

Analytical Methods

Rapid determination of organophosphorous pesticides in leeks by gas chromatography–triple quadrupole mass spectrometry

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ABSTRACT

A rapid multi-residue method was developed for the determination of 20 organophosphorous pesticide residues in leeks by gas chromatography coupled to triple quadrupole mass spectrometry (GC–QqQ–MS/MS). The method was based on the modified QuEChERS sample preparation method. After microwave pre-treatment, leek samples were extracted with acetonitrile containing acetic acid 0.1% and cleaned by dispersive solid phase extraction. The QqQ analyser acquired data in selected reaction monitoring (SRM) mode. Recoveries of 20 organophosphorous pesticides ranged from 81.0% to 109.4% with the relative standard deviations (RSD) below 10.4%. The limits of detection (LODs) were 0.07–1.5 µg/kg. The limits of quantitation (LOQs) ranged from 0.25 to 5 µg/kg. Ten leek samples were analysed for method application.

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1. Introduction

Leeks are one of the important vegetables in China, which are delicious and excellent material for the dumplings – the Chinese traditional food. They are not only tasty but also nutritious, as they are good source of carbohydrate, protein, vitamin, cellulose and mineral. In addition, leeks are reported to have the similar medicinal values as garlic, which show some anticancer activity (Chen, Li, Wang, Pan, & Jin, 2009).

However, the residues of pesticide especially organophosphorous pesticides in leeks are quite serious. Some of the organophosphorous pesticides, such as phorate, cannot only kill the pests, but also promote growth of leeks as fertiliser. Although organophos-

phorous pesticides have low environmental persistence and high effectiveness, overuse and abuse have resulted in residue problems and may cause risks to human health (John, Worek, & Thiermann, 2008).

Methods used to determine organophosphorous pesticide residues are mainly based on chromatographic analysis such as GC–NPD, GC–FPD, GC–MS, HPLC–MS, GC–MS/MS (de la Colina, Peña Heras, Dios Cancela, & Sánchez Rasero, 2002; Dömötöróvá & MatISOVÁ, 2008; Fernández-Alba & García-Reyes, 2008; Krueve, Kunnapas, Herodes, & Leito, 2008; Li et al., 2007; Patel, Fussell, Macarthur, Goodall, & Keely, 2004; Tahboub, Zaater, & Al-Talla, 2005; Tao et al., 2009; Walorczyk, 2008). However, there are many sulphur compounds in leeks, which influence the selective detectors such as FPD. Song, Ma, and Li (2007) combined GPC and SPE to efficiently eliminate the interferences, but the method was time-consuming and demanded a lot of solvent. Wang et al. (2009) determined pesticide residues by FPD in leeks using a microwave-assisted heating to dramatically reduce the interferences. Although the method had been simplified compared with the former one, yet it still involve two steps of concentration which renders the method time-consuming. Moreover, SPE is costly and time-consuming. Therefore, new methods in sample preparation and measurement should be studied and developed.

Many studies have been reported concerning the determination of pesticides in leeks by using GC–MS. Although GC–MS has some

Abbreviations: GC–QqQ–MS/MS, gas chromatography–triple quadrupole mass spectrometry; QqQ, triple quadrupole; QuEChERS, quick easy cheap effective rugged and safe; HAC, acetic acid; SRM, selected reaction monitoring; RSD, relative standard deviations; LOD, the limits of detection; LOQ, the limits of quantitation; GC–NPD, gas chromatography–nitrogen–phosphorus detector; GC–FPD, gas chromatography with flame photometric detector; GC–MS, gas chromatography–mass spectrometry; HPLC–MS, high performance liquid chromatography–mass spectrometry; GPC, gel permeation chromatography; SPE, solid phase extraction; PSA, primary secondary amine; GCB, graphitic carbon black; MgSO₄, magnesium sulphate anhydrous; EI, electron impact ionisation; CID, collision-induced dissociation.

