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Research Article

Microwave-Assisted "One-Pot" Acidolysis and Extraction for the Rapid Determination of Mancozeb in Fruit and Vegetable Samples

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Mancozeb is an extensively consumed fungicide, which often leaves high residue levels on agricultural products. The conventional method for detecting mancozeb involves a time-consuming process using gas chromatography (GC) after a 2-hour water-bath acidolysis, resulting in low efficiency and recovery rates. This study developed a rapid method for detecting mancozeb in fruits and vegetables using microwave-assisted acidolysis and extraction coupled with GC analysis. Mancozeb underwent "one-pot" acidolysis to generate CS_2 gas and was subsequently extracted from samples using microwave treatment, requiring only 50 seconds of pretreatment time. The average recoveries of mancozeb ranged from 81% to 112%. The limit of detection and limit of quantification were 0.003 and 0.01 mg kg^{-1}, respectively. The scanning electron microscope imaging showed that strong cell crumpling after microwave treatment improved the acidolysis rate significantly, where the acidolysis rate was 91.8% for mancozeb. In addition, this method is rapid, simple, and precise for detecting residues of mancozeb and other dithiocarbamate fungicides.

1. Introduction

Mancozeb is a dithiocarbamate (DTC) fungicide that is extensively consumed in agriculture, with a proportion of more than 20% and an annual consumption of approximately 30,000 tons and 1 billion dollars [1]. Mancozeb is widely used because it has a good effect in preventing fungal diseases of many crops [2, 3] and other aspects [4]. However, mancozeb exposure inhibits mitochondrial complexes in HT-29 cells [5], cardiotoxic effects in zebrafish [6], and neurodegenerative conditions such as Parkinson's disease [7]. Even though mancozeb is presently banned in the EU, both the EU and USA have established maximum residue limits (MRLs) for it. This is because there's a concern that it could still be used illegally within the EU or legally in other countries whose products may be imported. The current MRLs for mancozeb in the EU and USA are based on the content of dithiocarbamates, which include mancozeb, maneb, metiram, propineb, thiram, and ziram. These MRLs are expressed as CS_2 equivalents. The lowest MRLs for mancozeb in the EU and USA are 0.05 and 0.06 mg kg^{-1}, respectively, which are equivalent to 0.089 and 0.11 mg kg^{-1} of mancozeb. Therefore, a reliable and sensitive determination method for mancozeb and other DTCs is of great practical importance for safeguarding human health, protecting the environment, and strengthening pesticide residue monitoring.

Rapidly and accurately determining mancozeb and other DTCs residue in food samples has always been a big challenge. Various classical methods have been established for determining pesticide residues, such as methylated derivatization high-performance liquid chromatography-mass spectrometry (HPLC-MS) [8, 9], gas chromatography (GC) coupled with a flame photometric detector (FPD) with

a sulfur filter [10, 11], a surface-enhanced Raman scattering (SERS) [12, 13], atomic emission spectrometry [14], atomic absorption spectrometry [15], and electron capture detector (ECD) [16]. However, the determination of mancozeb using the HPLC-MS method requires a complicated methylation derivatization step [17, 18]. Furthermore, HPLC-MS is expensive to be accepted in all laboratories [19]. GC is another standard method for determining mancozeb, which is a more convenient and feasible instrument in the laboratory, with high sensitivity and good selectivity. Generally, before the determination of mancozeb by GC, classical water bath heating acidolysis is required to generate CS_2 gas for a long time (90–120 min) under 90°C. Subsequently, the generated CS_2 gas was absorbed by the hexane solvent, and the solvent was injected into the GC for CS_2 determination [20]. Considering the molecular weights of mancozeb and CS_2, one mole of mancozeb will generate two moles CS_2. The conversion factor μg of mancozeb × 0.564 equaled μg of CS_2 was established. The entire process usually requires at least 2 h with a traditional water-bath heater and sometimes even longer. Moreover, the acidolysis efficiency of this water-bath heater method is usually limited to 50–60% for mancozeb. The determination of mancozeb required additional correction according to the acidolysis efficiency, which reduced the accuracy and efficiency of the method [21].

Microwaves have high energy to heat solvents in contact with a sample to improve the efficiency of the chemical reaction or extraction of analytes from the sample matrix into the solvent [22]. As an alternative to conventional heating [23], microwave-assisted detection has been applied in various analyses [24]. Paiga et al. [25] developed a method for determining carbamate and urea pesticide residues in fresh vegetables using microwave-assisted extraction–liquid chromatography. Wu et al. [26] also determined organophosphorus pesticides in fruits by gas chromatography–mass spectrometry (GC–MS) with the aid of microwave-assisted extraction. Recently, microwave-assisted extraction also applied for simultaneous determination of mycotoxins and pesticide residues in soil and other samples [27, 28]. This indicates that the use of microwave-assisted sample pretreatment for the determination of pesticide residues has great application prospects [29–31]. In our previous study, we used the microwave-assisted hydrolysis reactor coupled molecular emission spectrometer (MES) to determination the mancozeb and other DTCs fungicide successfully [14]. However, the MES detector has poor sensitivity for the mancozeb at 0.5 mg kg^{-1} only, and the mechanism and influence of the microwave acidolysis were also not investigated.

