Analysis of triallate residue and degradation rate in wheat and soil by liquid chromatography coupled to tandem mass spectroscopy detection with multi-walled carbon nanotubes

Pengyue Zhao, Baoyong Huang, Kejia Gu, Nan Zou and Canping Pan

ABSTRACT
A modified quick, easy, cheap, effective, rugged and safe (QuEChERS) method for the analysis of triallate residue in wheat and soil was developed and validated. Multi-walled carbon nanotubes were used as clean-up sorbent. The residual levels and dissipation rates of triallate in wheat and soil were determined by liquid chromatography–tandem mass spectrometry. The limit of quantification was established as 0.01, 0.02 and 0.05 mg kg\(^{-1}\) for soil, wheat and wheat plant samples, respectively. The average recoveries of triallate ranged from 77% to 108% at fortified levels of 0.01–0.5 mg kg\(^{-1}\) with relative standard deviations of 3.0–8.4% (\(n = 5\)). From residue trials at three geographical experimental plots in China, the results showed that the half-lives of triallate in soils were 1.13–1.63 days. For trials applied according to the label recommendation, the final residues of triallate in wheat at harvest time were all below 0.05 mg kg\(^{-1}\) (the maximum residue levels of China, Japan, Korea and the US).

ARTICLE HISTORY
Received 20 September 2014
Accepted 3 October 2015

KEYWORDS
Triallate; multi-walled carbon nanotubes; dissipation; final residue; wheat

1. Introduction
Wheat (Triticum spp.) is one of the most popular crops in China, which is the third leading crop in China after rice (Oryza sativa) and maize (Zea mays) [1]. It is also one of the major crops in Chinese daily life. Wheat grain contains a lot of water, protein, carbohydrates, dietary fibre, minerals, fats and so on [2]. It can be grounded into flour to make bread, biscuits, cakes, pasta and noodles, for fermentation to make beer, other alcoholic beverages or biofuel and even the wheat straw can be used as fertiliser and feedstuff.

Triallate, S-2,3,3-trichloroallyl diisopropyl(thiocarbamate), with CAS number of [2303-17-5], belongs to the thiocarbamate chemical class producing a peripheral neuropathy (degeneration of nerve fibres) in experimental animals. Triallate chemical properties are as followed: water solubility 4.0 g mL\(^{-1}\), vapour pressure 16 mPa (25°C). It is a pre-emergent
herbicide used on barley, lentils, peas, triticale, wheat and canary grass (seed only) in the
fall or in the spring before targeted weed species germinate [3]. The chemical structure is
shown in Figure 1. It is a systemic herbicide inhibiting cell division and elongation in the
seedling shoots before emergence from the ground [4]. It was reported that 2,3,3-trichloro-
prop-2-en-sulfonic acid was a main metabolite for triallate [5]. The maximum residue limit
(MRL) established by China, Japan, Korea and the US for triallate in wheat is 0.05 mg kg\(^{-1}\). In
the EU, MRL for triallate has been set to 0.1 mg kg\(^{-1}\) in wheat [6].

Recently, few analytical methods have been reported for the determination of trial-
late. Traditionally, the vast majority of separation and analysis of triallate were per-
formed by gas chromatography or gas chromatography–tandem mass spectrometry
[7,8]. Several kinds of solvents were used to extract triallate, such as methanol, water–
acetonitrile and supercritical carbon dioxide [8,9,10]. During the clean-up procedure,
solid-phase extraction was the most popular method to remove the interferences from
the sample matrices [8,9,11]. In addition, the most common samples studied were soil,
honey and barley seedling, and no report on wheat sample has been published.

Since the first report in 1991 [12], carbon nanotubes (CNTs) have shown great possibi-
lities for a wide variety of processes and applications, which include their use as electrodes,
sensors (gas, enzymatic, etc.), nanopores, electronic materials, field emitters and so on. In
our previous study, it was shown that multi-walled carbon nanotubes (MWCNTs) could be
used as alternative reversed-dispersive solid-phase extraction (r-DSPE) sorbents to primary
secondary amine (PSA) or C18 in pesticide residue analysis in vegetable and fruit samples
[13,14]. They were also mixed with graphitised carbon black and PSA for r-DSPE clean-up of
acetonitrile extracts from tea samples [15].

