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Analytical Methods

# Microwave pretreatment and gas chromatography–mass spectrometry determination of herbicide residues in onion

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**Abstract**

A rapid multi-residue method was developed for the determination of 16 herbicides in onion. The analytical procedure was based on preventing formation of sulfur-containing compounds in onion by microwave inactivation of the enzyme alliinase. The onion samples which had been pretreated were extracted with acetonitrile and cleaned by solid-phase extraction. The herbicide residues in onion were detected by gas chromatography/mass spectrometry with selected ion monitoring. The recoveries of 16 herbicides ranged from 69.2% to 105.0% with the relative standard deviations (RSD) below 10.7%. The limit of quantitation (LOQ) ranged from 0.003 to 0.015 mg $kg^{-1}$. The method was applied to the analysis of herbicide residues in onion samples.


*Keywords:* Microwave; GC–MS; Herbicide; Onion

## 1. Introduction

During the planting period the onion is challenged by various plant diseases, insect pests and weeds, among them various miscellaneous weeds affect the yield of the onion. To increase the yield of onion, herbicides (such as Chlorotoluron, Acetochlor, etc.) are widely used. Although herbicides have low immediate toxicity, they easily accumulate in the body, where they can induce cancer and have a high endocrine disrupting potential (Environmental Protection Agency, 2004; Hurley, Hill, & Whiting, 1998; Lee et al., 2004; Ma et al., 2006). Hence many countries established maximum recommended limits (MRL) for herbicide residues in foodstuff (California Department of Food and Agriculture, 2007).

Methods used to determine herbicide residues in vegetables are mainly based on chromatographic analysis such as GC–ECD, GC–NPD, GC–MS, HPLC–MS, etc. (Albero, Sánchez-Brunete, Donoso, & Tadeo, 2004; Aramendía et al., in press; Tadeoa, Sánchez-Brunete, Pérez, & Fernández, 2000). But there are many sulfo-compounds in onion, which influence the detection of herbicides in onion. For example, GC-ECD and GC-MS could be influenced sharply by elemental sulfur (Ahmed, 2001; Tekel & Hatrík, 1996). These sulfo-compounds show no response with GC–AED (element-specific atomic emission detector), so it can be used to analyze pesticide residues in onion. Unfortunately, the sensitivity of AED was rather low (Gelencsér,

*Abbreviations*: GC–MS, gas chromatography–mass spectrometry; SIM, selected ion monitoring; MRL, maximum residue limits; GC–ECD, gas chromatography–electron capture detector; GC–NPD, gas chromatography–nitrogen–phosphorus detector; HPLC–MS, high-performance liquid chromatography–mass spectrometry; GC–AED, gas chromatography–element-specific atomic emission detector; SFE, supercritical fluid extraction; HPLC–UV, high-performance liquid chromatography-UV detector; SPE, solid phase extraction; LOD, limit of detection; LOQ, limit of quantitation; RSD, relative standard deviation.

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Szépvölgyi, & Hlavay, 1993; Stan, 2000). Supercritical fluid extraction (SFE) removes sulfo-compounds from onion extracts that are assayed for pesticides (Tilio, Kapila, Nam, Bossi, & Facchetti, 1994; Wang, Xu, & Jiao, 1998), but the assay is fussy. Herbicide residues in onion could be detected by GC–NPD and HPLC–UV (Tadeoa, Sánchez-Brunete, Pérez, & Fernández, 2000), but the limit of quantitation (LOQ) was poor. There is no literature report of the determination of herbicide residues in onion by GC–MS.

Sulfur-containing compounds exist in the onion only when onion bulbs are crushed, like other Allium plants. The vacuolar enzyme, alliinase, transforms alliin into the very unstable thiosulphinate allicin, then allicin is rapidly degraded into vinyldithiins and ajoenes. In the intact onion, alliinase is found in vacuoles and is thereby physically separated from its natural substrate alliin, which occurs in the cytosol (Lancaster & Collin, 1981; Lawson & Hughes, 1992). Only upon injuring the onion bulbs does the active enzyme come into contact with alliin, converting sulfur-containing compound alliin into allicin (Jacobsen, Yamaguchi, Mann, & Howard, 1968). Allicin is not a stable compound and readily degrades to form secondary products consisting of various sulfides, sulfonic ether, sulfonic aether etc. which contribute to the characteristic flavor and odor of onion (Ferary & Auger, 1996). Unfortunately, the aggregates of elemental sulfur affect the determination of herbicides. Our goal was to deactivate alliinase before the onion bulbs were crushed so as to eliminate interference by sulfur compounds.

