS/MS pressure to stabilize the retention time of the chromatography of the target compounds and ensure the retention times of the 186 pesticides were within the allowed range (±0.05 s). The quantitative ion collision voltage range for the 186 pesticides was 6–34 (eV) and the qualitative ion collision cover range was 6–30 (eV).
| No. | Pesticides      | RT/min | Qualitative Ion Pairs (m/z) | CE/eV | No. | Pesticides      | RT/min | Qualitative Ion Pairs (m/z) | CE/eV |
|-----|------------------|--------|----------------------------|-------|-----|------------------|--------|----------------------------|-------|
| 1   | dichlorvos       | 5.972  | 109.00 > 79.00 * 8         |       | 94  | op'-DDE          | 14.811 | 246.00 > 176.00 * 30       |       |
| 2   | dichlorobenzonitrile | 6.935  | 185.00 > 93.00 * 14        |       | 95  | paclobutrazol    | 14.893 | 236.10 > 125.00 * 28       |       |
| 3   | biphenyl         | 7.389  | 170.90 > 136.00 * 14       |       | 96  | butachlor        | 14.92  | 160.10 > 72.00 * 10        |       |
| 4   | etridiazole      | 8.034  | 154.10 > 128.10 * 22       |       | 97  | fenothiocarb     | 14.947 | 160.10 > 106.10 * 12       |       |
| 5   | propoxur         | 8.181  | 154.10 > 115.00 * 24       |       |     |                  |        |                            |       |
| 6   | isoprocarb       | 8.946  | 182.90 > 139.90 * 18       |       | 98  | ditalimfos       | 15.046 | 188.10 > 160.10 * 12       |       |
| 7   | tecnazene        | 9.553  | 152.00 > 110.10 * 10       |       | 99  | butamifos        | 15.065 | 286.10 > 202.10 * 14       |       |
| 8   | diphenylamine    | 9.941  | 160.00 > 82.00 * 8         |       |     |                  |        |                            |       |
| 9   | ethoprophos      | 10.016 | 121.10 > 77.00 * 22        |       | 100 | napropamide      | 15.155 | 128.00 > 72.10 * 6         |       |
| 10  | chlorpropham     | 10.263 | 121.10 > 109.00 * 12       |       | 101 | bromfenvinfos    | 15.164 | 148.00 > 130.10 * 10       |       |
| 11  | benfluralin      | 10.382 | 260.90 > 202.90 * 14       |       |     |                  |        |                            |       |
| 12  | sulfotep         | 10.414 | 262.00 > 142.90 * 24       |       | 103 | flutolanil       | 15.227 | 173.00 > 95.00 * 26        |       |
| 13  | monocrotophos    | 10.532 | 169.10 > 128.10 * 22       |       |     |                  |        |                            |       |
| 14  | phorate          | 10.629 | 202.90 > 160.00 * 10       |       | 104 | chlorfenson      | 15.236 | 175.00 > 111.00 * 12       |       |
| 15  | alpha BHC        | 10.735 | 231.00 > 121.00 * 14       |       | 105 | hexaconazole     | 15.263 | 175.00 > 75.00 * 28        |       |
| 16  | dimethoate       | 11.008 | 121.00 > 66.00 * 24        |       | 106 | prothiofos       | 15.272 | 214.00 > 159.00 * 20       |       |
| 17  | simazine         | 11.166 | 160.00 > 82.00 * 8         |       | 107 | fludioxonil      | 15.29  | 248.00 > 127.00 * 26       |       |
| 18  | atrazine         | 11.25  | 180.00 > 144.90 * 16       |       | 108 | pretilachlor     | 15.318 | 248.00 > 154.00 * 20       |       |
| 19  | beta BHC         | 11.261 | 201.10 > 173.10 * 6        |       | 109 | isoprothiolane  | 15.318 | 262.10 > 202.10 * 10       |       |
| 20  | clomazone        | 11.292 | 218.90 > 182.90 * 8        |       | 110 | profenofos      | 15.363 | 238.10 > 162.10 * 10       |       |
| 21  | propazine        | 11.313 | 201.10 > 173.10 * 6        |       |     |                  |        |                            |       |
| 22  | gamma-BHC        | 11.408 | 231.00 > 121.00 * 14       |       | 111 | pp'-DDE          | 15.435 | 231.10 > 189.00 * 10       |       |
| 23  | profluralin      | 11.429 | 231.00 > 182.90 * 8        |       |     |                  |        |                            |       |
| 24  | terbuthylazine   | 11.492 | 318.00 > 199.10 * 18       |       | 112 | oxadiazon       | 15.453 | 302.00 > 175.00 * 8        |       |
| 25  | terbufos         | 11.502 | 318.00 > 155.10 * 18       |       |     |                  |        |                            |       |
| 26  | fonofos          | 11.576 | 299.10 > 173.10 * 6        |       | 113 | DEF              | 15.489 | 202.00 > 147.00 * 6        |       |
| 27  | pronamide        | 11.586 | 299.10 > 144.90 * 14       |       | 114 | dieldrin        | 15.525 | 202.00 > 113.00 * 20       |       |
|     |                  |        | 299.10 > 144.90 * 14       |       |     |                  |        |                            |       |
|     |                  |        | 231.00 > 128.90 * 16       |       | 115 | myclobutanil    | 15.534 | 276.90 > 241.00 * 8        |       |
|     |                  |        | 231.00 > 174.90 * 14       |       |     |                  |        |                            |       |
|     |                  |        | 173.00 > 95.00 * 26        |       | 116 | op'-DDD         | 15.562 | 262.90 > 193.00 * 34       |       |
|     |                  |        | 173.00 > 145.00 * 24       |       |     |                  |        |                            |       |
|     |                  |        | 318.00 > 199.10 * 18       |       | 117 | oxyfluoren      | 15.571 | 317.00 > 300.00 * 14       |       |
|     |                  |        | 318.00 > 155.10 * 18       |       |     |                  |        |                            |       |
|     |                  |        | 299.10 > 173.10 * 6        |       | 118 | bupirimate      | 15.579 | 273.10 > 108.10 * 16       |       |
|     |                  |        | 299.10 > 173.10 * 6        |       |     |                  |        |                            |       |
|     |                  |        | 173.00 > 95.00 * 26        |       | 119 | kresoxim methyl | 15.605 | 273.10 > 193.10 * 8        |       |
|     |                  |        | 173.00 > 145.00 * 24       |       |     |                  |        |                            |       |