Therefore, in this study, a "one-pot" acidolysis and extraction method with microwave was established for the conversion of mancozeb to CS_2 gas in fruit and vegetable samples, and the classical GC-ECD method was used for further analysis to ensure the high sensitivity. The acidolysis time of the traditional water-bath heater will shorten significantly from 2 h to 50 s. The change in the microstructural morphology of the sample was also observed using a scanning electron microscope (SEM) to prove the efficiency of the microwave. The microwave-assisted acidolysis method is high efficiency, short time consumption, and low cost for the rapid determination of DTCs residues in fruits and vegetables.

2. Materials and Methods

2.1. Instrumentations and Equipment. A gas chromatograph (Agilent Technologies, USA) consisting of a 7890B GC system coupled with an ECD detector was used for the extracted pesticides, standard samples, and test samples in this study. A MARS microwave accelerated solvent extraction (CEM Corporation, USA) was used for the microwave-assisted acidolysis of DTCs to improve the CS_2 conversion efficiency. A high-speed refrigerated centrifuge (CR22N/21N, Hitachi Koki Co., Ltd., Tokyo, Japan) was used to rapidly separate the supernatant and the hypolimnion. A thermostatic water-bath (B-260, Shanghai Yarong Biochemical Instrument Factory, Shanghai, China) was used for traditional sample pretreatment water-bath heating.

A field-emission scanning electron microscope (ZEISS ∑IGMA, Germany) was used to observe the microstructure of the fruit and vegetable samples before and after microwave treatment. A vacuum freeze dryer LGJ-10D (Beijing Sihuanqihang Technology Co. Ltd., China) was used to dry the samples for SEM observation.

2.2. Reagents and Sample. All reagents used in this experiment were of analytical grade. Deionized water (DIW, 18.2 MΩ cm), prepared using a Milli-Q water purification system (Millipore, USA), was used in all trials. The main reagents, $SnCl_2$ and HCl, used in this study were procured from the Shanghai Sui-Test Company (Shanghai, China). Ascorbic acid was purchased from Shandong West Asia Chemical Engineering Co., Ltd. (Shandong, China), and hexane was purchased from Huate Gas Co., Ltd. (Guangzhou, China). Mancozeb, metiram, thiram, and propineb standards were purchased from Sichuan Lier Crop Science Co. Ltd. (Sichuan, China). High-purity chemicals ethylenediaminetetraacetic acid (EDTA) and NaOH were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). L-cysteine (L-cys) and CS_2 gas were purchased from Aladdin Shanghai Biochemical Technology Co., Ltd. (Shanghai, China).

Fruit and vegetable samples, including banana, mango, pineapple, cowpea, dragon fruit, lychee, apple, eggplant, and peanuts, were collected from the experimental base of the Analysis and Test Center of the Chinese Academy of Agricultural Sciences in Hainan Province, China. The required samples were broken up using a wall-breaker and stored at −20°C for further analysis.

2.3. Analysis Procedure. The mancozeb was dissolved with a mixed solution prepared using 12.5 g EDTA and 12.5 g L-cysteine (L-cys) in 800 mL of ultrapure water, where the pH value was adjusted to 9.0–10.0 with a NaOH solution. Standard stock solutions of 50 μg mL^{-1} mancozeb were prepared by weighing and dissolving 0.0025 g mancozeb standard in 50 mL mixed solution and then diluting the

stock solution to prepare standard working solutions with different concentrations. The solution was prepared on the day of the experiment and was stored in a refrigerator at 4°C. 0.100 g CS_2 was dissolved in hexane (100 mL) to obtain a mother solution with a mass concentration of 1000 μg mL^{-1}. The standard solution was gradually diluted with hexane to 0.2 μg mL^{-1}, which was used for the assessment of converted efficiency of mancozeb and other DTCs.

10 g of $SnCl_2$ was dissolved in 250 mL (5 mol L^{-1}) hydrochloric acid (HCl) solution and a 40 mg L^{-1} $SnCl_2$–HCl solution was obtained when $SnCl_2$ was completely dissolved into a colorless transparent liquid.

2.4. Chromatographic Conditions. A GC chromatographic column (GS-Gas Pro, 30 m × 0.32 mm) with nitrogen gas (>99.999%) at a flow rate of 2.0 mL min^{-1} was used as the carrier gas for the separation of pesticides. The inlet temperature was set to 130°C, and the detector temperature was set to 240°C. The injection volume was 2 μL with split mode and a split ratio of 2 : 1. The oven temperature was programmed as follows: the initial column temperature was 40°C, held for 4 min, increased at 25°C min^{-1} to 90°C, fixed for 4 min, then at 30°C min^{-1} to 240°C, and held for 3 min.