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selectivity, it could not eliminate the interference of sulphur compounds in leeks. Tao et al. (2009) used gas chromatography/ion trap mass spectrometry to detect multi-residues in vegetables. The ion trap mass spectrometry is good for qualitative analysis but not efficient for quantitative analysis. Walorczyk (2008) used gas chromatography/triple quadrupole mass spectrometry to analyze the multi-residue of pesticides in green leafy vegetables. Leeks are not the same as ordinary green leaf vegetables because they contain sulphur compounds. This article is aimed at the vegetables with sulphur compounds. It describes a gas chromatography–triple quadrupole (QqQ) mass spectrometry technique which can effectively avoid false-positive results. Moreover, it is more sensitive for the trace level detection of the pesticide residues. (Frenich, Bola-nos, & Martínez Vidal, 2007; Frenich, González-Rodríguez, Arrebola, & Martínez Vidal, 2005; Frenich, Martínez Vidal, Cruz Sicilia, González Rodríguez, & Bola-nos, 2006; Martínez Vidal, Arrebola Liébanas, González Rodríguez, Frenich, & Fernández Moreno, 2006; Walorczyk, 2007; Wang, Jia, & Zhang, 2008).

This paper is to describe a rapid, accurate and sensitive method to determine multi-residues by GC–MS/MS with the modified quick easy cheap effective rugged and safe (QuEChERS) sample preparation method in leeks. Leeks are more representative because they both have pigments and sulphur compounds. So the method could apply to other vegetables with slight changes. The method could be used in the determination of ordinary green leaf vegetables without microwave pre-treatment. It could also be used in the determination of vegetables such as garlic, onion and other vegetables with sulphur compounds, omitting the pigments removal step if not required. Furthermore, this paper is the first article to verify the selectivity of QqQ analyser by the sample of complex matrices. Leek samples with and without microwave pre-treatment were compared for the interference of sulphur compounds. It provides the basis for the determination of vegetables with sulphur compounds by GC–QqQ-MS/MS.

2. Experimental

2.1. Materials and standards

Organophosphorous pesticide standards ($100 \mu\text{g mL}^{-1}$) were obtained from Environment Inspect Department of China Agricultural Ministry. A standard mixture ($1 \mu\text{g mL}^{-1}$ of 17 pesticides, $4 \mu\text{g mL}^{-1}$ parathion, $5 \mu\text{g mL}^{-1}$ dimethoate and quinalphos) was obtained by diluting those stock solutions in *n*-hexane and stored at -18°C . All organic solvents and chemical reagents were chromatography grade (*n*-hexane and acetonitrile) or analytical grade (magnesium sulphate anhydrous, sodium acetate, and acetic acid), and purchased either from Fisher Scientific Co. or Sinopharm Chemical Reagent Company. Primary secondary amine (PSA) sorbent was obtained from Varian (Varian, Harbor City, CA). Graphitic carbon black (GCB) was purchased from Supelco (Bellefonte, PA, USA).

Uncontaminated leek samples produced in our own garden were used as blank samples. Real samples were obtained from the local market in Shandong province of China. Edible parts were taken as samples and stored at 4°C or use.

2.2. Apparatus

2.2.1. Laboratory equipment

The homogeniser was IKA® T25 digital Ultra-Turrax. The vortex shaker was QILINBELER® Vortex Shake QL-861 and the Refrigerated Centrifuge was Sigma® 3–18 K. The nitrogen-evaporator was N-EVAP® 112. The domestic microwave oven was G8023CTL23-K3 (Galanz Co., China).

2.2.2. GC–QqQ-MS/MS

TSQ Quantum GC (Thermo Fisher Scientific, USA) analysis was used throughout the study with a GC system TRACE GC Ultra and a triple quadrupole mass spectrometer Quantum (mass range from m/z 10–3000). Samples were injected with AS 3000 auto-sampler into a split/splitless injector. The capillary column was $30 \text{ m} \times 0.25 \text{ mm i.d.}$, TR-5MS and with $0.25 \mu\text{m}$ film thickness (Thermo Fisher Scientific, USA).