Table 1. GC-MS/MS parameters of 186 pesticides in selected reaction monitoring (MRM) mode.
| No. | Pesticides          | RT/min | Qualitative Ion Pairs (m/z) | CE/ eV | No. | Pesticides          | RT/min | Qualitative Ion Pairs (m/z) | CE/ eV |
|-----|---------------------|--------|----------------------------|--------|-----|---------------------|--------|----------------------------|--------|
| 28  | diazinon           | 11.639 | 304.10 > 179.10 *          | 10     | 121 | isoxathion          | 15.813 | 177.10 > 130.10 *          | 10     |
| 29  | pyrimethanil       | 11.723 | 179.10 > 137.10            | 18     |      |                     |         |                            |        |
| 30  | isazofos           | 11.886 | 198.10 > 183.10            | 14     | 122 | cyproconazole1      | 15.822 | 198.10 > 111.10 *          | 16     |
| 31  | etrimfos           | 11.967 | 257.00 > 162.00            | 8      |      | fluazifop butyl    | 15.9    | 222.10 > 125.10          | 12     |
| 32  | delta-BHC          | 11.989 | 257.00 > 119.00            | 18     | 123 | nitrofen            | 15.909 | 282.00 > 91.10            | 18     |
| 33  | triallate          | 11.998 | 180.90 > 144.90            | 16     |      | endrin              | 15.917 | 282.00 > 238.10          | 18     |
| 34  | tebupirimfos       | 12.099 | 218.90 > 182.90            | 8      | 124 | chlorobenzilate     | 16.064 | 202.00 > 139.00 *         | 24     |
| 35  | pirimicarb         | 12.13  | 268.10 > 184.00            | 20     |      |                     |         |                            |        |
| 36  | iprobenfos         | 12.15  | 270.10 > 186.00            | 20     | 125 | cyproconazole1      | 15.822 | 282.00 > 238.10          | 18     |
| 37  | formothion         | 12.282 | 271.00 > 137.10            | 18     |      |                     |         |                            |        |
| 38  | pentachloroaniline | 12.303 | 318.10 > 152.10            | 14     |      | nitrofen            | 15.909 | 282.00 > 238.10          | 18     |
| 39  | phosphamidon       | 12.425 | 238.10 > 166.10            | 12     |      |                     |         |                            |        |
| 40  | dichlofenthion     | 12.445 | 204.00 > 91.00             | 8      | 126 | fensulfothion       | 16.108 | 202.00 > 234.00          | 10     |
| 41  | desmetryn          | 12.475 | 204.00 > 91.00             | 8      |      |                     |         |                            |        |
| 42  | propanil           | 12.516 | 204.00 > 91.00             | 8      | 127 | chlorothiophos      | 16.264 | 235.00 > 165.00          | 24     |
| 43  | acetochlor         | 12.547 | 224.00 > 125.00            | 18     | 128 | diniconazole        | 16.151 | 235.00 > 165.00          | 24     |
| 44  | phenthoate         | 12.58  | 222.90 > 204.90            | 14     |      |                     |         |                            |        |
| 45  | malathion          | 12.618 | 213.00 > 171.10            | 6      | 129 | oxadixyl            | 16.212 | 237.00 > 165.00          | 28     |
| 46  | vinclozolin        | 12.658 | 213.00 > 171.10            | 6      |      |                     |         |                            |        |
| 47  | parathion methyl   | 12.709 | 230.00 > 190.90            | 12     | 130 | pp'-DDD             | 16.229 | 153.00 > 97.00            | 14     |
| 48  | tolclofos methyl   | 12.719 | 227.90 > 146.10            | 12     |      |                     |         |                            |        |
| 49  | alachlor           | 12.73  | 223.10 > 132.10            | 12     | 131 | fenthiophos         | 16.264 | 237.00 > 165.00          | 28     |
| 50  | ametryn            | 12.877 | 273.9/246.0                | 6      |      |                     |         |                            |        |
| 51  | metalaxyl          | 12.877 | 273.9/246.0                | 6      |      |                     |         |                            |        |
| 52  | ronnel             | 12.906 | 273.9/246.0                | 6      |      |                     |         |                            |        |
| 53  | prometryn          | 12.936 | 273.9/246.0                | 6      |      |                     |         |                            |        |
| 54  | prometryn          | 13.141 | 273.9/246.0                | 6      | 132 | propiconazole       | 16.829 | 237.00 > 165.00          | 28     |
| 55  | terbutryn          | 13.18  | 273.9/246.0                | 6      |      |                     |         |                            |        |
| No. | Pesticides       | RT/min | Qualitative Ion Pairs (m/z) | CE/eV | No. | Pesticides       | RT/min | Qualitative Ion Pairs (m/z) | CE/eV |
|-----|------------------|--------|----------------------------|-------|-----|------------------|--------|----------------------------|-------|
| 56  | fenitrothion     | 13.2   | 277.00 > 260.00 *          | 6     | 149 | pyridaphenthion  | 17.654 | 340.00 > 199.10 *          | 8     |
| 57  | ethofumesate     | 13.239 | 207.10 > 161.10 *          | 8     | 150 | iprodione        | 17.678 | 187.00 > 124.00 *          | 25    |
| 58  | bromacil         | 13.307 | 204.90 > 187.90 *          | 14    | 151 | phosmet          | 17.798 | 243.90 > 187.00 *          | 5     |
| 59  | phorate sulfoxide| 13.366 | 153.00 > 97.00 *           | 12    | 152 | bifenthrin       | 18.782 | 160.00 > 77.00 *           | 24    |
| 60  | malathion        | 13.376 | 199.00 > 171.10            | 6     | 153 | EPN              | 17.846 | 160.00 > 133.00            | 14    |
| 61  | diropetryn       | 13.444 | 255.00 > 222.20 *          | 9     | 154 | bromopropylate   | 17.869 | 181.10 > 166.10 *          | 12    |
| 62  | metolachlor      | 13.464 | 162.10 > 133.10 *          | 16    | 155 | piperonphos      | 17.877 | 156.90 > 77.00 *           | 24    |
| 63  | phoratesulfone   | 13.493 | 153.00 > 97.00 *           | 12    | 156 | tetramethrin     | 17.893 | 140.10 > 98.00             | 12    |
| 64  | chlorpyrifos     | 13.503 | 199.00 > 171.10            | 6     | 157 | methoxychlor     | 17.965 | 140.10 > 113.00            | 15    |
| 65  | thiobencarb      | 13.532 | 206.90 > 189.90            | 16    | 158 | etoxazole        | 17.973 | 227.10 > 182.90 *          | 18    |
| 66  | fenthion         | 13.591 | 278.00 > 109.00 *          | 20    | 159 | fenamidone       | 18.037 | 268.10 > 180.10            | 16    |
| 67  | parathion        | 13.659 | 148.90 > 119.00            | 5     | 160 | tebufenpyrad     | 18.1   | 333.10 > 171.10 *          | 20    |
| 68  | isofenphos oxon  | 13.689 | 229.10 > 201.00            | 10    | 161 | anilofos         | 18.131 | 333.10 > 276.10            | 8     |
| 69  | triadimefon      | 13.718 | 208.10 > 181.00            | 10    | 162 | bifenvox         | 18.162 | 226.10 > 157.00 *          | 14    |
| 70  | buprofezin       | 13.726 | 175.10 > 132.10 *          | 14    | 163 | tetradifon       | 18.354 | 340.90 > 309.90 *          | 10    |
| 71  | isocarbophos     | 13.737 | 289.10 > 236.00 *          | 14    | 164 | phosalone        | 18.462 | 340.90 > 189.90            | 20    |
| 72  | dicofol          | 13.803 | 139.00 > 111.00 *          | 12    | 165 | leptofo          | 18.47  | 328.90 > 313.90            | 14    |
| 73  | trichloronat     | 13.84  | 139.00 > 75.00             | 12    | 166 | pyriproxyfen     | 18.631 | 374.90 > 359.90 *          | 24    |
| 74  | pirimiphos ethyl | 13.915 | 297.00 > 269.00            | 15    | 167 | iambda cyhalothrin| 18.631 | 374.90 > 359.90 *          | 24    |
| 75  | bromophos        | 13.925 | 304.00 > 265.00            | 18    | 168 | mefenacet        | 18.708 | 367.90 > 361.90 *          | 24    |
| 76  | isofenphos methyl| 14.019 | 318.00 > 166.00            | 18    | 169 | acrinathrin      | 18.77  | 318.90 > 313.90            | 14    |
| 77  | fosthiazate      | 14.019 | 195.00 > 103.00 *          | 10    | 170 | pyrazophos       | 18.981 | 289.10 > 93.00 *           | 14    |
| 78  | pendimethalin    | 14.141 | 252.10 > 161.10 *          | 10    | 171 | fenarimol        | 19.003 | 289.10 > 77.00             | 26    |
| 79  | chlorfenvinphos  | 14.15  | 323.00 > 267.00            | 16    | 172 | azinphos ethyl   | 19.13  | 221.10 > 193.10 *          | 12    |
| 80  | cyprodil         | 14.169 | 224.10 > 197.10            | 22    | 173 | permethrin 1     | 19.598 | 221.10 > 149.10            | 14    |
| 81  | terbufos sulfone | 14.235 | 153.00 > 97.00 *           | 21    | 174 | coumaphos        | 19.712 | 183.10 > 153.10 *          | 14    |
| 82  | fipronil         | 14.244 | 199.00 > 97.00             | 21    | 175 | fluquinconazole  | 19.734 | 183.10 > 168.10            | 14    |
| 83  | penconazole      | 14.272 | 366.90 > 212.90 *          | 30    | 176 | pyridaben        | 19.756 | 340.00 > 298.00 *          | 20    |
### Table 1. Cont.