2.5. Sample Pretreatment. This procedure is schematically shown in Figure 1. Briefly, 2 g of each fruit and vegetable samples were accurately weighed and added into PTFE (polytetrafluoroethylene) the microwave digestion tubes. The mancozeb standard solution was added to the samples for further study. Also, 0.2 g of ascorbic acid was added separately. Then, 20 mL of the $SnCl_2$–HCl solution and 4 mL of hexane were added to the tubes separately. The mouths of the PTFE tubes were sealed with PFA (perfluoroalkoxy) cover seal to ensure no air leakage, followed by heating in a microwave oven at 720 W for 50 s. Subsequently, the reacted solution was cooled to room temperature and transferred to a plastic centrifugal tube, and the mixture was centrifuged for 5 min at 4000 r min^{-1}. The solution was stratified, and the upper hexane layer supernatant was aspirated into the injection vial for further analysis.

2.6. Microstructure Observation with SEM. To verify the reason for the high efficiency of microwave-assisted acidolysis, banana and mango samples were selected as typical samples through the SEM images for the investigation. Three kinds of samples, untreated, treated with bath, and treated with microwave, were prepared for the observation of microstructural morphology using SEM. To enhance the clarity of the SEM images, the samples were dried in a frozen vacuum and coated with gold before observation.

3. Results and Discussion

3.1. Feasibility of the Efficiency Using Microwave-Assisted Acidolysis. The traditional acidolysis from mancozeb to CS_2 used the water-bath heating method. Ultrasound and microwaves have been reported to enhance the efficiency of some chemical reactions such as the extraction of active compounds [21, 32]. Therefore, the initial experiment investigated the feasibility of microwave-assisted acidolysis. The water-bath acidolysis and ultrasound-assisted acidolysis methods were selected to compare the acidolysis efficiency with that of the microwave method, and the results are summarized in Figure 2. The samples were treated using water-bath heating at 60°C for 60, 120, and 180 min. The ultrasound method was used to assist the acidolysis method at 10, 30, and 60 min, and the microwave method was used to assist the acidolysis method at 10, 30, and 50 s. Surprisingly, the 50 s microwave treatment at 720 W of microwave power could completely convert mancozeb to CS_2, while the acidolysis efficiencies after 180 min of water-bath heating at 60°C and 60 min of ultrasonic-assisted water-bath heating at 60°C were only 50% and 61%, respectively, which is similar to the earlier report [33]. Hence, the microwave method is considered a high-efficiency method to improve the acidolysis efficiency of mancozeb, and the processing time is only 50 s.

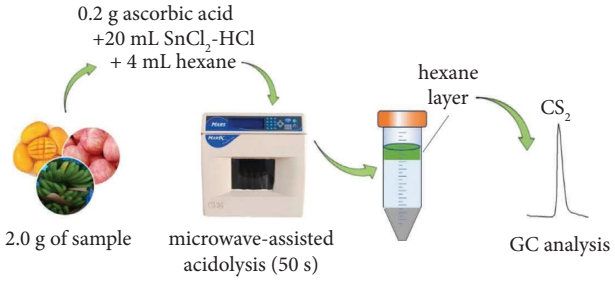

Figure 1: Schematic of microwave-assisted acidolysis for the rapid determination of mancozeb.

3.2. Microstructure of the Sample Treated with Microwave. To explore the reason for the improvement in acidolysis efficiency, the microstructures of the banana and mango samples were observed using SEM before and after water-bath heating and microwave treatment, and the results are presented in Figure 3. As shown in Figures 3(a) and 3(d), untreated mango and banana cell granules were closely arranged and the cell structure was well preserved. Figures 3(b) and 3(e) show that after 2 h of water-bath heating, mango and banana granule cells were loosely arranged, and the cell structure was slightly damaged. Compared with the untreated sample, there were no significant changes after treatment with water-bath heating.