Alliinase activities change with temperature, PH and metal ions (Kuettner, Hilgenfeld, & Weiss, 2002; Tobkin & Mazelis, 1979; Yoo & Pike, 2001), In the paper we studied factors that affect the alliinase activity. We report that microwave pretreatment of onion efficiently eliminated interferences, allowing rapid assay of 16 herbicides residues by GC–MS.

## 2. Materials and methods

### 2.1. Materials and standards

Herbicide standards, stocked at 1000 μg $mL^{-1}$ were obtained from Environment Inspect Department of China Agricultural Ministry. A standard mixture (10 μg $mL^{-1}$) was obtained by diluting those stock solutions in acetone. Standards were stored at −20 °C.

All organic solvents and chemical reagents were analytical (acetonitrile, acetone, n-hexane, sodium chloride), and purchased either from Concord Technology Co. or Tianjin Chemical Reagent Company. The SPE columns (Florisil, 6 mL, 1 g) used in the experiment were purchased from Supelco.

Uncontaminated red onion samples produced in our own garden were blank samples. Real samples were obtained from an onion plantation in shandong province of China. The samples were cut into 4 $cm^2$ slices without crushing and stored at 4 °C in a dark place.

### 2.2. Apparatus

#### 2.2.1. Laboratory equipment

The Rotary-evaporator was Heidolph Laborota 4001, and Nitrogen-evaporator was Organomation N-EVAP. Homogenizer was IKA-WERKE T25 Basic. A 12-port vacuum manifold Visiprep (Supelco, Madrid, Spain) was employed. The domestic microwave oven was WG800TL23-2W (Galanz Co., China). The water bath was HH-W420 (Jingbo Instrument Co., China).

#### 2.2.2. GC–MS

The system was Hewlett-Packard 6890 equipped with mass selective detector 5973 and 7683 autosampler. The capillary column was 30 m × 0.25 mm I.D, DB-5MS and with 0.25 μm film thickness (Agilent Technology Inc., USA).

The oven temperature program was: initial temperature isothermal at 50 °C for 1 min, then from 50 °C to 200 °C at 15 °C $min^{-1}$, then hold 5 min at 200 °C, then from 200 °C to 280 °C at 10 °C $min^{-1}$, then hold 5 min at 250 °C .

- Injector temperature was 280 °C .
- Carrier gas was Helium with constant flow rate (1.0 mL $min^{-1}$).
- Injector volume was 1.0 μL with splitless mode.
- Temperature of transfer line was 260 °C.
- Ion source was EI (70 eV, 230 °C).
- Temperature of quadrupole was 150 °C.
- Electron multiplier voltage was 1800 V.
- Scan mode was full scan (35–500 *m/z*) and selected ion monitoring (SIM) mode.

Analysis was performed with SIM based on the use of target and qualifier ions. Herbicides are identified according to the retention times, target ions and qualifier ions. The target and qualifier abundances were determined by injection of individual herbicide standards under the same chromatographic conditions in full scan from *m/z* 35 to 500. Quantification was based on the peak area ratio of the target ion divided by the peak area of the standard. Retention times, target ions and qualifier ions of 16 herbicides are listed in Table 3 and chromato gram of a standard solution of 16 herbicides is in Fig 1.