The injector temperature was set at 230°C . Injection volume was $1.0 \mu\text{L}$ with splitless mode. At 0.75 min, split mode was switched on with the split flow of 60 ml/min. At 2 min, gas saver was turned on with the flow of 20 ml/min.

The initial temperature of the column oven was 50°C (hold for 1 min). This temperature was increased at a rate of $25^\circ\text{C}/\text{min}$ up to 150°C ; next, the temperature was increased up to 240°C at a rate of $5^\circ\text{C}/\text{min}$; and finally, the temperature was increased up to 300°C at a rate of $30^\circ\text{C}/\text{min}$ (hold for 5 min).

Helium at a constant flow rate of 1.2 ml/min was used as carrier gas; argon at a pressure in the range of 1.0 mTorr was used as collision gas. The running time was 30 min, divided into 15 segments. The QqQ mass spectrometer was operated in EI at 70 eV in the selected reaction monitoring (SRM) mode. The transfer line and ionisation source temperatures were set at 280 and 250°C , respectively. A filament multiplier delay of 4.5 min was fixed in order to prevent instrument damages. The emission current was set at $100 \mu\text{A}$. The scan time ranged from 0.1 to 0.25 s, which resulted in dwell times (scan time divided by number of transitions). Peak widths of Q1 and Q3 were all set at 0.7 amu. The specific MS/MS conditions are shown in Table 1.

2.3. Sample preparation and clean-up

A total of 0.5 kg leek sample was cut into pieces of about 2 cm long and mixed thoroughly. A 3.0 g subsample was transferred into a 50 mL centrifugal tube and heated in a microwave oven for 10 s at 640 W, then rapidly cooled in an ice–water bath. HPLC-grade water (3 mL) and 15 mL of acetonitrile containing acetic acid 0.1% were added to the centrifugal tube and vigorously shaken with a vortex mixer. The sample was homogenised at 9000 rpm for 1 min in a homogeniser.

Magnesium sulphate anhydrous (4.0 g) and sodium acetate (2.0 g) were added to the mixture, and the mixture was shaken immediately for 2 min with a vortex mixer. The sample was centrifuged for 5 min at 5000 rpm using a refrigerated centrifuge at 4°C . The acetonitrile extract (4 mL) was transferred to a 20 mL centrifugal tube containing 100 mg PSA, 40 mg GCB and 600 mg MgSO_4 , followed by shaking for 2 min with a vortex mixer. PSA was used to remove fat and GCB was used to remove the pigments such as chlorophyll in the extract. The centrifugal tube was centrifuged at 10,000 rpm for 5 min at 4°C . The extract (2 mL) was transferred to 5 mL glass tube and dried with a gentle nitrogen stream. Finally, 1 mL *n*-hexane was added in the glass tube and shaken vigorously for 2 min with a vortex mixer. The extract was centrifuged at 15,000 rpm for 5 min at 4°C and transferred to the GC auto-sampler vial for GC–QqQ-MS/MS analysis.

3. Results and discussion

3.1. GC–QqQ-MS/MS analysis

For the optimisation of the MS parameters, all compounds were monitored in full scan mode in the range m/z 40–400 because the organophosphorous pesticides are always of low molecular weight. The range of m/z should be reduced to the smallest appropriate scope so as to increase the sensitivity of full scan. Full scan spectra

Table 1
Retention time (RT), scan time and MS/MS parameters.