In this study, we aimed to establish a modified quick, easy, cheap, effective, rugged and
safe (QuEChERS) preparation approach based on MWCNTs with highly selective liquid
chromatography–tandem mass spectrometry (LC-MS/MS) for the analysis of triallate in
wheat, wheat plant and soil. The dissipation dynamics of triallate in soil were investigated,
as well as the final residue in wheat, wheat plant and soil. The purpose of this paper was to
study the ultimate residue and dissipation rate of triallate in a wheat field ecosystem.

2. Experimental

2.1. Chemicals and equipment

Triallate standard material (purity 99.5%) and formulations (40% Triallate CS) were
supplied by China Agricultural University, Beijing, China. Acetonitrile of high
performance liquid chromatography (HPLC) grade was procured from Fisher Chemicals (USA). Deionised water was obtained from a Milli-Q water purification system (Millipore, USA). Analytical reagent grade anhydrous sodium chloride (NaCl) and magnesium sulfate (MgSO₄) were obtained from Sinopharm Chemical Reagent (Beijing, China). MWCNTs with average external diameters of 10–20 nm were provided by Tianjin Agela Co. Ltd (China).

An Agilent 6410 QqQ LC/MS was used to analyse the residue of triallate. Centrifugation was performed in two different instruments: an Anke TDL-40B centrifuge equipped with a bucket rotor (8 mL × 50 mL) (Shanghai, China) and a Sigma 3K15 microcentrifuge equipped with an angular rotor (24 mL × 2.0 mL) (BMH Instruments Co. Ltd, China). BS1100S analytical balance (Sartorius, Germany), IKA A11-basic grinder (IKA, Germany) and QL-901 Vortex (Kylin-bell Lab Instruments Co. Ltd, Jiangsu, China) were used for sample preparation.

2.2. Field experiment design

Field experiments including the residue dynamic and final residue in supervised field trials were designed according to recommendations on the pesticide label and were conducted in Beijing, Hunan and Jiangsu during 2012 according to ‘Guideline on pesticide residue trials’ [16] issued by the Institute of the Control of Agrochemicals, Ministry of Agriculture, the People’s Republic of China. Each experiment field consisted of three replicate plots and a control plot which was separated by irrigation channels; the area of each plot was 30 m² (10 m × 3 m). The distance between plots was kept at 1 m. According to the climatic conditions in different regions of China, the field experiment started in October in Beijing and in November in Hunan and Jiangsu. Winter wheat (Triticum aestivum) was used in the field experiments.

For dissipation experiments, 1800 g a.i/ha (1.5 times of the recommended dosage) was applied once on the wheat plant. A manual backpack-type sprayer (Seesa SX-LK-16, 16L, China) was used in the field experiments. Soil dissipation samples were collected at 2 h, 1, 3, 5, 7, 14, 21, 30 and 45 days after spraying. The climatic data at three sites during the residue dynamic trials are shown in Table 1.

The final residue experiments were carried out with a low dosage level of 1200 g a.i/ha (recommended dosage) and a high dosage level of 1800 g a.i/ha (1.5 times of the recommended dosage), respectively. Each dosage level was designed to spray one time. Spraying was conducted after sowing, and then the ground was covered with soil. Three replicates were carried out for each treatment and another untreated same size plot was used as a control. Representative wheat, wheat plant and soil samples (1 kg) were collected from each plot after maturity (about 6 months).