### 2.3. Sample preparation

Twenty-five grams of onion slices were weighed in a jar and heated in a microwave oven for 30 s, then rapidly cooled in an ice–water bath, and homogenized at 18,000 rpm for 1 min in a homogenizer. The resulting

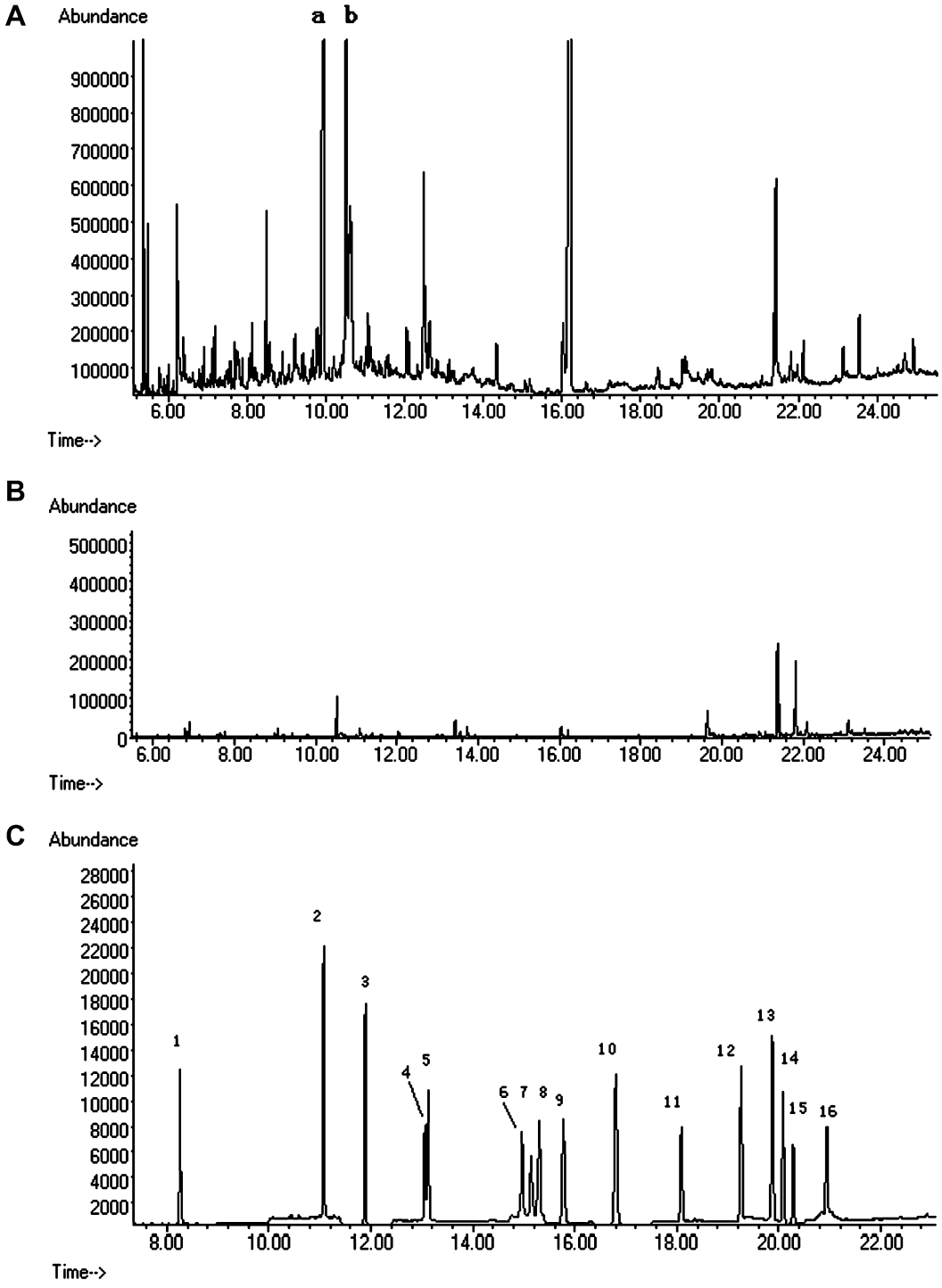


Fig. 1. (A) GC/MS (full scan) chromatogram of untreated onion. (a) *cis*-3,4-Diethyl-1,2,5-trithiane; (b) *trans*-3,4-Diethyl-1,2,5-trithiane. (B) GC/MS (full scan) chromatogram of onion pretreated by microwave oven. (C) GC/MS (SIM) chromatogram of a standard solution with 0.05 μg $mL^{-1}$ of 16 herbicides. Target compounds are numbered as follows: 1. Chlorotoluron; 2. Molinate; 3. Trifluralin; 4. Simazine; 5. Atrazine; 6. Acetochlor; 7. 2,4-D butylate; 8. Alachlor; 9. Prometryn; 10. Metolachlor; 11. Pendimethalin; 12. Butachlor;13. Pretilachlor; 14. Oxadiazon; 15. Oxyfluorfen; 16. Nitrofen.