Pesticide name	Segment	Scan time (s)	RT (min)	Precursor ion (<i>m/z</i>)	Product ion, <i>m/z</i> (collision energy, V)
Dichlorvos	1	0.25	6.22	185	109 (15), 93(15)
Sulfotep	2	0.25	11.74	322	294 (10), 202(15)
Phorate	3	0.25	12.22	260	75 (15), 231(5)
Dimethoate	4	0.25	12.98	125	47 (15), 93(10)
Diazinon	5	0.25	13.75	304	179 (15), 162(15)
Chlorpyrifos-methyl	6	0.25	15.56	286	271 (20), 208(15)
Parathion-methyl	7	0.10	15.90	263	109 (15), 246(5)
Fenclorphos	7	0.10	16.15	285	270 (15), 240(15)
Pirimiphos-methyl	8	0.25	16.51	305	290 (10), 180(10)
Fenitrothion	9	0.10	16.76	277	260 (8), 109(15)
Malathion	9	0.10	16.98	173	127 (5), 99(15)
Chlorpyrifos	9	0.10	17.20	314	258 (12), 286(10)
Fenthion	10	0.10	17.47	278	169 (15), 245(10)
Parathion	10	0.10	17.59	291	109 (15), 137(10)
Isofenphos-methyl	11	0.25	18.19	199	121 (10), 167(10)
Quinalphos	12	0.25	19.11	298	156 (10), 190(8)
Profenofos	13	0.25	20.84	339	269 (10), 251(25)
Ethion	14	0.25	22.44	231	129 (20), 185(10)
Triazophos	15	0.10	23.18	257	162 (10), 134(15)
Trithion	15	0.10	23.44	342	157 (10), 199(10)

Ions which are italics are quantification ions, the others are identification ions.

were obtained to select the appropriate precursor ions (Table 1). Selection of the precursor ion was carried out trying to choose the ion with higher *m/z* ratio (increase in selectivity) and abundance (increase in sensitivity) (Bola-nos, Frenich, & Martínez Vidal, 2007). High *m/z* ratio can effectively avoid the interference of impurities which usually occur with low *m/z* ratio. However, the highest *m/z* ratio was always with low abundance. So it is important to achieve a compromise between the two factors.

According to the selected precursor ion, product ion spectra were acquired by collision-induced dissociation (CID) with argon. Collision energies from 5 to 25 eV were applied. The aforementioned criterion was also applied to choose the suitable product ions, higher *m/z* ratio and abundance. The selected ions might be interfered with impurities in the real sample. So it is better to test three or four ions for each compound in the real sample and choose two ions that are more sensitive and less interfered in the final selected reaction monitoring mode.

The mass scanning speed of the analyser is a critical parameter which determines chromatographic peak shape (point across a peak) and sensitivity (Frenich, Fernández Moreno, Martínez Vidal, & Arrebola Liébanas, 2007). At least 8–10 points should be collected for each compound, which have been suitable for quantitative analysis. Scan time can be calculated as follows: the average peak width is 4 s. If the segment has only one compound and the peak contains eight points, the scan time is set at 0.5 s (4 s divided by eight points). However, two ions for one compound must be simultaneously detected in 0.5 s. The scan time should be set at 0.25 s (0.5 s divided by two ions). If the segment contains two compounds (simultaneously detect four ions), the scan time is about 0.125 s (0.5 s divided by four ions). This can help find a rough value, which should be verified in SRM experiment. This method facilitate the quantitative analysis of these organophosphorous pesticides in complex matrices.

3.2. Optimisation of extraction and clean-up

3.2.1. Extraction condition optimisation

Sample pre-treatment was based on the QuEChERS preparation method. Dispersive solid phase extraction for removing of co-extractives from acetonitrile extracts makes the clean-up step relatively fast, economical, and convenient. Acetonitrile is an effective solvent for the simultaneous extraction of pesticide multi-residues.

However, some of the pesticides are unstable in acetonitrile and prone to degradation, such as dicofol, chlorothalonil, captan. The acidification of acetonitrile solutions with 0.1% HAc helped reduce or sometimes eliminated the formation of the deltamethrin isomer. Moreover, the addition of HAc did not negatively affect the stability of the other pesticides (Maštovská & Lehotay, 2004).