2.3. Analytical procedure

2.3.1. Sampling and the modification of QuEChERS procedure

Soil samples were collected randomly from each plot using a soil auger to a depth of 0–15 cm. Small stones and other unwanted materials were removed. They were dried in the shade for 24 h at room temperature (25°C) and sieved through a 40-mesh sieve. Wheat plant samples were cut into small pieces and then ground with a blender. Wheat
### Table 1. Climatic data at three sites during the residue dynamic trials.

|        | Beijing |                | Hunan |                | Jiangsu |                |
|--------|---------|----------------|-------|----------------|---------|----------------|
|        | Days    | Temperature (°C) | Weather | Rainfall amount (mm) | Days    | Temperature (°C) | Weather | Rainfall amount (mm) | Days    | Temperature (°C) | Weather | Rainfall amount (mm) |
|        |         |                 |         |                  |         |                 |         |                  |         |                 |         |                  |
| 2 h    | 9–18    | Cloudy          | 0       | 8–11             | Rainy   | 1.1             | 7–15    | Sunny            | 0       |
| 1 day  | 11–22   | Sunny           | 0       | 9–12             | Rainy   | 1.4             | 6–16    | Cloudy           | 0       |
| 3 days | 6–15    | Cloudy          | 0       | 7–12             | Rainy   | 3               | 5–14    | Sunny            | 0       |
| 5 days | 2–14    | Sunny           | 0       | 7–12             | Cloudy  | 0               | 11–20   | Cloudy           | 0       |
| 7 days | 3–15    | Sunny           | 0       | 9–14             | Cloudy  | 0               | 14–22   | Cloudy           | 0       |
| 14 days| 1–11    | Rainy           | 1.0     | 4–18             | Sunny   | 0               | 8–13    | Cloudy           | 0       |
| 21 days| 1–11    | Sleety          | 1.2     | 6–11             | Cloudy  | 0               | 2–10    | Sunny            | 0       |
| 30 days| –7 to 1 | Cloudy          | 0       | 0–4              | Rainy   | 2.2             | –2 to 9 | Cloudy           | 0       |
| 45 days| –1 to –3| Snowy           | 2.1     | –2 to 0          | Sleety  | 3               | –2 to 5 | Sunny            | 0       |
samples were ground to powder. All samples (200 g of soil, 100 g of wheat plant and 100 g of wheat seed) were stored at −20°C until analysed.

For recovery test, the homogenised blank samples (10 g of soil, 5 g of wheat and 5 g of wheat plant) were spiked by the addition of the standard stock solutions (10 mg L⁻¹). The spiked samples were set aside for 30 min before extraction to allow the analyte fully permeate into the blank matrix. Both the blank samples and matrix-matched calibration solutions were prepared from soil and plant control samples.

A certain amount of previously homogenised samples (10 g of soil, 5 g of wheat and 5 g of wheat plant) were introduced into a 50 mL centrifuge tube, and then a small amount of water was added depending on the types of samples (2 mL of soil, 5 mL for wheat and wheat plant samples). The samples were allowed to stand for 5 min before extraction. After that, 10 mL of acetonitrile was added, and the tube was shaken vigorously for 1 min with a vortex mixer, ensuring that the solvent interacted well with the entire sample. Anhydrous NaCl (1 g) and anhydrous MgSO₄ (4 g) were added to the mixture. The shaking step was repeated for 1 min and then the tube was centrifuged for 5 min at 3802×g. A 1 mL of acetonitrile layer was transferred into a 2 mL microcentrifuge tube, which contained 5 mg of MWCNTs sorbent and 150 mg of MgSO₄. The sample was mixed vigorously by vortex for 1 min and centrifuge extracted for 3 min at 13,366×g. Acetonitrile layer was filtered through a 0.22 μm filter membrane and transferred into autosampler vial for LC-MS/MS analysis.