extract was filtered in the 100 mL graduated flask along with 15 g NaCl, shaken vigorously for 1 min then allowed to settle for 30 min to separate. The 50 mL upper layer was evaporated on a rotary evaporator to near dryness for clean-up.

### 2.4. Clean-up

Ten milliliters acetone/n-hexane (1:9 v/v) was added to condition the dry SPE column. The florisil cartridge for SPE was loaded with the extract after being activated

Table 1
Inactivation of alliinase activity (%) by pretreatment with microwave for various times

| Pretreatment time (sec) | Weight of onion (g) | | |
|---|---|---|---|
| | 25 | 50 | 100 |
| 15 | 22% | – | – |
| 20 | 1.5% | – | – |
| 25 | 0.2% | 25% | – |
| 30 | 0.1% | 15% | – |
| 40 | – | 2% | – |
| 50 | – | 0.2% | – |
| 60 | – | 0.1% | 30% |
| 80 | – | – | 2.5% |
| 100 | – | – | 1.5% |
| 120 | – | – | 0.2% |

and eluted with 10 mL mixture of acetone/n-hexane (1:9 v/v). Finally, the eluate was reduced to about 5 mL with a gentle nitrogen stream and then made up to 5 mL with *n*-hexane for analysis.

## 3. Results and discussion

### 3.1. Inactivation of alliinase

The interference of sulfur-containing compounds in onion would disappear if alliinase was inhibited. Alliinase showed the highest activity at 30 °C. The activity slowly disappeared with the decrease of temperature to 0 °C, and dropped sharply at temperatures higher than 60 °C. Accordingly, we developed a microwave heating method to inactivate alliinase.

Alliinase activity was evaluated by measuring the amount of a representative sulfide, 3,4-diethyl-1,2,5-trithiane, produced by the action of alliinase in crushed onion (peaks a and b in Fig. 1).

Twenty, 50, and 100 g onion slices were heated in a microwave oven (800 W) for 15–120 s and assayed for the presence of sulfides. The results are showed in Table 1. The degree of alliinase inactivation was proportional to the amount of sample and the time of microwave heating. When the ratio of microwave heating time and sample amount was higher than 1.0 s $g^{-1}$ at intensity (800 W), the enzyme lost its activity completely. So the sample quantity with this method was not too high. When more than 50 g were microwaved, heating asymmetry resulted.

### 3.2. Herbicides' stability

The stability of herbicides mostly depends on their own properties and different factors such as temperature. Therefore, it was important to study microwave heating conditions. Twenty-five and 50 g onion slices were fortified a mixed standard solution at concentrations of 0.1 mg $kg^{-1}$. After the solvent was naturally air-dried, the samples were heated in the microwave oven (800 W) for different times, and analyzed for herbicide recovery. The data are presented in Table 2.

The results indicated that recovery was related to sample quantity and heating time. Increased heating time reduced the recovery of all herbicides, but had the greatest effect on Molinate, Trifluralin, 2,4-Dbutylate, Pendimethalin, Oxyfluorfen, and Nitrofen. All the recoveries were higher than 75% when the ratio of heating time to gram of onion was 1.0 s $g^{-1}$ and all the recoveries were higher than 70% when the ratio was 1.2 s $g^{-1}$. However, when the ratio was higher than 1.2 s $g^{-1}$, most analytical recoveries were less than 70% because the herbicide degraded with increased heating time. Moreover, it was essential to chill the samples quickly in an ice–water bath after heating to avoid low recovery.