| No. | Pesticides        | RT/min | Qualitative Ion Pairs (m/z) | CE/ eV | No. | Pesticides     | RT/min | Qualitative Ion Pairs (m/z) | CE/ eV |
|-----|-------------------|--------|-----------------------------|--------|-----|----------------|--------|-----------------------------|--------|
| 84  | phosfolan         | 14.301 | 255.00 > 227.00 *           | 6      | 177 | dioxathion     | 19.77  | 152.90 > 96.90 *           | 10     |
|     |                   |        | 255.00 > 140.00             | 22     |     |                |        | 185.00 > 129.00            | 12     |
| 85  | isofenphos        | 14.338 | 213.00 > 121.00 *           | 15     | 178 | fenbuconazole  | 20.121 | 198.10 > 129.10 *          | 10     |
|     |                   |        | 213.00 > 185.00             | 6      |     |                |        | 129.10 > 102.10            | 18     |
| 86  | beflubutamid      | 14.46  | 176.00 > 91.10 *            | 15     | 179 | cyfluthrin     | 20.136 | 226.10 > 206.10 *          | 14     |
|     |                   |        | 221.00 > 193.00             | 12     |     |                |        | 198.90 > 170.10            | 25     |
| 87  | quinalphos        | 14.47  | 146.10 > 118.00 *           | 10     | 180 | cypermethri    | 20.46  | 163.10 > 127.10 *          | 6      |
|     |                   |        | 146.10 > 91.00              | 24     |     |                |        | 163.10 > 91.00             | 14     |
| 88  | mephosfonol       | 14.498 | 196.00 > 140.00 *           | 12     | 181 | boscalid       | 20.522 | 140.10 > 112.10 *          | 12     |
|     |                   |        | 196.00 > 168.00             | 6      |     |                |        | 140.10 > 76.00             | 24     |
| 89  | procymidone       | 14.535 | 283.00 > 96.00 *            | 10     | 182 | flucythrin     | 20.626 | 199.10 > 157.10 *          | 10     |
|     |                   |        | 285.00 > 96.00              | 10     |     |                |        | 157.10 > 107.10            | 12     |
| 90  | triadimenol       | 14.545 | 168.10 > 70.00 *            | 10     | 183 | fenvalerate    | 21.338 | 225.10 > 119.10 *          | 20     |
|     |                   |        | 128.10 > 65.00              | 22     |     |                |        | 225.10 > 147.10            | 10     |
| 91  | bromophos ethyl   | 14.721 | 358.90 > 302.90 *           | 16     | 184 | fluvulinate    | 21.452 | 250.10 > 55.00 *           | 20     |
|     |                   |        | 302.90 > 284.90             | 18     |     |                |        | 250.10 > 200.00            | 20     |
| 92  | methidathion      | 14.739 | 145.00 > 85.00 *            | 8      | 185 | difenoconazole | 21.793 | 323.00 > 265.00 *          | 14     |
|     |                   |        | 145.00 > 58.00              | 14     |     |                |        | 265.00 > 202.00            | 20     |
| 93  | chlordane trans   | 14.757 | 374.80 > 265.90 *           | 26     | 186 | deltamethrin   | 22.109 | 180.90 > 151.90 *          | 22     |
|     |                   |        | 372.80 > 263.90             | 28     |     |                |        | 252.90 > 93.00             | 20     |

Note: "*" in the table represents quantitative ion pairs. RT represents retention time. CE represents collision energy.

#### 3.2. Optimization of QuEChERS Procedure

Although eagle tea is caffeine-free, it still contains other complex matrices such as pigments, carbohydrates, polyphenols, fat, and other substances. When dealing with complicated dry samples like hawk tea, selecting the appropriate pretreatment method and optimizing it during the sample preparation procedure can effectively reduce the amount of co-extracts and lower the matrix effect, at the same time keeping excellent accuracy. In our early-stage preparations, we found that with the QuEChERS original unbuffered method, the extraction procedure produced the fewest co-extracts and released the lowest heat compared with the acetate-buffered and citrate-buffered QuEChERS methods. Therefore, the original QuEChERS method was adopted and modified in this work. Then, affecting factors such as the absorbents and solvents were investigated successively.

