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# Thermal dissociation atmospheric chemical ionization ion trap mass spectrometry with a miniature source for selective trace detection of dimethoate in fruit juices

Yongzhong Ouyang,[a] Xinglei Zhang,[a] Jing Han,[a] Xiali Guo,[b] Zhiqiang Zhu,[a] Huanwen Chen[a] and Liping Luo*[b]

A miniature thermal dissociation atmospheric chemical ionization (TDCI) source, coupled with LTQ-MS, has been developed for rapid trace detection of pesticide residues such as dimethoate in highly viscous fruit juice samples. Instead of toxic organic solvents and the high electric field used in the conventional ionizations, an ionic liquid, a "green solvent", was employed to directly generate reagent ions in the TDCI process, followed by the proton or charge transfer with the analytes prior to the LTQ instrument for mass analysis. Trace amounts of dimethoate in fresh orange juices have been quantitatively detected, without any sample pretreatment or aid of high-pressure gas. A low limit of detection (LOD = $8.76 \times 10^{-11}$ g $mL^{-1}$), acceptable relative standard deviation (RSD = 3.1–10.0%), and reasonable recoveries (91.2–102.8%) were achieved with this method for direct detection of dimethoate in highly viscous orange juice samples. The average analysis time for each single sample was less than 30 seconds. These experimental results showed that the miniature TDCI developed here is a powerful tool for the fast trace detection of pesticide residues in complex viscous fruit juices, with the advantage of high sensitivity, high speed, and high-throughput, ease of operation, and so on. Because of no chemical contamination and high voltage damage to the analytes and the environment, the technique has promising applications for online quality monitoring in the area of food safety.

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## Introduction

Organophosphorus pesticides are a group of effective insecticides, which have been widely used for decades. As one of the highly yielded organophosphorus pesticides, dimethoate is commonly used to kill insects on contact. Even at relatively low levels of residues in food or the environment, dimethoate may be hazardous to human health due to its high toxicity. To ensure the food safety for the consumers, the maximum residue limit (MRL) of dimethoate in pomegranate was set at 0.02 mg $kg^{-1}$ by the European Union (EU) (http://ec.europa.eu/sanco_pesticides /public/). In recent years, monitoring dimethoate and similar pesticide residues in food has become a very important governmental task in some countries. A wide variety of analytical methods have been developed for determination of pesticide residues in fruits, vegetables, and fruit juices, such as gas chromatography-mass spectrometry,[1–3] liquid chromatography-mass spectrometry,[4–6] liquid–liquid microextraction chromatography,[7] liquid–liquid extraction (LLE),[8] solid-phase microextraction (SPME),[9] matrix solid-phase dispersion method (MSPD),[10] enzyme inhibition,[11] and so on. However, complicated sample pretreatments such as extraction and purification required by these traditional techniques for complex sample analysis make the whole analysis process laborious and time consuming (>40 min), making it difficult to achieve fast detection of pesticide residues in complex food samples. Thus, the development of analytical techniques appropriate for high-throughput, high sensitivity, and nondestructive food analysis is highly desired.

Mass spectrometry (MS) has been considered to be the best "sensor" available for food analysis due to its superior sensitivity and selectivity. Recently developed ambient ionizations are rapidly becoming a growing field attributed to the advantage of minimal or no sample pretreatment for trace compound analysis in complex matrices. Due to the limitations of the desorption electrospray ionization (DESI) method,[12] a variety of ambient ionization methods have been proposed for trace analysis in a complex matrix, such as direct analysis in real time (DART),[13] desorption atmospheric pressure photoionization (DAPPI),[14] atmospheric pressure solids analysis probe (ASAP),[15] dielectric barrier discharge ionization (DBDI),[16] low-temperature plasma (LTP),[17,18] surface desorption atmospheric pressure chemical ionization (DAPCI),[19] atmospheric pressure glow discharge desorption ionization (APGDI),[20] fused-droplet