### 3.3. Pretreatment conditions

From tests of alliinase inactivation and herbicide stability, we found conditions suitable for testing herbicide

Table 2
Recovery (%) of 16 herbicides in 25 g and 50 g onion samples pretreated by microwave oven for different times

| Compound | Pretreatment time (25 g onion slices) | | | | Pretreatment time (50 g onion slices) | | | |
|---|---|---|---|---|---|---|---|---|
| | 25 s | 30 s | 40 s | 50 s | 50 s | 60 s | 80 s | 100 s |
| Chlorotoluron | 90.6 | 88.6 | 73.9 | 70.5 | 95.3 | 82.5 | 65.6 | 62.5 |
| Molinate | 88.4 | 90.8 | 75.5 | 64.3 | 79.8 | 82.5 | 70.6 | 69.9 |
| Trifluralin | 85.5 | 74.5 | 66.8 | 47.8 | 88.2 | 74.3 | 65.9 | 35.5 |
| Simazine | 92.5 | 85.1 | 78.5 | 70.6 | 97.6 | 86.6 | 71.5 | 74.0 |
| Atrazine | 96.7 | 90.5 | 84.8 | 91.6 | 95.6 | 79.5 | 82.4 | 79.0 |
| Acetochlor | 98.7 | 86.7 | 85.0 | 79.5 | 98.5 | 92.5 | 88.4 | 79.7 |
| 2,4-D-butylate | 75.9 | 70.9 | 55.4 | 30.9 | 80.4 | 72.8 | 61.4 | 42.3 |
| Alachlor | 97.1 | 85.7 | 90.2 | 85.0 | 98.2 | 104.5 | 91.6 | 88.6 |
| Prometryn | 105.3 | 90.4 | 87.9 | 80.0 | 101.6 | 91.4 | 84.2 | 78.4 |
| Metolachlor | 99.8 | 91.7 | 85.9 | 79.4 | 89.0 | 94.6 | 88.6 | 93.5 |
| Pendimethalin | 80.7 | 85.6 | 67.5 | 68.8 | 82.6 | 76.2 | 65.1 | 50.6 |
| Butachlor | 102.6 | 95.8 | 84.2 | 71.5 | 98.3 | 92.1 | 80.4 | 83.9 |
| Pretilachlor | 90.9 | 85.7 | 92.4 | 88.2 | 95.5 | 100.5 | 86.3 | 74.0 |
| Oxadiazon | 82.5 | 78.8 | 80.3 | 76.6 | 80.6 | 84.3 | 73.1 | 68.8 |
| Oxyfluorfen | 96.7 | 89.0 | 68.8 | 63.4 | 78.4 | 70.6 | 62.8 | 50.9 |
| Nitrofen | 97.8 | 82.7 | 65.8 | 63.6 | 92.2 | 89.9 | 70.8 | 64.5 |

Table 3
Retention time (RT, min), Monitor ions, Recovery results (%) ± RSD (%), LOD, LOQ and correlation coefficients ($r^2$) of the herbicides studied