The sodium chloride was replaced with the sodium acetate, which was added to make a buffer solution with HAc in order to control pH 6–7. Many organophosphorous pesticides are easily hydrolysed, especially in acidic or alkaline conditions. So neutral pH condition was selected to make them relatively stable, in which condition the pesticides also prefer acetonitrile to water. Compared to QuEChERS method, this buffer system has two advantages: on one hand, HAc was added with acetonitrile to protect the target compounds; on the other hand, it is more suitable for the pesticides which prefer neutral condition because the buffer solution of QuEChERS method is set at pH 5–5.5.

3.2.2. Clean-up optimisation

The chlorophyll of leeks was excessive. Using plenty of GCB can sufficiently remove the chlorophyll, but it can also resulted in loss of target compounds. The amount of GCB should be suitably added (Nguyen et al., 2008). To reduce the chlorophyll in the extraction, the amount of weighed subsample was decreased to 3.0 g. A small quantity of the extraction solvent was removed for clean-up and analysis. Owing to the high sensitivity of the QqQ mass spectrometry, there was a good compromise between detection limit and sample clean-up.

3.2.3. Microwave pre-treatment comparison

sulphur-containing compounds exist in leeks only when leek bulbs are crushed, like other Allium plants. The sulphur-containing compounds have the similar characteristic as the pesticides and they are not easy to separate from target compounds. As many articles reported, microwave pre-treatment was often used to deactivate alliinase before the leek samples were homogenised so as to reduce interference by sulphur compounds. The QqQ mass spectrometry has good selectivity for target ions and it can effectively eliminate interference (Fig. 1). This method prolonged the running time to separate all the organophosphorous pesticides and observe the baseline. Fig. 1 shows the baseline was hardly influenced by the