[a]*Jiangxi Key Laboratory for Mass Spectrometry and Instrumentation, East China Institute of Technology, Nanchang, Jiangxi Province 330013, P. R. China*
[b]*State Key Laboratory of Food Science and Technology, School of Life Sciences and Food Engineering, Nanchang University, Nanchang, Jiangxi 330047, P. R. China. E-mail: lluo2@126.com; Fax: +86-791-83969519; Tel: +86-791-83969519*

electrospray ionization (FD-ESI),[21] electrospray assisted laser desorption/ionization (ELDI),[22] extractive electrospray ionization (EESI),[23,24] easy ambient sonic ionization (EASI),[25] plasma assisted multiwavelength laser desorption ionization (PAMLDI-MS),[26] and so on. These techniques can be usually divided into two categories based on the chosen ionization methods: atmospheric pressure chemical ionization-based (APCI) and electrospray ionization-based (ESI) ambient ionization techniques.[27] However, the use of organic solvents (*e.g.*, methanol) as electrospray solutions can pollute food samples for ESI-based ambient ionization (ESI) techniques (*e.g.*, DESI, FD-ESI, EESI, ELDI, *etc.*). The high-voltage or high electric field (*e.g.*, DART, LTP, DAPCI, APGDI, PAMLDI-MS, *etc.*) applied in the APCI-related methods (APCI) can cause damage to the practical food samples (*e.g.*, fresh meat, vegetables, fruit juice, *etc.*) analysis to some extent. In a sense, all these techniques are not the ideal ionization sources favorable for food sample analysis.

In our previous study[28] a simple ambient ionization technique, thermal dissociation atmospheric chemical ionization (TDCI) method, in which an ionic liquid instead of high-voltage or high electric field was used for primary ion formation, was proposed for fast detection of complex food samples. A wide variety of analytes including polar (*e.g.*, amino acids) and non-polar (*e.g.*, naphthalene) have been successfully detected and identified.[28] In this study, a home-made miniature TDCI source coupled to an ion trap mass spectrometer has been developed for trace detection of pesticide residues (dimethoate) in fruit juice samples. An ionic liquid, 1-butyl-3-methylimidazolium bromide salt, was employed for ionization of dimethoate in orange juices under ambient conditions. The present study showed that the TDCI-MS developed here is a promising tool for fast trace detection of pesticide residues such as dimethoate in highly complex heterogeneous samples, with the advantages of high sensitivity, high-throughput, nondestructiveness, and ease of operation. Because of no chemical contamination and high voltage damage to the analytes and the environment, it is especially useful for fast analysis of food samples with a complex matrix.

## Experimental

### Instrumental setup

The experimental apparatus used for ion thermal dissociation at atmospheric pressure consisted of a commercial linear ion trap mass spectrometer (LTQ-XL, Finnigan, and San Jose, CA) and a home-made miniature TDCI source with an atmospheric pressure interface including a heated transfer capillary (Fig. 1). A stainless steel cylindrical tube (8.8 mm outer diameter, 6.8 mm inner diameter, length 4.5 cm) wrapped with metal heating wire (nichrome: 80% nickel, 20% chromium) outside the wall was placed in front of the mass spectrometer as the miniature TDCI source. The distance between the outer end of the tube and the transfer capillary of the mass spectrometer was varied over the range 0.1 to 2 cm. The sample mixtures containing ionic liquids and analytes (1–60 μL) were deposited on the center of the tube to be heated. The temperature of the tube was controlled by adjusting the voltage applied to the heating wire and the

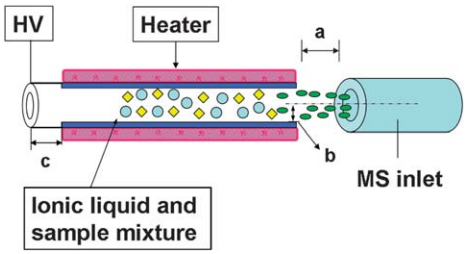


**Fig. 1** Profile map of the TDCI source setup. High concentrations of primary ions were produced from the thermal dissociation of ionic liquids, followed by proton or charge transfer with the analytes in the raw samples with a complex matrix under ambient conditions. Note that the scheme is not proportionally scaled.