| Compound | RT (min) | Monitor ions ($m/z$)* | Recovery (%) ± RSD (%) ($n = 5$) (mg/kg) | | | LOD (mg/kg) | LOQ (mg/kg) | $r^2$ |
|---|---|---|---|---|---|---|---|---|
| | | | 0.02 | 0.1 | 0.5 | | | |
| Chlorotoluron | 8.25 | 132, 167, 104 | 80.5 ± 9.2 | 90.5 ± 2.5 | 97.5 ± 2.5 | 0.003 | 0.010 | 0.9991 |
| Molinate | 11.06 | 126, 187, 55 | 76.9 ± 8.8 | 81.5 ± 10.2 | 89.1 ± 6.2 | 0.002 | 0.006 | 0.9983 |
| Trifluralin | 11.87 | 306, 264, 335 | 78.5 ± 5.5 | 89.0 ± 7.8 | 89.0 ± 6.3 | 0.003 | 0.010 | 0.9958 |
| Simazine | 13.02 | 201, 186, 173 | 92.1 ± 3.7 | 92.4 ± 6.9 | 101.9 ± 2.9 | 0.002 | 0.006 | 0.9972 |
| Atrazine | 13.09 | 200, 215, 173 | 103.5 ± 10.7 | 90.4 ± 5.3 | 97.6 ± 4.7 | 0.002 | 0.006 | 0.9989 |
| Acetochlor | 14.94 | 146, 223, 162 | 95.6 ± 8.3 | 95.7 ± 6.6 | 98.3 ± 3.8 | 0.002 | 0.006 | 0.9993 |
| 2,4-D-butylate | 15.11 | 276, 175, 220 | 69.2 ± 9.7 | 78.2 ± 5.1 | 81.3 ± 4.3 | 0.005 | 0.015 | 0.9976 |
| Alachlor | 15.27 | 160, 188, 237 | 89.9 ± 3.7 | 92.0 ± 7.0 | 97.6 ± 4.6 | 0.002 | 0.006 | 0.9988 |
| Prometryn | 15.72 | 241, 184, 226 | 95.3 ± 4.3 | 101.9 ± 6.5 | 98.1 ± 2.4 | 0.0015 | 0.005 | 0.9995 |
| Metolachlor | 16.77 | 162, 238, 211 | 92.2 ± 7.7 | 94.9 ± 5.2 | 96.8 ± 1.8 | 0.001 | 0.003 | 0.9985 |
| Pendimethalin | 18.07 | 252, 281, 220 | 76.6 ± 8.0 | 83.4 ± 6.1 | 81.0 ± 5.9 | 0.003 | 0.010 | 0.9978 |
| Butachlor | 19.24 | 176, 160, 188 | 93.8 ± 6.7 | 98.0 ± 1.2 | 95.8 ± 2.4 | 0.0015 | 0.005 | 0.9990 |
| Pretilachlor | 19.85 | 238, 162, 176 | 105.0 ± 4.5 | 96.7 ± 3.9 | 101.0 ± 1.9 | 0.001 | 0.003 | 0.9966 |
| Oxadiazon | 20.06 | 175, 258, 344 | 80.0 ± 8.8 | 87.4 ± 5.5 | 92.5 ± 2.0 | 0.002 | 0.006 | 0.9968 |
| Oxyfluorfen | 20.26 | 252, 300, 361 | 91.8 ± 5.9 | 89.8 ± 4.4 | 96.7 ± 1.9 | 0.003 | 0.010 | 0.9992 |
| Nitrofen | 20.92 | 283, 202, 253 | 77.4 ± 8.0 | 84.6 ± 4.9 | 93.1 ± 6.2 | 0.003 | 0.010 | 0.9979 |

* Ions which are underlined are target ions, the others are qualifier ions.

residues in onions. Fig. 2 shows that a microwave time of 1–1.2 s $g^{-1}$ of onion was sufficient to eliminate interferences and to yield adequate recoveries.

### 3.4. Recovery, LOD and LOQ, linearity

The blank samples (25 g) were spiked with 16 herbicides at concentrations of 0.02, 0.1, 0.5 mg $kg^{-1}$ and the samples were heated in a microwave oven for 30 s, then extracted with acetonitrile and cleaned up with Florisil SPE, finally detected by GC–MS. The recovery of each herbicide was replicated five times and the data are presented in Table 3. The table shows that the recoveries were in the range 69.2–105.0%, the relative standard deviation (RSD) ($n = 5$) varied from 1.2% to 10.7%. The method is applicable for the determination of sixteen pesticides in onion.

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. Table 3 summarizes the detection and quantification limits obtained for each herbicide.

The linearity of all the herbicides was satisfied with $r^2 > 0.995$ from 0.01 μg $mL^{-1}$ to 5.0 μg $mL^{-1}$. Correlation coefficients of each herbicide are presented in Table 3.