The microwave system has a strong radiation ability, which can cause rapid internal warming or destruction of the sample tissue (cell) structure, increasing the solubility of the target compounds in the sample in the extraction solvent [34]. Moreover, the rapid warming ability of the electromagnetic field generated by microwaves increases the diffusion rate of the target compounds, and high-frequency electromagnetic waves penetrate the solvent to reach the vascular bundle and glandular cell system in the fruit and vegetable tissue. Figures 3(c) and 3(f) depict that after 50 s of microwave treatment, mango and banana cell walls were

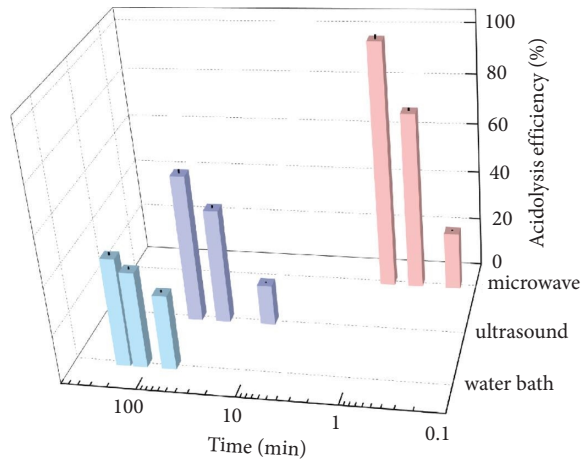

Figure 2: Effects of different acidolysis methods for the analytical results.

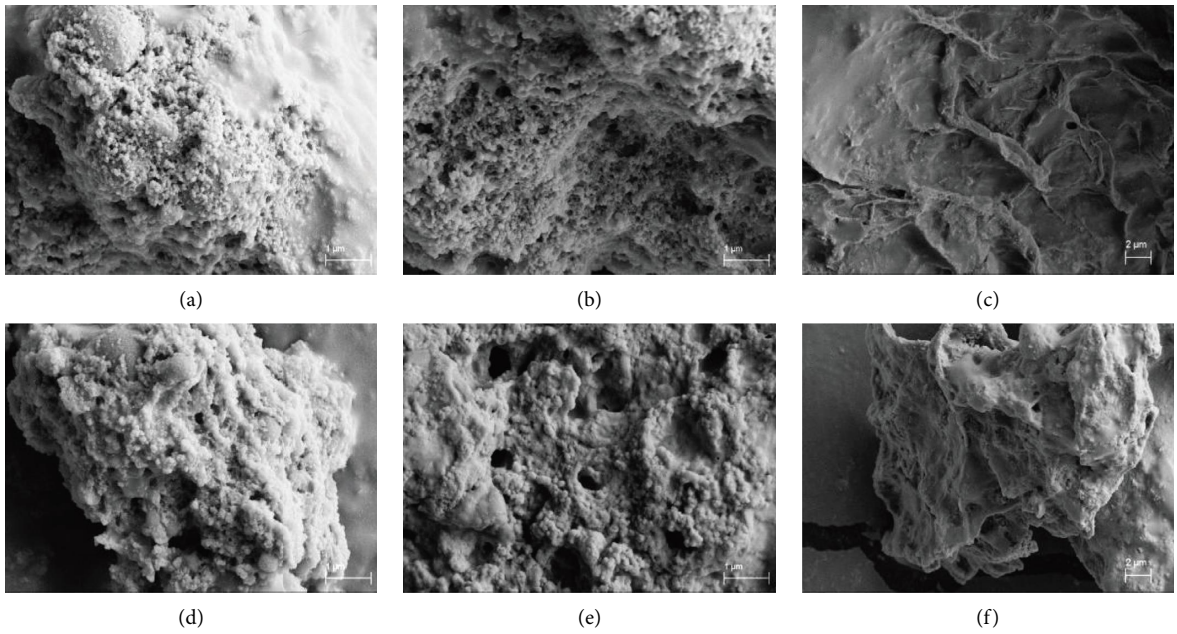

Figure 3: Microstructure of banana and mango after different treatment. (a) Mango untreated; (b) mango water bath for 2 h; (c) mango microwave heating for 50 s; (d) banana untreated; (e) banana water bath for 2 h; (f) banana microwave heating for 50 s.

strongly ruptured, and cell crumpling was evident. Although both Figures 3(c) and 3(f), were microwave treated, mango cell rupture in Figure 3(c) is more evident, and wrinkling is also more obvious owing to the high-water content in mango. Because water-containing materials have deep transient heating characteristics to microwaves, mango is more likely to have cell rupture during this process, whereas the starch content in a banana is high and the starch structure is less affected by the microwaves [35], resulting in a weaker degree of banana cell rupture.

3.3. Optimization of Operating Parameters. Microwave power is an important factor in the acidolysis of mancozeb into CS_2. The microwave power in the range of 80 to 800 W was then tested for the best converted efficiency, and the results are presented in Figure 4(a). A mancozeb concentration of 10 μg mL^{-1} was used to test the acidolysis efficiency. When the concentration of the $SnCl_2$–HCl solution was set at 40 mg L^{-1} and the microwave time was adjusted to 50 s, the response of the mancozeb standard increased with the microwave power and reached a plateau at 720 W. This may be because, with the increase in microwave heating power, mancozeb and $SnCl_2$–HCl solution undergo cohesive acidolysis to completely generate CS_2 gas. Therefore, 720 W microwave power was selected for further study.