##### 3.2.1. The Application of EMR-Lipid

The fat in hawk tea is twice that in green tea, so EMR-Lipid was considered to remove the fat. With high selectivity, EMR-Lipid could efficiently remove lipids based on volume exclusion and hydrophobic interaction mechanisms without loss of target analytes. Extraction and purification were included in the sample preparation procedure, so when applying EMR-Lipid, adding it to the extraction or the purification procedure should be taken into account. EMR-Lipid needs to be activated by water and the hawk tea powder also needs to soak in water to improve the extraction efficiency. To simplify the steps, the hawk tea sample was weighed into a 50 mL tube containing the EMR-Lipid to remove the fat in the extraction step instead of in the purification step; the water was then added to activate the EMR-Lipid materials at the same time to promote the dissolution of target components. The comparison experiment was also carried out. The EMR-Lipid was activated in the purification step; the purification capacity was almost the same as when adding it in the extraction step, and so was the recovery result. Yet, when using it this way, there is one more purification and salting out procedure. As shown in Figure 1, it is obvious that the combination of MgSO$_4$ + PSA + MWCNTs plus EMR-Lipid in the extraction procedure provided the better clean-up performance. After analysis of the hawk tea blank sample via the Q3scan mode, EMR-Lipid plus the combination of
MgSO₄ + PSA + MWCNTs showed the lower matrix effect (Figure S5). At the spike level of 0.1 mg/kg, the recovery rates of 167 of 186 pesticides (about 89.78%) were in the range of 70–120% (Table S2).

3.2.2. Selection of the Salt Composition

The different versions of QuEChERS have different salt composition; the original un-buffered QuEChERS adopted the combination of 4 g MgSO₄ + 1 g NaCl. Magnesium sulfate will release a lot of heat when dissolved in water, which will accelerate the dissolution of all substance and then lead to a stronger matrix effect (which was also why AOAC 2007.01 and CEN15662 QuEChERS were excluded in this work). The comparison experiment proceeded by adding 4 g NaCl in the extraction procedure. Gravimetric analysis and temperature monitoring were conducted for the two kinds of salt composition. The average amounts of five replicates were evaluated for each salt composition (Table 2). The average weight of 5 mL co-extracts in the combination of 4 g MgSO₄ + 1 g NaCl and 4 g NaCl was about 0.13103 g and 0.10930 g, respectively. In addition, the thermometer showed that the highest value in the extraction process can rise from room temperature to 40.5 °C using the combination of 4 g MgSO₄ + 1 g NaCl. However, the temperature was almost unchanged when used 4 g NaCl. MgSO₄ was exothermic when dissolved in water whereas the NaCl was not; a relatively high dose of MgSO₄ may have not only caused the degradation of some pesticides but also promoted the dissolution of other substances and exacerbated the matrix effect, so the weight of the co-extracts was heavier with the salt combination of 4 g MgSO₄ + 1 g NaCl. It goes without saying that single NaCl was better for sample extraction.

Table 2. Weight of 5 mL co-extracts in the two salts’ composition.

| No.    | 4 g NaCl Co-Extracts (g) | 4 g MgSO₄ + 1 g NaCl Co-Extracts (g) |
|--------|--------------------------|-------------------------------------|
| replicate 1 | 0.10805                  | 0.12837                              |
| replicate 2 | 0.10925                  | 0.13428                              |
| replicate 3 | 0.11082                  | 0.13125                              |
| replicate 4 | 0.10892                  | 0.13172                              |
| replicate 5 | 0.10977                  | 0.12953                              |
| average   | 0.10930                  | 0.13103                              |
3.2.3. Pretreatment Effects of Different Combinations of Adsorbents

The original unbuffered QuEChERS method involved extraction with acetonitrile and purification with a certain quantity of adsorbents, including PSA and/or C18 and/or GCB. Acetonitrile turned out to be an optimal solvent in analyzing pesticide residues with relatively fewer total extracts [31]. For the sample purification procedure, PSA forms hydrogen bonds through amine groups and polar matrix components, which is mainly in favor of removing organic acids, polar pigments, fatty acids, and sugars in the sample; [32] MgSO₄ is mainly used to absorb water and ensure the adsorption capacity of PSA. GCB has a strong adsorption capacity and can effectively remove chlorophyll in tea [33]. However, in recent years, the MWCNTs have been proven to perform better when combined with PSA or some other materials in QuEChERS. The GCB was replaced by MWCNTs in the purification procedure in some research [18]. C18 was not adopted in the purification procedure, because EMR-Lipid was used in the extraction procedure to remove the fat. Based on this situation, three combinations of adsorbents were investigated for the purification procedure: MgSO₄ + PSA, MgSO₄ + PSA + GCB, MgSO₄ + PSA + MWCNTs. In Figure 1, it can be visually observed that the combination of MgSO₄ + PSA + MWCNTs in the extraction procedure provided preferable clean-up performance. Besides, the recoveries also suggested that the combination of MgSO₄ + PSA + MWCNTs was better: at the spike level of 0.1 mg/kg, 162 of 186 (87.10%) pesticides were in the range of 70–120% while the GCB combination gave the result that 158 of 186 (84.94%) pesticides were in the range of 70–120% (Table S2). Although both GCB and MWCNTs had the characteristics of adsorbing planar structure pesticides, such as quinoxyfen, ditalimfos, and cyprodinil, MWCNTs reduced the adsorbability to a certain extent for some of the pesticides, such as aclonifen and boscalid, according to our results. When GCB was used, the recovery of some pesticides was lower, compared with the same dose of MWCNTs. The reason may be that the multi-ring planar structure of GCB has a certain adsorption effect on planar structure pesticides, leading to a low recovery rate of planar structure pesticides, while the hollow structure of MWCNTs has less adsorption effect on these pesticides [34]. Therefore, the combination of MgSO₄ + PSA + MWCNTs was selected as the absorbent in this experiment.