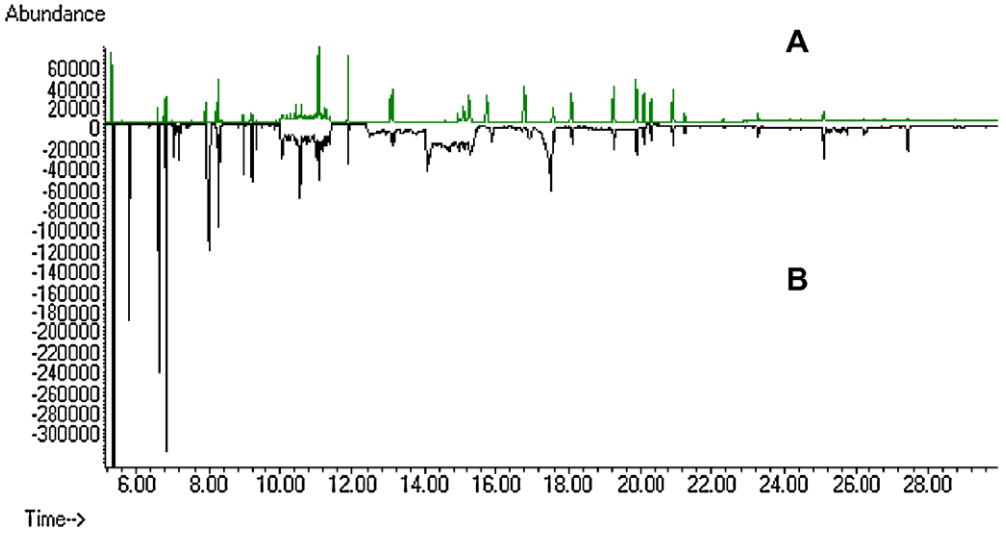


Fig. 2. Comparison of chromatograms: chromatogram A (upper) onion extract spiked with 0.02 mg $kg^{-1}$ herbicide mixture after pretreatment with microwave; chromatogram B (lower) onion extract spiked with 0.02 mg $kg^{-1}$ herbicide mixture but without microwave pretreatment.

Table 4
Herbicide concentrations (mg kg$^{-1}$) of real onion samples coming from onion plantation in Shandong province of China

| Compound | Real onion sample | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| Chlorotoluron | ND | ND | ND | ND | ND | ND |
| Molinate | ND | ND | ND | ND | ND | ND |
| Trifluralin | ND | ND | ND | ND | 0.078 | ND |
| Simazine | ND | ND | ND | ND | ND | ND |
| Atrazine | ND | ND | ND | ND | ND | ND |
| Acetochlor | ND | ND | 0.033 | ND | ND | ND |
| 2,4-D-butylate | ND | ND | ND | ND | ND | ND |
| Alachlor | ND | ND | ND | ND | ND | ND |
| Prometryn | ND | ND | ND | 0.10 | ND | ND |
| Metolachlor | ND | ND | ND | ND | ND | ND |
| Pendimethalin | ND | ND | ND | ND | ND | ND |
| Butachlor | ND | ND | ND | ND | ND | ND |
| Pretilachlor | ND | ND | ND | 0.015 | ND | ND |
| Oxadiazon | ND | ND | ND | ND | ND | ND |
| Oxyfluorfen | ND | ND | ND | ND | ND | ND |
| Nitrofen | ND | 0.022 | ND | ND | ND | ND |

### 3.5. Real samples

Six samples were obtained from an onion production base in Shandong province of China and assayed for herbicide content according to the method described above. The results are shown in Table 4. It was clear that five kinds of herbicides were detected in four samples, with values range from 0.015 to 0.10 mg kg$^{-1}$.

## 4. Conclusion

A rapid multi-residue method was developed for the determination of 16 herbicides in onion. On the basis of the results it could be stated that a microwave processing method before the onion bulbs were crushed could make alliinase lose its activity, which eliminated the interference from alliinase sulfo products. Strict microwave processing time may keep herbicides stable in the experiment. Treated onions were extracted with acetonitrile and cleaned by SPE; GC-MS/SIM was used to determine the herbicide residues. All herbicide recoveries ranged from 69.2 to 105.0% and relative standard deviations were in the range 1.2–10.7% for spiked samples. The limits of quantification below 0.02 mg kg$^{-1}$ were achieved with this procedure. In a word, this analytical method opens a fast, convenient and economical approach to determine herbicide residues levels in onion.

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