temperature of the outer wall of the tube was monitored by a Pt 100 thermocouple sensor. The accuracy of the temperature measurements was better than ±1 °C up to about 600 °C. A thin cylindrical gasket (material: nichrome; dimensions: 8.8 mm o.d., 6.4 mm i.d.; thickness: 0.5 mm) was placed coaxially about 1.5 cm in front of the sample inlet of the source tube. A high voltage of about 3–4 kV was applied to the gasket to enable more ionized ions to be collected into the LTQ ion trap mass spectrometer for mass analysis. The gasket was fixed to the sample inlet of the tube using electrical insulating materials, and thus it was insulated from the stainless steel source tube. A higher signal intensity was observed at smaller distances, probably because more ions from the tube outlet were collected into the MS inlet. The fragment ions emerging from the tube were monitored using the LTQ mass spectrometer. The samples were taken from concentrated solutions, which were prepared in about a 1 : 2 ratio of their volume of the sample and ionic liquid.

The LTQ-XL mass spectrometer was set to run in a positive ion detection mode, and TDCI-MS spectra were acquired in the mass range of $m/z$ 50–600 D. The capillary voltage was set to 44 V, the tube lens voltage was set to 60 V, and the temperature of the LTQ transfer capillary was kept at 150 °C throughout the experiments. Other parameters were automatically optimized by the LTQ-MS system. The ions of interest were isolated with a mass-to-charge window width of 1.6 units for collision-induced dissociation (CID) experiments by applying a collision energy (CE) of 20–30% (arbitrary units defined by the LTQ mass spectrometer). The optimal experimental parameters depend to a large degree on the working mode and physical chemistry properties (*e.g.*, thermal stability, polarity, volatility, *etc.*) of analytes and ionic liquids. Source optimization was performed to achieve the highly stable signal of the dimethoate, and the following optimal conditions of the TDCI source were adopted: the repelling voltage applied in the front end of the tube was 4.0 kV, the temperature of the tube was set at 160.0 °C, the least horizontal linear distance ($a$) from the outlet of the tube to the MS inlet was 0.2 cm and the vertical distance between the low inner wall of the tube and the central axis of the MS inlet ($b$) was 0.4 cm (Fig. 1).

### Materials and reagents

Dimethoate (40% effective concentration) was dissolved in deionized water to prepare stock solutions ($4 \times 10^{-4}$ g mL$^{-1}$).

The dimethoate stock solutions were further diluted using deionized water, and the working solutions were made at $10^{-7}$ to $10^{-11}$ g mL$^{-1}$ for actual measurements. Five different types of orange juice samples were directly prepared for residue analysis by crushing in a blender, without any pretreatment. The whole fruit samples purchased in the local supermarkets of Southeast China were immediately crushed into viscous juice samples without washing or any kind of pretreatment. All juice samples were kept at 4 °C. The ionic liquid of 1-butyl-3-methylimidazolium bromide salt was synthesized following the description in the previous ref. 29. The actual ionic liquid with a concentration of $10^{-6}$ g mL$^{-1}$ solution was used. The water used was deionized water provided by the chemistry facilities in East China Institute of Technology (ECIT).

## Results and discussion

### Investigation of the ionization mechanism

The elimination of organic solvent pollution and damage from high-voltage is one of the most important goals in the field of green chemistry (*e.g.*, food sample analysis). Ionic liquids (ILs) are proving to be increasingly promising as viable media for potential "green" synthesis and catalysis,[30,31] owing to their many excellent physicochemical properties. In this study, a "green solvent", an ionic liquid, was employed for chemical ionization of the pesticide dimethoate in the TDCI process, instead of toxic solvents and high-voltage used as in the ESI or APCI related ionization techniques. Two key steps, thermal evaporation and chemical ionization, are involved in the TDCI process. The heat transferred into the tube first allows emission of cations from the ionic liquid as the reagent ions, followed by the chemical ionization of thermally evaporated analytes from the sample mixture through charge and proton transfer.