The effect of microwave time on the acidolysis efficiency was investigated between 10 and 70 s. As shown in Figure 4(b), the response of the mancozeb standard solution significantly increases with the increasing microwave heating time until 50 s and reached a plateau. Which indicated microwave heating time affects the CS_2 generation,

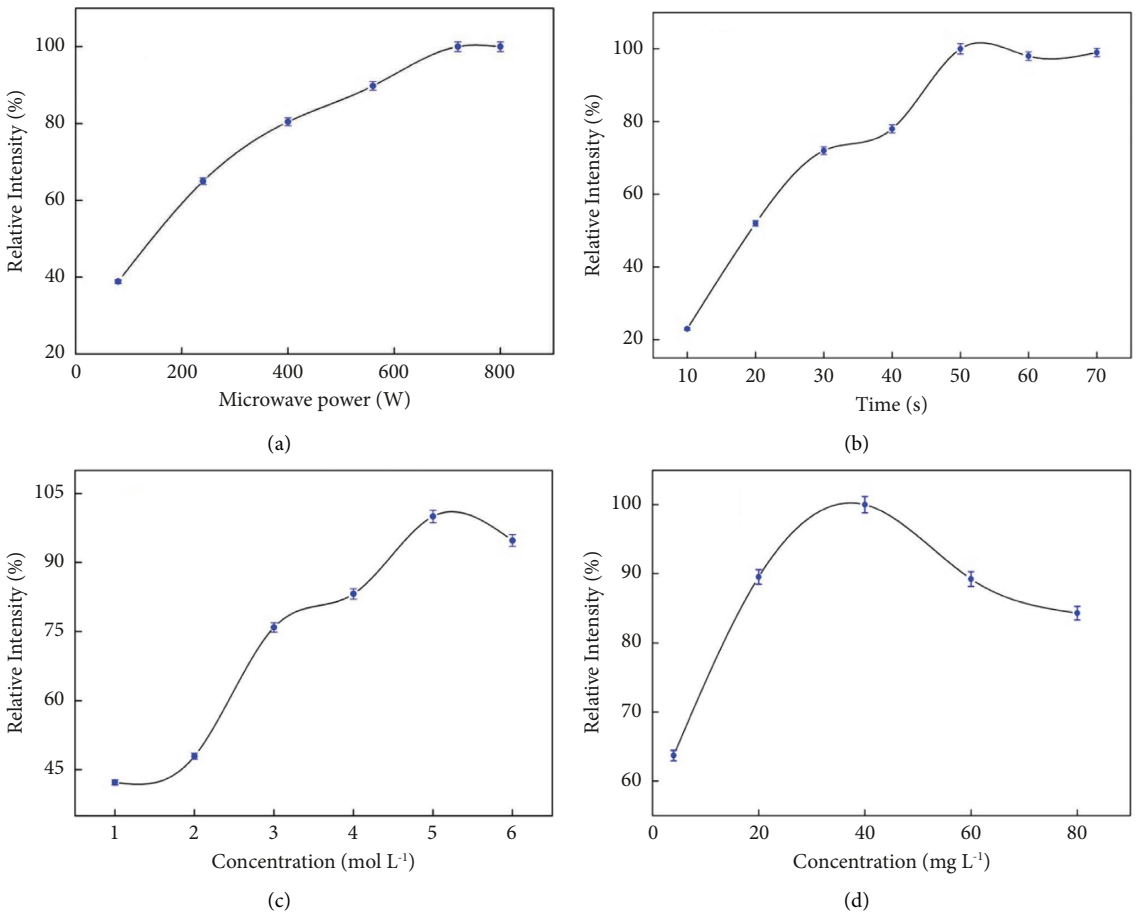

Figure 4: Optimization of influencing factors with an online microwave-assisted acidolysis. (a) Microwave power. (b) Microwave time. (c) Hydrochloric acid concentration. (d) Stannous chloride concentration.

and it is completely converted to CS_2 at 50 s. Therefore, optimum microwave time was set as 50 s for this study.

Further experiments were performed to determine the effects of HCl concentration on acidolysis by ranging it from 1 mol L^{-1} to 6 mol L^{-1} and constant amount of $SnCl_2$ (0.8 g) was then added. As summarized in Figure 4(c), the response increased with the increase in HCl concentration and reached a plateau after 5 mol L^{-1}. Hence, the concentration of HCl affects the dissolution of $SnCl_2$ crystals, which in return affects the acidolysis of mancozeb in the $SnCl_2$–HCl solution. When the concentration of HCl reached 5 mol L^{-1}, $SnCl_2$ was entirely dissolved and mancozeb acidolysis completely generated CS_2 gas. Therefore, the concentration of 5 mol L^{-1} was selected for further experiments.