3.2.4. The Addition of Toluene

Even though MWCNTs are an efficient sorbent in removing complex matrices and provided good clean-up performance, there still remains the stubborn problem that MWCNTs may absorb certain pesticides with a planar structure and reduce their recovery. For further improving the recovery of these target pesticides that possessed planar structure, toluene was added after the upper extractant was transferred to the tube for purification. The benzene ring from toluene may compete with MWCNTs and reduce the tendency of pesticides to be absorbed by MWCNTs [17]. In this way, the recovery showed breakthrough improvement: 184 of 186 pesticides were in the range of 70–120%, which was a proportion of 98.92%. The exceptions were phosfolan and quinoxyfen. These two pesticides not only have a planar structure but also have weak solubility in water, especially phosfolan, so their recovery rates were 59.0% and 65.4%, as shown in Table 3.
| No. | Pesticides               | R²      | Spiked 0.02 mg/kg |          | Spiked 0.05 mg/kg |          | Spiked 0.1 mg/kg |          | LODs mg/kg | LOQs mg/kg |
|-----|-------------------------|---------|------------------|----------|------------------|----------|------------------|----------|------------|------------|
| 1   | dichlorvos              | 0.9985  | 81.9             | 6.1      | 88.7             | 5.2      | 106.3            | 4.2      | 0.01       | 0.02       |
| 2   | dichlorobenzonitrile    | 0.9901  | 64.8             | 11.6     | 78.6             | 3        | 94               | 5.7      | 0.01       | 0.02       |
| 3   | biphenyl                | 0.9906  | 100.3            | 21.5     | 87               | 5        | 89.3             | 3.5      | 0.005      | 0.01       |
| 4   | etridiazole             | 0.9973  | 118.7            | 3.3      | 87.6             | 1.8      | 101.2            | 7.2      | 0.005      | 0.01       |
| 5   | propan ocarb            | 0.9965  | 56.2             | 5.2      | 68.8             | 8.4      | 73.6             | 8.4      | 0.02       | 0.05       |
| 6   | isocrocarb              | 0.9976  | 85               | 6.4      | 71.8             | 9.4      | 96               | 6.7      | 0.005      | 0.01       |
| 7   | tecnazene               | 0.9942  | 61.9             | 6.4      | 64.9             | 11       | 104.9            | 11.3     | 0.01       | 0.02       |
| 8   | diphenylamine           | 0.9962  | 103.8            | 15.5     | 95.6             | 10.5     | 103.5            | 5.9      | 0.005      | 0.01       |
| 9   | ethoprophos             | 0.9981  | 97.8             | 12.6     | 98.7             | 1.8      | 101.2            | 7.2      | 0.005      | 0.01       |
| 10  | propoxur                | 0.9965  | 56.2             | 5.2      | 68.8             | 8.4      | 73.6             | 8.4      | 0.02       | 0.05       |
| 11  | isoprocarb              | 0.9976  | 85               | 6.4      | 71.8             | 9.4      | 96               | 6.7      | 0.005      | 0.01       |
| 12  | tecnazene               | 0.9942  | 61.9             | 6.4      | 64.9             | 11       | 104.9            | 11.3     | 0.01       | 0.02       |
| 13  | diphenylamine           | 0.9962  | 103.8            | 15.5     | 95.6             | 10.5     | 103.5            | 5.9      | 0.005      | 0.01       |
| 14  | ethoprophos             | 0.9981  | 97.8             | 12.6     | 98.7             | 1.8      | 101.2            | 7.2      | 0.005      | 0.01       |
| 15  | propoxur                | 0.9965  | 56.2             | 5.2      | 68.8             | 8.4      | 73.6             | 8.4      | 0.02       | 0.05       |
| 16  | isoprocarb              | 0.9976  | 85               | 6.4      | 71.8             | 9.4      | 96               | 6.7      | 0.005      | 0.01       |
| 17  | tecnazene               | 0.9942  | 61.9             | 6.4      | 64.9             | 11       | 104.9            | 11.3     | 0.01       | 0.02       |
| 18  | diphenylamine           | 0.9962  | 103.8            | 15.5     | 95.6             | 10.5     | 103.5            | 5.9      | 0.005      | 0.01       |
| 19  | ethoprophos             | 0.9981  | 97.8             | 12.6     | 98.7             | 1.8      | 101.2            | 7.2      | 0.005      | 0.01       |
| 20  | propoxur                | 0.9965  | 56.2             | 5.2      | 68.8             | 8.4      | 73.6             | 8.4      | 0.02       | 0.05       |
| 21  | isoprocarb              | 0.9976  | 85               | 6.4      | 71.8             | 9.4      | 96               | 6.7      | 0.005      | 0.01       |
| 22  | tecnazene               | 0.9942  | 61.9             | 6.4      | 64.9             | 11       | 104.9            | 11.3     | 0.01       | 0.02       |
| 23  | diphenylamine           | 0.9962  | 103.8            | 15.5     | 95.6             | 10.5     | 103.5            | 5.9      | 0.005      | 0.01       |
Table 3. Cont.