To test whether the primary ions are produced from the ionic liquid and whether the repelling voltage has any effect on the generation of ions, further experiments were carried out under the optimized conditions. Fig. 2 gives the relative ion currents of the protonated dimethoate (*m*/*z* 230) recorded during the TDCI process with or without expelling voltage or ionic liquid. As shown in Fig. 2, no signal of dimethoate was detected when a 50 μL dimethoate solution (1 ng mL$^{-1}$) was injected into the TDCI source without using any ionic liquids in the sample mixtures during the first minute, even though the source temperature and the repelling voltage were optimally set at 160 °C and 4.0 kV, respectively. This demonstrated that primary ions cannot be generated just by heating organic compounds of dimethoate, although the emission of cations for organic salts and ionic liquids can be achieved when their heater temperature is increased to some degree. Meanwhile, it was also implied that the repelling voltage applied did not have any effect on the generation of ions. However, a relatively high intensity of the signal corresponding to the protonated dimethoate (*m*/*z* 230) was observed after addition of the same 100 μL concentration of 1-butyl-3-methylimidazolium bromide solutions, even breaking the repelling voltage from 1–2 minutes, indicating that the ionic liquid plays the key role in the reagent ion formation. As expected, the signal for analytes (*m*/*z* 230) was increased by about one-third when the repelling voltage was applied (from 2–3 minutes), and was then returned to the original intensity when the repelling voltage was disconnected (from 3–4 minutes), implying that addition of the repelling voltage led to the collection of more product ions into the mass spectrometer for detection, and did not have any influence on the generation of analyte ions at all. Note that the voltage applied to the heating wire and the thin gasket was controlled separately.

These experiments also demonstrated that the primary ions used for analyte ionization were from the ionic liquid by heating in the TDCI process. The charge or proton transfer between the cations and analytes could provide a reasonable interpretation for chemical ionization of analytes, since the base peak corresponding to the protonated dimethoate (*m*/*z* 230) was observed in the TDCI-MS spectrum. The generation of the analyte ions was electric field-independent or high voltage-independent during these thermal ionization processes.[34] Such an ionization method not only avoids contamination by organic solvents but also prevents the damage caused by the high voltage or high electric field in food sample analysis.

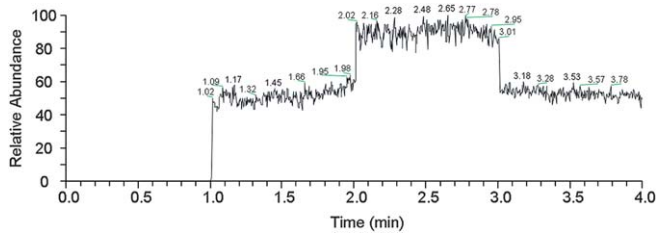


**Fig. 2** Relative currents of the protonated dimethoate (*m*/*z* 230) recorded during TDCI of dimethoate for the case: (a) with heat and repelling high voltage and without addition of ionic liquid (in the range of 0–1 minutes), (b) with heat and ionic liquid but without repelling high voltage (1–2 minutes), (c) with heat, repelling voltage, and ionic liquid (2–3 minutes), and (d) breaking repelling voltage based on the case of (c) (3–4).

### Optimization of the TDCI source

A remarkable number of experimental parameters affects TDCI performance. As discussed above, the source temperature has direct effects on the generation of ions, while the geometrical parameters and repelling voltage have important effects on the ion collection efficiency and hence on the sensitivity of the method. To optimize the TDCI parameters, 50 μL of dimethoate solution ($1.0 \times 10^{-6}$ g mL$^{-1}$) together with 100 μL of the same concentration of 1-butyl-3-methylimidazolium bromide solution was injected into the source. A positive ion detection mode was employed for detection of the dimethoate, and thus the 1-butyl-3-methylimidazolium cation was generated as reagent ions. The dependence of signal intensity on the geometrical parameters *a* and *b* was shown in Fig. 3. It was found that a highly stable signal of dimethoate (*m*/*z* 230) was detected when the horizontal linear distance (*a*) was in the range of 0.2–0.3 cm and the vertical distance between the inner wall of the source tube and the central axis of the MS inlet (*b*) is 0.4 cm. Therefore, the geometrical parameters (*a*) and (*b*) were set to be 0.2 cm and 0.4 cm, respectively.