2.3.2. LC-MS/MS analysis
An Agilent 1200 HPLC (Agilent Technologies, USA), equipped with a degasser and an autosampler, was used for the chromatographic analysis. Separation was achieved on an Eclipse Plus C18 column, 50 mm × 2.1 mm, 3.5 μm (Agilent), with a flow rate of 0.3 mL min⁻¹. The isocratic elution condition employed a mobile phase of acetonitrile and 0.1% formic acid in ultrapure water (v/v = 80:20). The injection volume was 10 μL, and column temperature was maintained at 30°C. Nitrogen was used for both nebulizer and collision gas. The mass spectrometric parameter option was initially performed by full scan and selected ion scan for the compounds. The [M + H]⁺ ion was chosen as the precursor ion for triallate. Product ion mass spectra were obtained in electrospray ionisation using collision-induced dissociation and the collision energy was optimised for two selective ion transitions. Both pairs of multiple reaction monitoring (MRM) transitions (m/z 304→m/z 143, m/z 304→m/z 86) were used for confirmation analysis, which met the requirements of the EU decision [17], and the most sensitive transition (m/z 304→m/z 143) was selected for quantification analysis. For these two transitions, the dwell times were both 300 ms, fragmentor was 120 V and the collision energy was 25 and 15 eV, respectively. The drying gas temperature was 350°C with the flow rate of 8.0 L min⁻¹. The nebulizing gas pressure was 35 psi.

2.3.3. Statistical analysis
The dissipation process follows the first-order kinetic reaction. The degradation rate constant was calculated using the first-order rate equation: \( C_t = C_0e^{-kt} \), where \( C_t \) represents the concentration of the pesticide residue at time \( t \), \( C_0 \) represents the initial concentration after application and \( k \) is the dissipation degradation rate constant (days). The half-life (\( t_{1/2} \)) was calculated from the \( k \) value for each experiment (\( t_{1/2} = \ln 2/k \)).
3. Results and discussion

3.1. Optimisation of extraction procedure

Taking into account that according to the QuEChERS method samples with a water content between 25% and 80% require the addition of water to achieve the same amount of sample and water, the addition of water was considered [18]. A certain amount of water was added to achieve sufficient partition of the target analytes among the matrix, water and an organic solvent such as acetonitrile. The water contents of wheat and wheat plant sample were 10–13%, and the soil samples were dried in the shade at room temperature before extraction (moisture: 4%). Due to the low content of water in wheat and wheat plant, it might be necessary to add a small amount of water to the samples before the analytes are extracted by acetonitrile. To evaluate the effect of water, different amounts of water were investigated with the same extraction procedure. The amount of water was progressively increased from 0 to 5 mL (i.e. 0, 1, 2, 3 and 5 mL). As shown in supplementary table S1, for wheat and wheat plant samples, the recoveries of triallate increased gradually to 93–107% as the amount of water increased. For soil samples, 2 mL of water was enough to obtain the best recoveries (83–108%). Therefore, 5 mL of water for wheat and wheat plant samples and 2 mL of water for soil samples were added before extraction, which was used in the study.

3.2. Optimisation of clean-up procedure

In our previous study, we found that MWCNTs could be used as alternative r-DSPE materials in pesticide multiresidue analysis with the QuEChERS method [13,14] and better clean-up performances were obtained than the other sorbents. The r-DSPE clean-up with MWCNTs was employed to reduce the matrix effects (MEs). In this study, in order to find out the optimum amount of MWCNTs used in the clean-up procedure, the r-DSPE procedure was performed using 1 mL of the acetonitrile extract at the spiked level of 0.5 mg kg\(^{-1}\) for wheat and wheat plant samples. They were placed into 2.0 mL microcentrifuge tubes containing 150 mg MgSO\(_4\) and different amounts of MWCNTs (i.e. 5, 10, 15 and 20 mg). As shown in supplementary table S2, when the amount of MWCNTs increased to 10, 15 and 20 mg, the recoveries decreased gradually. As a result, 5 mg was used as the optimum amount for the r-DSPE clean-up in the further studies since acceptable recoveries were obtained.