| No. | Pesticides            | R$^2$ | Spiked 0.02 mg/kg | Spiked 0.05 mg/kg | Spiked 0.1 mg/kg | LODs mg/kg | LOQs mg/kg |
|-----|-----------------------|-------|-------------------|-------------------|-----------------|------------|------------|
|     |                       |       | Recovery (%) | RSD | Recovery (%) | RSD | Recovery (%) | RSD |         |            |            |
| 55  | terbutryn             | 0.9975| 79.4           | 6   | 82.4          | 4.2 | 79.9         | 4.2 | 0.005    | 0.01      |
| 56  | fenithion             | 0.9959| 91.1           | 6.4  | 99.6          | 0.1 | 108.5        | 5.8  | 0.005    | 0.01      |
| 57  | ethofumesate          | 0.9962| 95.5           | 6.5  | 100.5         | 4.3 | 107.4        | 3.6  | 0.005    | 0.01      |
| 58  | bromacil              | 0.9989| 77             | 6.2  | 73.6          | 10.7 | 88.6         | 4.6  | 0.005    | 0.01      |
| 59  | phorate sulfoxide     | 0.9964| 78             | 7    | 93.3          | 4.9 | 117          | 5.6  | 0.01     | 0.02      |
| 60  | malathion             | 0.9969| 88.7           | 5.9  | 95.3          | 4.2 | 111.5        | 2    | 0.005    | 0.01      |
| 61  | dipropetryn           | 0.9921| 82.5           | 6    | 85.9          | 1.3 | 87.9         | 2.4  | 0.005    | 0.01      |
| 62  | metolachlor           | 0.9962| 76.9           | 9.2  | 73.5          | 6   | 93.3         | 1.4  | 0.005    | 0.01      |
| 63  | phorate sulfone       | 0.9971| 50             | 9    | 69.9          | 10.3| 95.3         | 4.2  | 0.01     | 0.02      |
| 64  | chlorpyrifos          | 0.9971| 86.9           | 3.5  | 90.6          | 3.4 | 94.2         | 3.7  | 0.005    | 0.01      |
| 65  | thiobencarb           | 0.9971| 70.7           | 5.7  | 69.9          | 10.3| 95.3         | 4.2  | 0.01     | 0.02      |
| 66  | parathion             | 0.9971| 86.9           | 6.6  | 76.8          | 4.9 | 91.3         | 2.9  | 0.005    | 0.01      |
| 67  | isofenphos oxon       | 0.9963| 59.5           | 6.2  | 67.4          | 2   | 75.4         | 2.7  | 0.02     | 0.05      |
| 68  | isofenphos methyl     | 0.9963| 84.9           | 5.7  | 88.3          | 4.3 | 97.1         | 0.7  | 0.01     | 0.02      |
| 69  | fenthion              | 0.9963| 79.2           | 9.2  | 86.2          | 4.1 | 93.2         | 2.7  | 0.005    | 0.01      |
| 70  | terbufos sulfate      | 0.9963| 59.5           | 6.2  | 67.4          | 2   | 75.4         | 2.7  | 0.02     | 0.05      |
| 71  | bromochlor            | 0.9971| 82.5           | 6    | 85.9          | 1.3 | 87.9         | 2.4  | 0.005    | 0.01      |
| 72  | isofenphos ethyl      | 0.9963| 59.5           | 6.2  | 67.4          | 2   | 75.4         | 2.7  | 0.02     | 0.05      |
| 73  | isofenphos methyl     | 0.9974| 74.7           | 5.3  | 87.6          | 2.1 | 99.9         | 0.8  | 0.005    | 0.01      |
| 74  | fenthion              | 0.9971| 84.9           | 5.7  | 88.3          | 4.3 | 97.1         | 0.7  | 0.01     | 0.02      |
| 75  | cyprodinil            | 0.9963| 79.2           | 9.2  | 86.2          | 4.1 | 93.2         | 2.7  | 0.005    | 0.01      |
| 76  | chemochlor            | 0.9963| 59.5           | 6.2  | 67.4          | 2   | 75.4         | 2.7  | 0.02     | 0.05      |
| 77  | isofenphos methyl     | 0.9974| 74.7           | 5.3  | 87.6          | 2.1 | 99.9         | 0.8  | 0.005    | 0.01      |
| 78  | fenthion              | 0.9971| 84.9           | 5.7  | 88.3          | 4.3 | 97.1         | 0.7  | 0.01     | 0.02      |
| 79  | cyprodinil            | 0.9963| 59.5           | 6.2  | 67.4          | 2   | 75.4         | 2.7  | 0.02     | 0.05      |
| 80  | terbufos sulfate      | 0.9963| 79.2           | 9.2  | 86.2          | 4.1 | 93.2         | 2.7  | 0.005    | 0.01      |
| 81  | terbufos sulfate      | 0.9971| 84.9           | 5.7  | 88.3          | 4.3 | 97.1         | 0.7  | 0.01     | 0.02      |
| 82  | terbufos sulfate      | 0.9963| 79.2           | 9.2  | 86.2          | 4.1 | 93.2         | 2.7  | 0.005    | 0.01      |
| 83  | terbufos sulfate      | 0.9971| 84.9           | 5.7  | 88.3          | 4.3 | 97.1         | 0.7  | 0.01     | 0.02      |
Table 3. Cont.