 

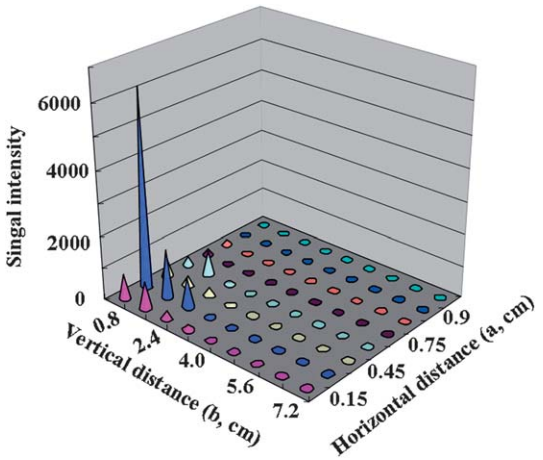


**Fig. 3** The effect of geometrical parameters of TDCI on the signal intensity. *a* and *b* represent the least horizontal linear distance from the outlet of the tube to the MS inlet, and the vertical distance between the low inner wall of the tube and the central axis of the MS inlet, respectively.

As clearly shown in Fig. 4(a), almost no signal was observed when the temperature was below 115 °C, but the signal intensity of *m*/*z* 230 (protonated dimethoate) was increased rapidly, with the source temperature increasing from 115 °C to 160 °C, and it did not change upon a further increase of temperature above 160 °C. Actually, the high temperature facilitates the generation of a high concentration of primary ions, thus enhancing the ionization efficiency. It can be found that the signal intensity is starting to be observed only when the source temperature is above the boiling point of dimethoate (117 °C), indicating that the reaction between the reagent ions and sample molecules can occur only when enough energy is provided. In contrast, the signal level was gradually increased with the increase of the repelling voltage from 1 kV to 4 kV, and a highly stable signal was sustained with a relatively high voltage (4 kV). High voltage enables much more procured ions to be collected into the MS inlet for detection, hence leading to a highly stable TDCI-MS signal for analytes. There is no evident increase for further improving the voltage. Thus, the optimal settings for the source temperature and voltage were 160 °C and 4.0 kV, respectively.

The choice of appropriate ionic liquids in the favor of analyte ionization is also an important part that needs to be optimized in the TDCI process,[28] since the performance of the TDCI has been strongly depended on the physicochemistry properties of the ionic liquid. The physicochemistry properties of the ionic liquid (*e.g.*, PA, IP, solubility, thermal stability, melting point, *etc.*) should be taken into account for chemical ionization of different analytes. Sometimes, the physicochemistry properties of the ionic liquid can be distinguished from the species of cations and anions as well as the length of the alkyl groups on the cations. A variety of ionic liquids were applied to evaluate the performance of the TDCI source for dimethoate analysis. As a result, an ionic liquid of 1-butyl-3-methylimidazolium bromide salt was found to be especially favorable for the dimethoate analysis, and thus it was chosen as the target reagent in this study. During the heating process, the produced energetic reagent ions, such as 1-butyl-3-methylimidazolium bromide cation, can collide and react with the vaporized sample molecules in a micro-space between the parallel sample plates, and then produce the analyte ions by a series of proton-transfer or charge-transfer reactions (Fig. 1). The predominant reaction that occurred in the ionization mainly depended on the comparable proton affinity (PA) or ionization potential (IP) between these reactants. Certainly, both of these two kinds of reactions can simultaneously occur provided that they were exothermic. In the present study, the proton-transfer reaction between the reagent ions and analyte takes absolute advantage.