3.3. Method validation

The EU SANCO/10684/2009 guidelines [19] were followed in this study. In order to reduce MEs, the linearity of wheat, wheat plant and soil samples was studied by matrix-matched standard calibration method in the range of 0.01–0.25 mg L\(^{-1}\), 0.025–0.5 mg L\(^{-1}\) and 0.01–10 mg L\(^{-1}\), respectively. Linear calibration graphs were constructed by least-squares regression of concentration versus peak area of calibration standards. Linearity values of wheat, wheat plant and soil samples, calculated as determination coefficients (\(R^2\)), were 0.9935–0.9994. Accuracy and precision of the sample preparation method was evaluated by spiking blank samples with triallate working solution.
The occurrence of MEs is regarded as a signal suppression or enhancement of the analyte due to the co-elution of matrix components [20–23], playing an important role in the quality of the quantitative data generated by the method. The ME was measured according to the original work of Matuszewski and Badoud [24,25]. If one depicts the peak areas of triallate obtained in neat solution standards as $A$, the corresponding peak areas for standards spiked after extraction as $B$, the values can be calculated as follows:

$$\text{ME}(%)= \frac{B}{A} \times 100$$

As the ME data listed show in Table 2, almost no ME appeared for soil samples. However, it can be seen the matrix enhancement effect for wheat plant samples and the matrix suppression effect for wheat samples, which was probably due to the different substances or compounds in the wheat and wheat plant samples.

The recovery and reproducibility experiments were carried out for each sample in five replicates at three fortification levels (0.02, 0.05 and 0.5 mg kg$^{-1}$ in wheat, 0.05, 0.2 and 0.5 mg kg$^{-1}$ in wheat plant and 0.01, 0.05 and 0.5 mg kg$^{-1}$ in soil). The average recoveries of triallate were in the range from 77% to 108% with relative standard deviations (RSDs) ≤8.4%, as shown in Table 2.

The limits of detection (LODs) and limits of quantification (LOQs) were calculated as the concentration giving signal-to-noise ratios of 3 ($S/N = 3$) and 10 ($S/N = 10$), respectively, which was analysed by the MassHunter Workstation software qualitative analysis version B.03.01/build 3.1.346.0 and Microsoft Excel. Quantification was accomplished using the standard curve constructed by plotting analyte concentrations against peak areas. LOQ was used for the determination of these parameters.

**Figure 2** shows a total ion current chromatogram, an MRM chromatogram with the transition of $m/z$ 304→$m/z$ 86 and an MRM chromatogram with the transition of $m/z$ 304→$m/z$ 143 for a wheat sample, respectively. All control samples showed no evidence of chromatographic interference.

In the previous studies [9,11], LODs for soil and cereal samples were 0.01–0.02 mg kg$^{-1}$, and in the proposed method, lower LODs and LOQs of 0.003–0.005 mg kg$^{-1}$ were obtained. MWCNTs were used as r-DSPE sorbents combined with the QuEChERS

### Table 2. Average recovery, calibration curve, matrix effect, LODs and LOQs of triallate in the wheat, wheat plant and soil samples ($n = 5$).  

| Samples  | Fortified level (mg kg$^{-1}$) | Average recovery (%) | RSD (%) | Calibration curve | $R^2$ | Matrix effect (%) | LOD (mg kg$^{-1}$) | LOQ (mg kg$^{-1}$) |
|----------|-------------------------------|----------------------|---------|--------------------|------|------------------|-------------------|-------------------|
| Wheat    | 0.02                          | 93                   | 6.7     | $y=(11586 \pm 1002)$ | 0.9935 | 67.7             | 0.003             | 0.02              |
|          | 0.05                          | 89                   | 7.6     | $x=(223.84 \pm 18.43)$ |       |                  |                   |                   |
|          | 0.5                           | 77                   | 3.9     |                    |       |                  |                   |                   |
| Wheat plant | 0.05                         | 107                  | 5.3     | $y=(28098 \pm 2142)$ | 0.9976 | 120              | 0.005             | 0.05              |
|          | 0.2                           | 104                  | 3.0     | $x=(53.343 \pm 4.53)$ |       |                  |                   |                   |
|          | 0.5                           | 96                   | 5.1     |                    |       |                  |                   |                   |
| Soil     | 0.01                          | 83                   | 8.4     | $y=(19190 \pm 1764)$ | 0.9994 | 93.5             | 0.003             | 0.01              |
|          | 0.05                          | 108                  | 5.6     | $x=(228.52 \pm 17.66)$ |       |                  |                   |                   |
|          | 0.5                           | 103                  | 5.9     |                    |       |                  |                   |                   |
preparation method for the extraction of triallate, instead of SPE, which was more tedious and costly. In this study, comparable recoveries with the other clean-up methods were obtained.