The effects of the concentration of $SnCl_2$–HCl from 10 to 80 mg L^{-1} were studied, and the results are shown in Figure 4(d). The best results were obtained by choosing 40 mg L^{-1} of $SnCl_2$–HCl solution. Since the concentration of the $SnCl_2$–HCl solution affects the acidolysis of mancozeb to produce CS_2; the acidolysis rate of stannous chloride hydrochloric acid solution with different concentrations is different, and a more suitable acid digestion concentration was obtained when the concentration of $SnCl_2$–HCl was 40 mg L^{-1}, which ensured the accuracy of the test.

3.4. Analysis Characteristics. The analytical performance was evaluated by directly injecting of converted CS_2 in hexane solution with different concentrations of mancozeb standard under optimal conditions. The typical chromatograms of blank, standard solution, and spiked samples in banana, mango, pineapple, and cowpea are shown in Figure 5. The results were evaluated following the criteria outlined in the standard SANTE 11312/2021, which provides guidelines for analytical quality control and method validation procedures for analyzing pesticide residues in food and feed. No interfering peaks were detected at the retention time of 5.64 minutes for mancozeb in blank tested samples, which were extracted and analyzed under the same conditions. The retention time falls within the standard requirement with a deviation of ±0.1 minute. The concentrations of mancozeb standard solution were in the range from 0.005 to 5.0 μg mL^{-1}, and the test was repeated for 6 times, indicating that the peak area exhibited a clear linear response ($R^2 = 0.9995$). The obtained regression equation was $Y = 4.05 \times 10^4 X = 3.76 \times 10^2$. And the deviation of back-calculated concentration from true concentration $\leq \pm 20\%$.

The limit of detection (LOD) of the method was 0.003 mg kg^{-1} at three times the signal-to-noise ratio of analytes (3 signal/noise). The limit of quantification (LOQ)