| No. | Pesticides     | $R^2$ | Spiked 0.02 mg/kg | Spiked 0.05 mg/kg | Spiked 0.1 mg/kg | LODs mg/kg | LOQs mg/kg |
|-----|----------------|-------|-------------------|-------------------|------------------|------------|------------|
|     |                |       | Recovery (%) | RSD | Recovery (%) | RSD | Recovery (%) | RSD |
| 109 | isoprothiolane | 0.9991 | 68.9 | 11.7 | 74.1 | 4.8 | 83.2 | 3 |
| 110 | profenofos     | 0.9963 | 76   | 5.3 | 83.6 | 1.6 | 95  | 2.8 |
| 111 | pp'-DDE        | 0.9921 | 68.4 | 12.7 | 72.7 | 2.6 | 83.3 | 2.1 |
| 112 | oxadiiazon     | 0.9974 | 73.9 | 7.1 | 83.6 | 5.6 | 88.8 | 4.2 |
| 113 | DEF            | 0.9952 | 75.6 | 1.3 | 85   | 6.5 | 92.2 | 3.3 |
| 114 | dieldrin       | 0.9908 | 66.9 | 3.9 | 67.5 | 7   | 72.8 | 2.7 |
| 115 | myclobutanil   | 0.9962 | 86.3 | 6   | 88.1 | 3.2 | 102.9 | 1.6 |
| 116 | op'-DDD        | 0.9989 | 69.7 | 7.3 | 78.2 | 3.9 | 90.1 | 1.3 |
| 117 | oxyfluorfen    | 0.9979 | 119.3 | 5.4 | 106.7 | 10.1 | 119.7 | 1.6 |
| 118 | bupirimate     | 0.9911 | 52.2 | 4.3 | 52.9 | 1.3 | 71.4 | 1.2 |
| 119 | kresoxim methyl| 0.9963 | 92.1 | 7.9 | 89.9 | 3.7 | 97.2 | 1.2 |
| 120 | cyfluorenmid   | 0.9921 | 82.6 | 3.8 | 83.9 | 8.4 | 92.1 | 4.6 |
| 121 | isoaxathion    | 0.9974 | 79.8 | 3.8 | 95.4 | 7.5 | 102.9 | 5.4 |
| 122 | cyproconazole 1| 0.9952 | 88.1 | 6.1 | 73.2 | 22.3 | 99.5 | 3.2 |
| 123 | fluazifop butyl| 0.9922 | 92.5 | 5.9 | 86.4 | 3.4 | 104.3 | 3.2 |
| 124 | nitrofen       | 0.9962 | 86.1 | 9.1 | 86.1 | 5.7 | 98.7 | 5.3 |
| 125 | endrin         | 0.9989 | 77.8 | 2.8 | 83.4 | 5.8 | 116.2 | 11.1 |
| 126 | chlorobenzilate| 0.9979 | 103.4 | 3.8 | 99.2 | 2.2 | 95.9 | 2.2 |
| 127 | fensulfothion  | 0.9991 | 86.1 | 2.3 | 97.3 | 5.4 | 103.3 | 5.7 |
| 128 | diniconazole   | 0.9963 | 71.2 | 2.7 | 70.5 | 1.3 | 87.8 | 2.7 |
| 129 | oxadixyl       | 0.9974 | 93   | 4.6 | 91.1 | 1.5 | 102.7 | 2.5 |
| 130 | pp'-DDD        | 0.9952 | 86.3 | 3.5 | 94.5 | 3.2 | 109.9 | 2 |
| 131 | ethion         | 0.9952 | 86.3 | 9.1 | 86.1 | 5.7 | 98.7 | 5.3 |
| 132 | op'-DDT        | 0.9998 | 73.9 | 4.2 | 77.7 | 3.1 | 90.5 | 1.5 |
| 133 | chlorothiophos | 0.9962 | 90.8 | 2.9 | 88   | 7.6 | 98  | 0.5 |
| 134 | aclonifen      | 0.9989 | 108.3 | 5.5 | 94.5 | 8.8 | 103.4 | 7.2 |
| 135 | triazophos     | 0.9979 | 122.5 | 5.5 | 101.5 | 3.5 | 108.7 | 3 |
| 136 | famphur        | 0.9991 | 68.9 | 2.5 | 74   | 3   | 78.9 | 0.8 |
| 137 | benalaxyl      | 0.9923 | 81   | 6.5 | 91.1 | 1.5 | 104.1 | 0.6 |
| 138 | carbutanil     | 0.9921 | 90.8 | 8.9 | 88.1 | 2.2 | 100.9 | 2.6 |
| 139 | triflonylsorb  | 0.9974 | 85.6 | 4.8 | 86.4 | 2.9 | 99.5 | 2.2 |
| 140 | edifenphos     | 0.9952 | 84.8 | 0.6 | 86.9 | 3.9 | 101.5 | 1.2 |
| 141 | quinoxylen     | 0.9991 | 52.1 | 13.3 | 60.5 | 3.8 | 65.1 | 3.1 |
| 142 | propiconazole  | 0.9962 | 85.5 | 4.1 | 88.2 | 10.4 | 97.9 | 7 |
| 143 | pp'-DDT        | 0.9989 | 66.7 | 5.7 | 78.5 | 0.9 | 85.2 | 1.1 |
| 144 | hexazinone     | 0.9929 | 66.7 | 5.3 | 72.1 | 2.2 | 79  | 1.1 |
| 145 | tebuconazole   | 0.9991 | 83.4 | 3.4 | 85.7 | 3.2 | 92.6 | 3.9 |
| 146 | diclofop methyl| 0.9963 | 82.1 | 3.9 | 90.3 | 5.3 | 100.1 | 0.4 |
| 147 | piperonylbutoxide| 0.9921 | 71.6 | 5.2 | 81.4 | 1 | 89.7 | 1.3 |
| 148 | epoxiconazol   | 0.9904 | 75.6 | 4.9 | 78.5 | 3.4 | 90.7 | 4.7 |
| 149 | pyridazinone   | 0.9952 | 68.8 | 1.9 | 70.9 | 5.5 | 77.1 | 1 |
| 150 | iprodione      | 0.9808 | 123  | 6.7 | 113.1 | 7.7 | 106.8 | 3.4 |
| 151 | phosmet        | 0.9962 | 69.2 | 8.4 | 68.3 | 1.8 | 76.4 | 2.9 |
| 152 | bifenthion     | 0.9902 | 63.4 | 4.1 | 77.2 | 0.4 | 87  | 1.6 |
| 153 | EPN            | 0.997 | 99.2 | 10.2 | 97.6 | 6 | 107.5 | 3.6 |
| 154 | bromopropionate| 0.9921 | 70.6 | 4.1 | 81.9 | 3.1 | 93.7 | 0.4 |
| 155 | pirimiphos     | 0.9913 | 79.7 | 1.2 | 82.8 | 2 | 93.6 | 2.1 |
| 156 | tetramethrin   | 0.9921 | 74.4 | 5.4 | 82.1 | 1.2 | 92.1 | 0.9 |
| 157 | methoxychlor   | 0.9904 | 71.7 | 5.4 | 86.3 | 4.3 | 95.5 | 1.4 |
| 158 | etoxazole      | 0.9952 | 76.7 | 8.5 | 95.4 | 10.4 | 102.6 | 1.7 |
| 159 | fenamidone     | 0.9908 | 79.5 | 5.3 | 88.4 | 2.7 | 99  | 1.6 |
| 160 | tebufenpyrad   | 0.9962 | 81.7 | 9.2 | 84   | 2.8 | 90.5 | 0.7 |
| 161 | anilofos       | 0.9989 | 80.5 | 6.5 | 93.3 | 3.4 | 102.8 | 3.7 |
3.2.5. The Exchange of Solvent

Despite the fact that the recovery of the pesticides was increased dramatically by adding toluene, it was still essential to exchange the solvent before analysis by GC-MS/MS, especially for the targets with RT less than 14 min. We found that when using the mixture of acetonitrile and toluene as the solvent directly determined by GC-MS/MS, this often caused a dilemma that was ignored in some previous work [17]. Although the accuracy was guaranteed by toluene, with high molecular polarity, tailing of peaks was more likely to occur when using acetonitrile as the solvent. In addition, due to the solvent effect caused by mixing the solvents acetonitrile and toluene, the chromatographic peaks broadened and bifurcated, retention time drifted, and double peaks happened more frequently, which would significantly influence the qualitative and quantitative results. Ethyl acetate was a splendid choice to resolve this contradictory situation, as it is less volatile than n-hexane and more environmentally friendly than toluene. The comparison of some typical pesticides verified by the two solvents is shown in Figures S1–S4. The chromatographic peaks immediately became symmetrical and smooth and better qualitative and quantitative results were obtained after exchange by ethyl acetate. For long-term monitoring, the exchange of solvent also has crucial benefits for instrument life and maintenance.

3.3. Matrix Effects Study

The QuEChERS methods are widely used in vegetables, fruit, and teas, and the matrix effect is greatly influenced by the materials applied in modification and optimization processes [35,36]. Matrix effects were assessed by comparing the slopes of six matrix-matched calibration curves to the slopes of the calibration curves in solvent. Matrix effects were calculated with Equation [37]: ME (%) = \left( \frac{\text{slope of calibration curve in matrix}}{\text{slope of calibration curve in solvent}} - 1 \right) * 100. Calibration curves (6 points from 0.01 to 0.4 mg/L) were plotted by solvent (ethyl
acetate) and matrix (blank hawk tea solutions obtained from the preparation procedure by modified QuEChERS). When the ME% is within $-20$ and +20 it is considered a low matrix effect and if ME% is within $-50$ to $-20$ and +20 to +50 it is considered a medium matrix effect. If more than $-50$ or +50, the matrix effect was evaluated as a strong matrix effect. The MEs (%) for the modified QuEChERS method are depicted in Figure 2. It was obvious that there existed enhanced matrix effects by GC-MS/MS overall in our study. However, compared to standard solution peaks, matrix effects also possess the merits of improving peak shapes with less tailing, more symmetry, and higher intensity [29]. Even though the matrix effect will always exist when applying GC-MS/MS, the modified QuEChERS with the combination of MgSO$_4$ + PSA + MWCNTs plus EMR-Lipid succeeded in minimizing the matrix effect to the weakest level compared with other work [38]: 117 of 186 pesticides (62.9%) had weak matrix effects, 45 pesticides (24.2%) had moderate matrix effects, and 24 pesticides (12.9%) had strong matrix effects. In contrast, the matrix effect of the QuEChERS without EMR-lipid and MWCNTs was the stronger: 62 pesticides (33.3%) showed weak matrix effects, 69 pesticides (37.1%) had moderate matrix effects, and 55 pesticides (29.6%) had strong matrix effects. In order to visually observe which modified QuEChERS method provided better cleaning of the extracts, gas chromatography tandem mass spectrometry (GC-MS/MS) analysis of the extracts in full scan mode was carried out as a complementary evaluation (Figure S5). The chromatogram verified the above matrix effect calculation results.