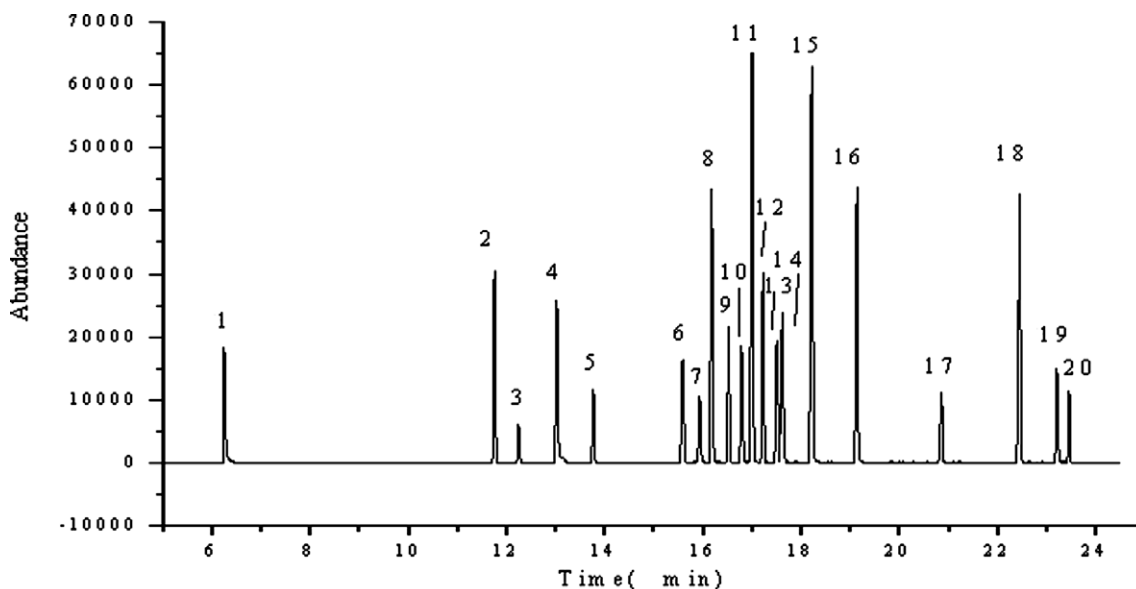


Fig. 1. GC-MS/MS (SRM) chromatogram of a matrix-matched standard solution with $0.02 \mu\text{g mL}^{-1}$ of 20 organophosphorous pesticides. Target compounds are numbered as follows: 1. Dichlorvos; 2. Sulfofep; 3. Phorate; 4. Dimethoate; 5. Diazinon; 6. Chlorpyrifos-methyl; 7. Parathion-methyl; 8. Fenchlorphos; 9. Pirimiphos-methyl; 10. Fenitrothion; 11. Malathion; 12. Chlorpyrifos; 13. Fenthion; 14. Parathion; 15. Isofenphos-methyl; 16. Quinalphos; 17. Profenofos; 18. Ethion; 19. Triazophos; 20. Trithion.

impurities with microwave pre-treatment and QqQ mass spectrometry.

Fig. 2 compared the two chromatograms with and without microwave pre-treatment. It is obvious that the response of most organophosphorous pesticides increased in the lower chromatogram. Organophosphorous pesticides are easily affected by matrix-induced enhancement. Sulphur-containing compounds may contribute to the higher concentration of sample matrix, which can cause an enhancement in the observed chromatographic response (Poole, 2007). Although the baseline of the lower chromatogram is not as smooth as the upper one, the QqQ mass spectrometry still shows the predominant selectivity.

However, dirty sample may pollute the injection port and the column and shorten their life span. It is better to carry out microwave pre-treatment which can help with the clean-up of the

extract. The time of microwave pre-treatment should be suitably controlled according to the articles reported (Wang, Zhang, Tang, & Liu, 2005; Zhang et al., 2008). Microwave pre-treatment may cause loss of recovery because organophosphorous pesticides are thermally labile. But if it was immediately followed with ice water cooling, recoveries could be enhanced especially for the volatile compounds such as dichlorvos.

3.3. Recovery, LOD and LOQ, linearity

One of the main problems in trace analysis of complex matrices is the matrix-induced response enhancement. In this work, matrix-matched standard calibration was used for quantification purposes in order to avoid matrix effect.

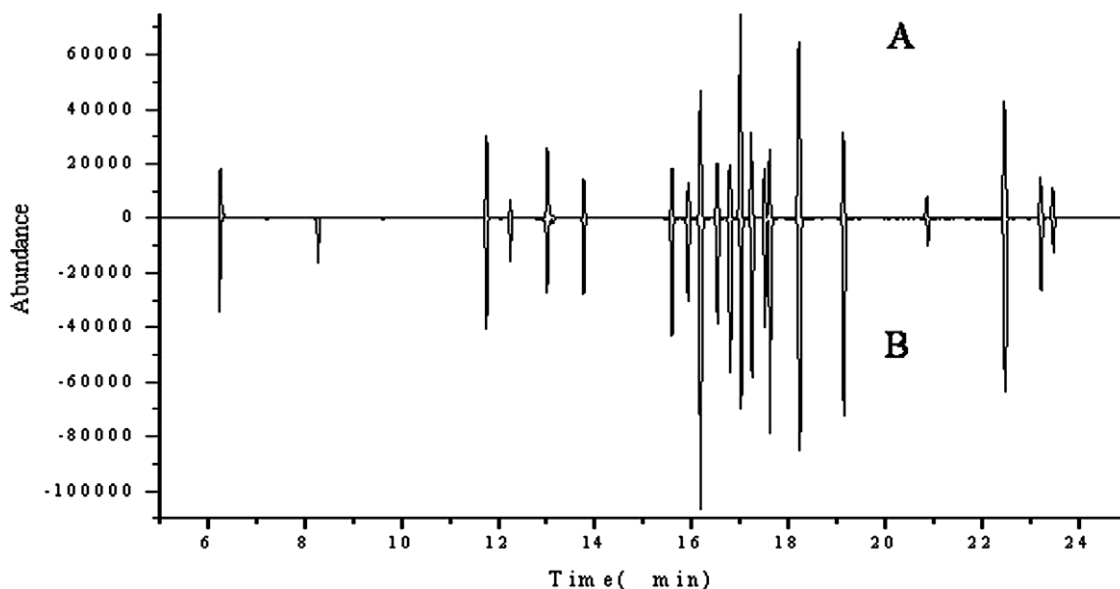


Fig. 2. Comparison of chromatograms: chromatogram A (upper) leek extract spiked with $50 \mu\text{g/kg}$ organophosphorous pesticide mixture after microwave pre-treatment; chromatogram B (lower) leek extract spiked with $50 \mu\text{g/kg}$ organophosphorous pesticide mixture but without microwave pre-treatment.