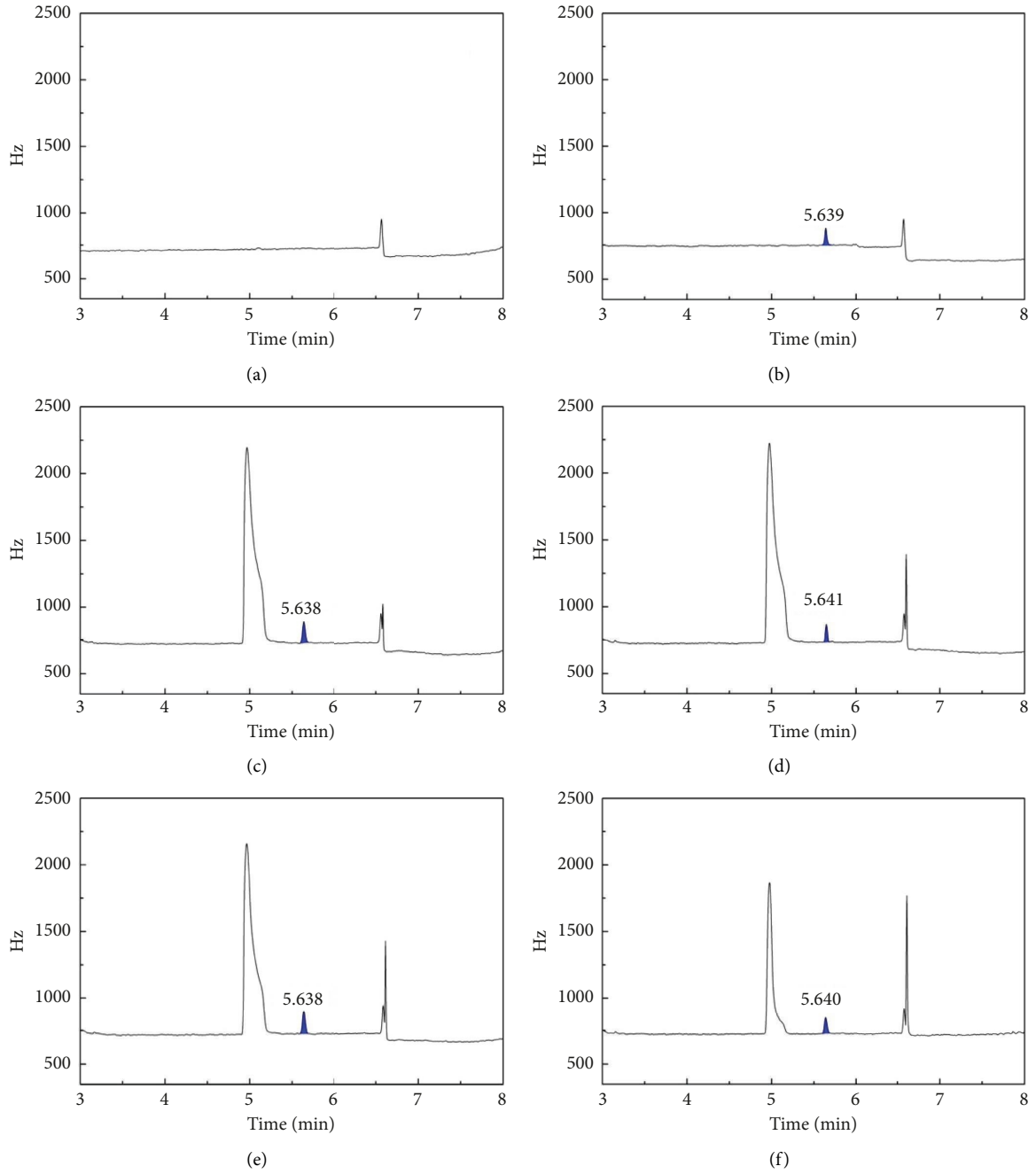

FIGURE 5: The typical chromatograms of standard solution and spiked samples. (a) Blank; (b) mancozeb standard solution at 0.005 μg mL^{-1}; (c) spiked banana sample at 0.01 mg kg^{-1}; (d) spiked mango sample at 0.01 mg kg^{-1}; (e) spiked pineapple sample at 0.01 mg kg^{-1}; (f) spiked cowpea sample at 0.01 mg kg^{-1}.

of the method was 0.01 mg kg^{-1} at the content corresponding to 10 signal/noise. The LOQ of 0.01 mg kg^{-1} met the requirement for accurate determination, considering that the lowest MRLs for mancozeb in the EU and USA are 0.089 and 0.11 mg kg^{-1}, respectively.

Mancozeb was spiked at 0.01, 1.0, and 10 mg kg^{-1} into the banana, mango, pineapple, and cowpea samples to test the method accuracy, and the analytical results are presented in Table 1. Overall recovery rates of mancozeb in the fruit and vegetable test samples spiked at 3 fortification levels ranged from 81% to 112% with relative standard deviations was 1.4% to 8.1%. The method satisfied the criteria with a recovery range falling within 70–120% and precision achieving a relative standard deviation (RSD) of ≤20%. Moreover, the proposed method is faster than traditional GC methods, as summarized in Table 2. Microwave-assisted acidolysis significantly improved the pretreatment time and conversion efficiency, with only 50 s required for conversion and absorption.

Table 1: The results for precision and recoveries of mancozeb ($n = 6$).

Samples	Spiked (mg kg^{-1})	Found (mg kg^{-1})	Recovery (%)	RSD (%)
Banana	0.01	0.112 ± 0.0063	112 ± 6.3	3.8
	1.0	0.832 ± 0.041	83 ± 4.1	2.8
	10	9.41 ± 0.20	94 ± 2.0	1.4
Mango	0.01	0.108 ± 0.0092	108 ± 9.2	7.3
	1.0	0.844 ± 0.040	84 ± 4.0	3.0
	10	9.73 ± 0.70	97 ± 7.0	5.1
Pineapple	0.01	0.0851 ± 0.0070	85 ± 7.0	4.6
	1.0	9.86 ± 0.065	99 ± 6.5	3.4
	10	8.46 ± 0.38	85 ± 3.8	2.0
Cowpea	0.01	0.0811 ± 0.0020	81 ± 2.0	8.1
	1.0	8.28 ± 0.013	83 ± 1.3	3.1
	10	8.52 ± 0.75	85 ± 7.5	4.2

Table 2: Comparison of the pretreatment time and LOD with those reported in references ($n = 6$).

Methods	Time of pretreatment	LOD (mg kg^{-1})	LOQ (mg kg^{-1})	References
LC–MS/MS	20 min	0.015	0.05	[17]
GC-FPD	2 h	0.026	0.089	[11]
SERS	15 min	0.1	—	[12]
LC-DBD-MES	10 min	0.3	1	[14]
Water bath heating acidolysis GC-ECD	2 h	0.053	0.18	[16]
Microwave assisted acidolysis GC-ECD	50 s	0.003	0.01	This method

Note. "—" means not mentioned.

Table 3: CS_2 conversion of mancozeb and other DCTs fungicides ($n = 6$).

Compounds	Added of DTCs (μg)	Theoretical content of CS_2 (μg)	Actual measured content of CS_2 (μg)	Conversion rate (%)
Mancozeb	0.25	0.141	0.129 ± 0.0041	91.5 ± 2.9
Metiram	0.25	0.140	0.128 ± 0.0060	91.4 ± 4.3
Thiram	0.25	0.158	0.114 ± 0.011	72.2 ± 7.0
Propineb	0.25	0.131	0.108 ± 0.0072	82.4 ± 5.5

Note. The theoretical conversion rate is based on molar mass. 1 g of mancozeb produces 0.562 g of CS_2, 1 g of metiram generated 0.559 g CS_2, 1 g of thiram generated 0.632 g CS_2, and 1 g of propineb generated 0.525 g CS_2.