3.4. Dissipation of triallate wheat field ecosystem

The data relating to the decline regression equation and half-life are summarised in Table 3. The dissipation curves of triallate in soil samples carried out in Beijing, Hunan and Jiangsu are shown in Figure 3. The residues of triallate were detected after the application of pesticide. The dissipation process follows the first-order kinetic reaction. As shown in Figure 3 and Table 1, the decline of triallate in Hunan was drastic as

Table 3. Half-life and other statistical parameters for triallate dissipation in soil.

| Experiment site | Regression equation  | Determination coefficient ($R^2$) | Degradation constant (day$^{-1}$) | Half-life (days) |
|-----------------|----------------------|----------------------------------|-----------------------------------|-----------------|
| Beijing         | $y = 13.577x^{-0.392}$ | 0.7048                           | 0.392 ± 0.040                     | 1.63 ± 0.19     |
| Hunan           | $y = 3.321x^{-0.624}$  | 0.8210                           | 0.424 ± 0.044                     | 1.55 ± 0.17     |
| Jiangsu         | $y = 11.811x^{-0.649}$ | 0.7461                           | 0.649 ± 0.069                     | 1.13 ± 0.13     |
compared to that in Beijing and Jiangsu because it was rainy in the first three days during the dynamic trials in Hunan while it was sunny or cloudy in Jiangsu and Beijing. Because triallate had a good water solubility at 4.0 g/mL and a high vapour pressure at 16 mPa (25°C), the rainfall has an important effect on the decline. In general, the temperature was the highest in Jiangsu during the residue dynamic trials, so the half-life was the shortest (1.13 days) in this trial site.

The initial deposits of triallate residue in Beijing, Hunan and Jiangsu were 14.1, 10.6 and 12.4 mg kg\(^{-1}\) in soils, which declined to 2.54 (45 days), 0.51 (45 days) and 0.68 (30 days) mg kg\(^{-1}\), respectively, and half-lives were observed to be 1.63, 1.55 and 1.13 days. During

Figure 3. Dissipation curves of triallate in soil samples in the three experiment fields: (a) Beijing, (b) Hunan and (c) Jiangsu.
the first three days, the triallate residue declined faster, as the dissipation rate reached 80.8% (Beijing), 84.9% (Hunan) and 71.7% (Jiangsu), and after 3 days, it declined slowly.

3.5. Final residue of triallate

Wheat, wheat plant and soil samples for the final residue analysis were collected after maturity. In Table 4, it is shown that the final residues of triallate in wheat and wheat plant samples were undetectable at harvest. The residues of triallate in soil samples ranged from 0.01 to 0.072 mg kg\(^{-1}\) at harvest time.

4. Conclusions

A modified QuEChERS–LC-MS/MS method has been successfully applied to the determination of triallate in wheat, wheat plant and soil samples. The recoveries ranged from 77% to 108% with RSDs ≤8.4%. The LOQs of this method were 0.02, 0.05 and 0.01 mg kg\(^{-1}\) for the wheat, wheat plant and soil samples, respectively. The dissipation dynamics showed that triallate dissipated fast in soil, and the half-lives were 1.13–1.63 days. For trials applied according to the label recommendation, the final residues of triallate in wheat could not be detected at harvest time and were all below 0.05 mg kg\(^{-1}\) (the MRL of China, Japan, Korea and the US).

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by an instrumentation special project [no. 2013YQ510391] from the Chinese Ministry of Science and Guangxi Special Invited Scientist (2013) programme in Agric-Environment and Agro-products Safety.