The blank samples (3.0 g) were spiked with 20 organophosphorous pesticides at concentrations of 0.01, 0.05, 0.1 mg kg⁻¹ and the samples were heated in a microwave oven for 10 s, then extracted with acetonitrile and cleaned up with dispersive solid phase extraction (PSA and GCB), finally detected by GC–QqQ–MS/MS. The linearity of all the organophosphorous pesticides was from 0.002 to 0.20 µg mL⁻¹ by the calculation of a seven-point plot. Determination coefficient (R^2) ranged between 0.9897 and 0.9997 for all the target compounds. The recovery of each compound at each concentration was replicated three times and the data are presented in Table 2 which indicates that the recoveries were in the range of 81.0–109.4%. Precision was expressed as relative standard deviation (RSD). RSD ($n = 3$) varied from 1.3% to 10.4%. The results obtained satisfies SANCO/2007/313 criteria (i.e. average recoveries in the range of 70–120% with RSD less than and equal to 20%).

The limit of detection (LOD) of the proposed method was determined by considering a value three times the background noise obtained for blank samples, whereas the limits of quantification

(LOQ) were determined considering a value 10 times the background noise. The LODs of Tao et al. (2009) for 12 organophosphorous pesticides are 10 times or even higher than our values. Tao et al. used gas chromatography/ion trap mass spectrometry which is different from our GC–QqQ–MS/MS. The LODs of Bola-nos et al. (2007) are mostly lower compared to our values because they used eggs as samples and the matrices are different. In the work of Walorczyk (2008), only LOQs are provided which are mostly three times higher than the LOQs in our current work. Walorczyk (2008) analysed multi-residues in green leaf vegetables by GC–QqQ–MS/MS. As the leek samples are more complex than ordinary vegetables, the results of current work are satisfactory. Table 2 summarises the detection and quantification limits obtained for each organophosphorous pesticide.

3.4. Application to real samples

Ten samples were obtained from the local market in Shandong province of China and assayed for organophosphorous pesticide

Table 2
Recovery results (%), RSD (%), LOD, LOQ and determination coefficient (R^2) of the organophosphorous pesticides studied.

Pesticide name	R^2	10 µg/kg		50 µg/kg		100 µg/kg		LOD (µg/kg)	LOQ (µg/kg)
		R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)		
Dichlorvos	0.9987	97.1	4.7	95.7	8.1	100.6	6.5	1.50	5.00
Sulfotep	0.9973	87.4	9.6	86.5	2.1	87.5	3.2	0.22	0.75
Phorate	0.9948	83.9	6.3	81.8	4.2	87.9	1.4	0.62	1.87
Dimethoate	0.9996	102.5	2.2	103.7	3.3	109.4	6.1	1.12	3.75
Diazinon	0.9994	97.3	1.3	94.8	7.2	93.1	5.6	0.37	1.25
Chlorpyrifos-methyl	0.9974	87.1	1.7	88.9	3.1	93.5	6.0	0.50	1.50
Parathion-methyl	0.9990	93.2	2.4	91.2	7.7	90.5	6.8	0.75	2.50
Fenclorphos	0.9983	92.2	6.7	91.5	7.1	102.8	10.4	0.18	0.62
Pirimiphos-methyl	0.9974	88.0	5.8	86.3	2.3	94.1	9.7	0.60	2.00
Fenitrothion	0.9897	95.5	9.0	86.9	5.8	94.3	7.8	0.37	1.25
Malathion	0.9992	94.9	4.9	100.4	6.1	105.9	4.2	0.22	0.75
Chlorpyrifos	0.9979	92.1	4.6	90.2	7.9	90.7	3.5	0.18	0.62
Fenthion	0.9978	90.5	8.9	96.2	3.6	101.5	4.7	1.05	3.50
Parathion	0.9926	98.7	7.0	101.8	2.9	102.6	6.5	1.50	5.00
Isofenphos-methyl	0.9997	83.6	5.6	81.0	4.9	85.8	5.2	0.07	0.25
Quinalphos	0.9973	98.5	1.8	99.0	4.4	100.1	6.2	1.50	5.00
Profenofos	0.9965	100.4	3.7	92.2	5.8	95.6	3.1	0.75	2.50
Ethion	0.9992	94.2	7.5	91.1	4.8	92.3	1.4	0.15	0.50
Triazophos	0.9981	97.7	9.6	99.4	6.0	105.4	1.8	0.45	1.50
Trithion	0.9938	93.3	8.2	92.7	6.1	98.6	5.5	0.60	2.00