3.5. Acidolysis Efficiency of Microwave Treatment. The efficiency of microwave-assisted acidolysis is the most important factor affecting accuracy. Therefore, 0.25 μg mancozeb was selected to add the $SnCl_2$–HCl solution and hexane, which were then moved into the microwave oven for 50 s acidolysis. The generated CS_2 was absorbed by hexane and injected into the GC instrument to determine its CS_2 content. Pure CS_2 was also injected as a standard to quantify the yield of mancozeb acidolysis. The theoretical yield of CS_2 from mancozeb was calculated using the molar mass of CS_2 in mancozeb. Then, an acidolysis efficiency of 91.4% was calculated relative to the measured yield for the theoretical yield (set as 100%). The results are shown in Figure 4, suggesting that the acidolysis efficiency is high.

Furthermore, to confirm the feasibility of this microwave-assisted acidolysis method for other types of DTCs fungicides, it was used to determine the residues of other dithiocarbamate pesticides, including metiram, thiram, and propineb. The principle behind the acidolysis of mancozeb and other DTCs to CS_2 involved a chemical reaction where mancozeb underwent hydrolysis in acidic conditions to yield CS_2 as one of the reaction products. This reaction typically involved the cleavage of the carbon-sulfur bonds present in the mancozeb molecule, resulting in the formation of CS_2 along with other byproducts. The specific mechanism and intermediates were not clear yet, which involved in this acidolysis process may vary depending on the reaction conditions and the presence of catalysts or other factors. Considering that one mole of mancozeb produces two moles of CS_2, a conversion factor of μg of mancozeb multiplied by 0.564 is established as equivalent to μg of CS_2. As shown in Table 3, under optimal conditions, all tested DTCs exhibited acidolysis efficiencies exceeding 72.2% of CS_2, with mancozeb achieving a conversion rate of 91.5%.

Table 4: Results of 10 kinds of mancozeb spiked positive samples ($n = 6$).

Sample	Added (μg)	Found (μg)	
		Water-bath acidolysis method	This method
Banana	0.25	0.20 ± 0.014	0.21 ± 0.0063
Mango	0.25	0.20 ± 0.025	0.21 ± 0.0030
Dragon fruit	0.25	0.21 ± 0.017	0.23 ± 0.0075
Lychee	0.25	0.18 ± 0.0087	0.19 ± 0.012
Apple	0.25	0.20 ± 0.019	0.21 ± 0.012
Eggplant	0.25	0.21 ± 0.022	0.23 ± 0.0025
Cowpea	0.25	0.21 ± 0.019	0.24 ± 0.0053
Peanuts	0.25	0.20 ± 0.024	0.23 ± 0.0055

3.6. Analysis of Real Samples. Fifty fruit and vegetable samples purchased from a local market were analyzed to preliminarily demonstrate the potential application of the proposed method. The results showed no DTCs residues in the tested fifty samples (data not shown). Mancozeb was spiked at 0.25 μg into nine different real fruit, vegetable, and rice samples (banana, mango, dragon fruit, lychee, apple, eggplant, cowpea, and peanuts) to test the accuracy, and the results are presented in Table 4. The results produced by the proposed method are not significantly different from those obtained by traditional water bath heating acidolysis method (90°C for 120 min) at a confidence level of 95% through the t-test. This indicates that this method (microwave-assisted acidolysis) has good precision and accuracy, and it is suitable for the analysis of different types of matrix samples.

4. Conclusion

In this study, a rapid method for mancozeb determination was established using microwave-assisted acidolysis coupled with GC-ECD. Compared to traditional water-bath heating acidolysis, microwave-assisted acidolysis had a high conversion efficiency, where the acidolysis time was directly reduced from 2 h of the original water-bath to 50 s. Moreover, microwave-assisted acidolysis greatly shortens the pretreatment time to reduce the probable gas leakage during the heating process, which improves the recovery of the method. Finally, rapid and high-efficiency acidolysis coupled with the high sensitivity of the GC-ECD method, mancozeb, and other DTCs fungicides in the fruit and vegetable samples could be determined with high sensitivity and accuracy. The proposed method is fast and accurate to operate and possibly applied as a standard method for the determination of mancozeb and other DTCs residues. Further exploration into an online and continuous flow microwave-assisted acidolysis coupled with the GC method could be beneficial for determining mancozeb and other DTCs in food.

Data Availability

The data used to support the findings of this study are made available from the corresponding authors upon reasonable request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Qiaoxia Tian performed the experiments and wrote the original draft of the manuscript. Hongxing Li performed the experiments. Lixia Chen had discussions on the experimental design and performed the experiments. Bingjun Han conceived, designed, and wrote the manuscript. All authors have reviewed the manuscript.

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