References

[1] F. Wang, Z. He, K. Sayre, S. Li, J. Si, B. Feng and L. Kong, Field Crops Res. 111, 3 (2009). doi:10.1016/j.fcr.2008.12.004.
[2] K. Stuper-Szablewska, M. Buśko, T. Góral and J. Perkowski, Food Chem. 153 (2014). doi:10.1016/j.foodchem.2013.12.059.
[3] F. Broeckaert, A. Li, D. Goldstein, J. Acquavella and M. Martens, Toxicol. Lett. **144** (Supplement 1), s189–s190 (2003).
[4] California Department of Pesticide Regulation Public Report 2007-5. Triallate, Tracking ID Number: 215144 (California Environmental Protection Agency, Sacramento, CA, 2013).
[5] W. Wang, R. Kreuzig and M. Bahadir, Fresenius’ J. Anal. Chem. **360**, 5 (1998).
[6] Global MRL database. (2013). <http://www.globalmrl.com>.
[7] E. Fuentes, M.E. Báez and D. Reyes, Chim. Acta. **578**, 2 (2006).
[8] B. Albero, C. Sánchez-Brunete and J.L. Tadeo, J. Agric. Food Chem. **52**, 19 (2004).
[9] C. Sanchez-Brunete, T. Salto, J.M. Garcia-Baudin and J.L. Tadeo, J. Chromatogr. B **562**, 1 (1991). doi:10.1016/0378-4347(91)80604-B.
[10] J.L. Bernal, J.J. Jiménez, J. Atienza and A. Herguedas, J. Chromatogr. A **754**, 1 (1996). doi:10.1016/S0021-9673(96)00446-3.
[11] P.C. do Nascimento, A.L.B. Rohlfes, D. Bohrer, L.M. de Carvalho and E.J. Pilau, Talanta **65**, 1 (2005). doi:10.1016/S0039-9140(05)00091-3.
[12] S. Iijima, Nature **354** (1991). doi:10.1038/354056a0.
[13] P. Zhao, L. Wang, L. Zhou, F. Zhang, S. Kang and C. Pan, J. Chromatogr. A **1225** (2012). doi:10.1016/j.chroma.2011.12.070.
[14] P. Zhao, L. Wang, J. Luo, J. Li and C. Pan, J. Sep. Sci. **35**, 1 (2012).
[15] P. Zhao, L. Wang, Y. Jiang, F. Zhang and C. Pan, J. Agric. Food Chem. **60**, 16 (2012). doi:10.1021/jf203440b.
[16] Guideline on pesticide residue trials, the Institute of the Control of Agrochemicals, Ministry of Agriculture, the People’s Republic of China (China Agriculture Press, Beijing, 2004).
[17] European Council 2002/657/EC Implementing Council Directive 96/23/EC Concerning the Performance of Analytical Methods and the Interpretation of Results, European Council, Brussels, Belgium, 2002.
[18] A. Michelangelo, J.L. Steven and S. Darinka, J. AOAC Int. **86**, 2 (2003).
[19] European Commission Directorate General Health and Consumer Protection, Guidance Document on Method Validation and Quality Control Procedures for Pesticide ResiduesAnalyses in Food and Feed, SANCO/10684/2009, 1 January, 2010.
[20] C. Jansson, T. Pihlstrom, B.-G. Osterdahl and K.E. Markides, J. Chromatogr. A **1023**, 1 (2004). doi:10.1016/j.chroma.2003.10.019.
[21] A. Kruve, A. Kunnapas, K. Herodes and I. Leito, J. Chromatogr. A **1187**, 1 (2008). doi:10.1016/j.chroma.2008.01.077.
[22] W.M.A. Niessen, P. Manini and R. Andreoli, Mass Spectrum Rev. **25**, 6 (2006). doi:10.1002/mas.20097.
[23] J. Zrostlikova, J. Hajísla, J. Poustka and P. Begany, J. Chromatogr. A **973**, 1 (2002). doi:10.1016/S0021-9673(02)01196-2.
[24] B.K. Matuszewski, M.L. Constanzer and C.M. Chavez-Eng, Anal. Chem. **75**, 13 (2003). doi:10.1021/ac020361s.
[25] F. Badoud, E. Grata, L. Perrenoud, M. Saugy, S. Rudaz and J.-L. Veuthey, J. Chromatogr. A **1217**, 25 (2010). doi:10.1016/j.chroma.2009.11.001.