## Identification and confirmation of dimethoate by TDCI-MS/MS

Under the optimized experimental conditions, we recorded the TDCI-LTQ-MS spectra of dimethoate using 1-butyl-3-methylimidazolium bromide salt as a reagent, as shown in Fig. 5.

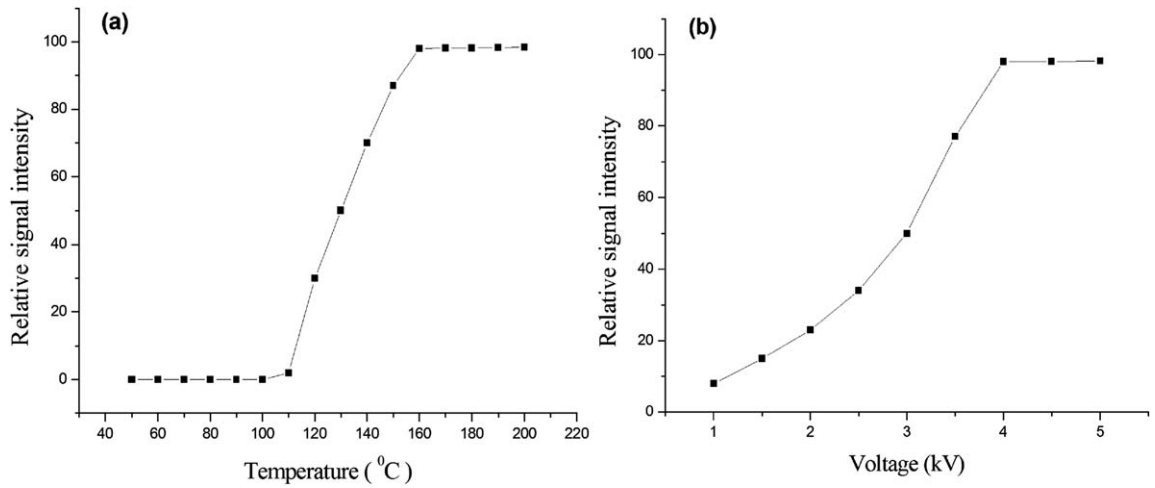


**Fig. 4** Optimization of the TDCI source temperature and repelling potential for dimethoate detection: (a) effect of source temperature on the signal intensity of the peak at *m*/*z* 230 and (b) effect of the repelling high voltage on the signal intensity of the peak at *m*/*z* 230. Note that the signal intensities were normalized to 100% based on the highest signal detected. Each point designates an average of 6 measurements.

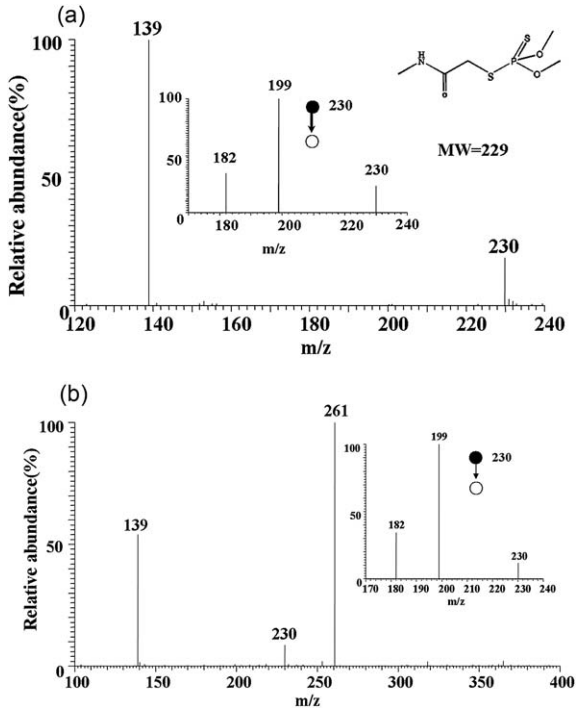


**Fig. 5** Mass spectra for dimethoate observed in standard and practical samples. (a) MS spectrum of standard dimethoate solution with the concentration of $10^{-9}$ g mL$^{-1}$ and (b) MS spectrum of the practical orange juice sample. The peak at *m*/*z* 230 is assigned to the molecular ion $[M + H]^+$ of dimethoate. The insets show the MS/MS of the peak at *m*/*z* 230.