![Figure 2](image-url)

**Figure 2.** The comparison of matrix effect by modified QuEChERS and unmodified QuEChERS.

### 3.4. Recoveries and RSDs

The 186 pesticides of mixed standard solution were added to pesticide-free hawk tea powders, and the recovery rates and variabilities of the modified QuEChERS were evaluated at concentrations of 0.02 mg/kg, 0.05 mg/kg, and 0.1 mg/kg with three replicates. The results are presented in Table 3 and Table S2. By comparing reproducibility and recovery rates, it was found that the QuEChERS modified by the MWCNTs and EMR-Lipid improved the recovery of some of the pesticides. Moreover, it was apparent that the addition of toluene distinctively raised the recoveries of planar structure pesticides, keeping the recoveries at an ideal range of 70–120% for 184 pesticides at the concentration of 0.1 mg/kg. Relative standard deviations (RSDs, %) were less than 14.4%. Comparing these results with the published SPE method, the modified QuEChERS combined with GC-MS/MS performed much better in efficiency, recovery, and repeatability [39] in comparison with some other modified extraction methods: the extraction efficiency and general suitability all improved, meanwhile the matrix effect was lower [40,41]. These excellent results
showed that the QuEChERS has irreplaceable superiority, with wide applicability, stability, accessibility, and simplicity. Even dicofol, which was said to perform better in QuEChERS acetate, showed a decent recovery at the concentration of 0.1 mg/kg by this method [42,43], which indicated that the QuEChERS method had preeminent accuracy for quantification of multi-pesticide residues in hawk tea. At the concentration of 0.02 mg/kg, the recoveries of 93.01% pesticides were in the range of 60–130% and the RSDs of 180 pesticides were less than 15. At the concentration of 0.05 mg/kg for the modified QuEChERS, the recoveries of 86.02% pesticides were in the range of 70–120% and the RSDs of 182 pesticides were below 15.

3.5. Linearity

Working standard solutions of 0.01, 0.025, 0.05, 0.1, 0.2, and 0.4 mg/L were prepared by the modified QuEChERS method to obtain the matrix-matched linearity. Linear ranges and correlation coefficients are summarized in Table 3. It is conspicuous that the correlation coefficients for the tested 182 pesticide residues were all higher than 0.99, and those of propazine, desmetryn, iprodione, and difenoconazole were more than 0.98. The calibration curves were linear within the range.

3.6. Limits of Detection and Limits of Quantitation

Limits of detections (LODs) and limits of quantifications (LOQs) were determined by adding different concentrations of pesticide standards to the hawk tea blank samples. When the signal-to-noise ratio reached three for each pesticide, the corresponding concentration was regarded as the LOD of the method. Meanwhile, when the signal-to-noise ratio reached 10 for each pesticide, the corresponding concentration was fixed as the limit of quantification (LOQ) of the method [44]. The LODs and LOQs of the 186 pesticides are listed in Table 3. For the 186 pesticides, the LODs and LOQs ranged from 0.001 to 0.02 mg/kg and 0.005 to 0.05 mg/kg, respectively. The results indicated that analyzing the pesticide residues by GC/MS/MS in hawk tea produced good quantitative detection limit findings. In addition, the LOQs for the analysis compounds were lower than the maximum residue limits (MRLs) specified by China and the Codex Alimentarius Commission (CAC). Therefore, the established GC/MS/MS analysis method is worth using for routine analysis of pesticide residues in hawk tea or other kinds of herbal tea.

3.7. Real Samples

Twenty-six samples of eagle tea were purchased from the major hawk tea producing areas in Wulong and Wushan District, Chongqing, China to verify the method. Among all the tested analytes, chlorpyrifos and bifenthrin were detected with a concentration of 0.0054 mg/kg and 0.0106 mg/kg in two samples from Wulong District, which meant eagle tea in this area has a potential risk of pesticide contamination. The international Codex Alimentarius Commission (CAC) standards and China national standards GB2763-2021 provided that the MRLs of chlorpyrifos poisoning in tea were 0.1 mg/kg and 2 mg/kg, and the MRLs of bifenthrin were 5 mg/kg and 30 mg/kg, respectively. The obtained results indicated that the abuse of some pesticides is unavoidable, although the residue levels of pesticides were lower than MRLs established by different countries and organizations. Regular monitoring of hawk tea samples for multi-residue pesticides is still necessary and important, and a tighter management and regulation of pesticides needs to be implemented in hawk tea production and marketing to guarantee the safety of the tea drinking public.

4. Conclusions

In this paper, the QuEChERS method was modified using EMR-Lipid and MWCNTs to lower the matrix effect and improve recovery, and then applied in the determination of 186 pesticides in hawk tea combined with GC–MS/MS for the first time. The addition of toluene was the crucial part for improving the recovery of planar structure pesticides. Moreover, the exchange of solvent also played an important role in wiping out the solvent
effect and improved the chromatographic peak for better qualitative and quantitative analysis purposes. The recoveries for all pesticides were excellent; even dicofol recovery worked well with the modified QuEChERS although the literature has reported that acetate-buffered QuEChERS is more fit for these kinds of pesticides. The calibration parameters for the modified QuEChERS method including recovery, precision, linear range, LOD, and LOQ were examined, which indicated that modified QuEChERS coupled with GC-MS/MS was suitable for rapid multi-pesticides analysis in hawk tea. Analysis of real samples revealed that the abuse of pesticides still exists. Therefore, regular and long-term monitoring of pesticide residues in hawk tea and herbal tea is of great significance.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ijerph191912639/s1, Figure S1: Chromatogram of etrimfos in the mixed solvent of acetonitrile and toluene; Figure S2: Chromatogram of etrimfos in ethyl acetate; Figure S3: Chromatogram of chlorpyrifos in the mixed solvent of acetonitrile and toluene; Figure S4: Chromatogram of chlorpyrifos in ethyl acetate; Figure S5: The hawk tea blank sample under the Q3scan mode after purification by different materials; Table S1: The major constituents of hawk tea processed by different methods; Table S2: The comparison of different adsorbent combination on recoveries and RSDs for 186 pesticides.

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