Table 3
Organophosphorous pesticide concentrations (mg kg⁻¹) of real leek samples coming from supermarket in Shandong province of China.

Pesticide name	Real leek sample (mg kg ⁻¹)									
	1	2	3	4	5	6	7	8	9	10
Dichlorvos	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sulfotep	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Phorate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dimethoate	0.0110	ND	ND	ND	ND	ND	ND	ND	ND	ND
Diazinon	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorpyrifos-methyl	ND	ND	ND	ND	ND	ND	ND	0.0032	ND	ND
Parathion-methyl	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.0035
Fenclorphos	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pirimiphos-methyl	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Fenitrothion	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Malathion	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorpyrifos	ND	0.0410	ND	ND	0.0030	0.0036	ND	ND	ND	ND
Fenthion	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Parathion	ND	ND	ND	0.0230	ND	ND	ND	ND	ND	ND
Isofenphos-methyl	0.0020	ND	ND	ND	0.0015	ND	ND	ND	ND	ND
Quinalphos	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Profenofos	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethion	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Triazophos	ND	ND	ND	ND	ND	0.0040	ND	ND	ND	ND
Trithion	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

The precision results are given with the addition of a decimal place for in some parts of the tables.

content according to the method described above. The results are shown in Table 3. It was clear that seven kinds of organophosphorous pesticides were detected in seven samples, with values range from 0.0015 to 0.041 mg kg⁻¹. The highest concentrations were found with chlorpyrifos (0.041 mg kg⁻¹) and parathion (0.023 mg kg⁻¹). The concentration of the two pesticides conform to the legislation of EU (chlorpyrifos and parathion both set at 0.05 mg kg⁻¹) and People's Republic of China (National Standard Compilation of Pesticides, 2004).

4. Conclusion

A rapid, economical, efficient multi-residue method was developed for the determination of 20 organophosphorous pesticides in leeks. The amount of analysed sample was reduced to 3.0 g so as to reduce the chlorophyll in the extraction. The leek samples were heated in a microwave oven for 10 s to inactivate enzymes. HAC (0.1%) was added with acetonitrile as the extracting solvent to prevent the target compounds from degradation. HAC also made a buffer solution with the sodium acetate in order to regulate pH 6–7. The extracts were cleaned up using dispersive solid phase extraction by PSA and GCB to remove polar matrix components.

The method could effectively decrease the chlorophyll of the final extract and protect the chromatographic system. Moreover, compared to other analytical methods described for pesticide residue detection in leeks, this proposed analytical method is easy, convenient, time-saving and also economical. This approach can be applied to other green leaf vegetables containing large amount of chlorophyll. Moreover, the selectivity of QqQ analyser was clearly demonstrated in this investigation which proved to be efficient in the determination of organophosphorous pesticides the vegetables with sulphur-containing compounds.

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