Fig. 5(a) shows the TDCI-MS and tandem mass spectrum of the standard aqueous solution of dimethoate, with a concentration of $10^{-9}$ g mL$^{-1}$. As shown, a strong signal (*m*/*z* 139), which corresponds to the reagent ions, 1-butyl-3-methylimidazolium cation, was clearly observed, and the peak at *m*/*z* 230, with a remarkable intensity, was assigned to the molecular ions $[M + H]^+$ of dimethoate. To ensure that the peak at *m*/*z* 230 was the signal of protonated dimethoate, the MS/MS experiments were further performed on this molecular ion $[M + H]^+$. The MS/MS spectrum is illustrated as the inset figures. The major product ions were detected at *m*/*z* 199 and 182, corresponding to the characteristic fragments of protonated dimethoate generated by the loss of $CH_3NH_2$ and $CH_3SH$, respectively. The MS/MS results are completely consistent with the previous Nano-DAPCI-MS/MS experimental results,[32] which supports the confirmation of dimethoate, proving the reliability and accuracy of this home-made miniature TDCI source. Although the low level of pesticide residue in juice samples was also successfully detected by the DAPCI-MS with Nano sampling,[32] the use of a nanoliter level sampling device is not suitable for large amounts of real sample analysis. Especially for non-volatile compounds such as melamine, the signal of analytes can be hardly obtained using the DAPCI. Instead, the TDCI source has the predominant advantage for nonvolatile analyte analysis due to its independent heater device.

Further experiments were rapidly performed to analyze the practical orange juice samples with the same ionic liquid, as shown in Fig. 5(b). In these spectra, the signal ion of *m*/*z* 230 was also detected and the corresponding MS/MS spectrum further confirmed that this signal belonged to the dimethoate in juice. And the signal ion of *m*/*z* 261 in Fig. 5(b) may be another unknown component.

## Sensitivity and dynamic response range

In order to evaluate the sensitivity of the method, the blank samples (dimethoate-free juice samples) that did not produce any dimethoate signal in the MS/MS (*i.e.*, *m*/*z* 199, 182) were spiked with different amounts of dimethoate solutions. A series of orange juice samples containing dimethoate at five different concentrations (0.01 ng mL$^{-1}$, 0.1 ng mL$^{-1}$, 1.0 ng mL$^{-1}$, 10 ng mL$^{-1}$, 100 ng mL$^{-1}$) were prepared for TDCI-MS/MS analysis. These standard juice samples were used to make the calibration curve for quantification of the dimethoate content in actual orange juice samples. To reduce the possibility of a false positive signal, the most abundant characteristic fragment ions at *m*/*z* 199, produced by dissociation of protonated dimethoate $[M + H]^+$ (*m*/*z* 230) in the MS/MS experiment, were chosen as the target ion for quantitative analysis of dimethoate in juice samples when the signal intensities reached 3 times the noise level. Note that the real data were the results which have subtracted the background from the detected signal intensity. The duration of active CID was 30 ms for each mass analysis scan. The averaged signal intensity of *m*/*z* 199 obtained using 40 scans was actually used for quantification, and thus this confirmed the reliability of this method. As a result, a working curve for quantification of dimethoate in juice samples was obtained using a series of authentic fruit juice samples spiked with different amounts of dimethoate (Fig. 6). As shown in Fig. 6, in the range of $10^{-7}$ to $10^{-11}$ g mL$^{-1}$, the signal intensity linearly responded to the analyte concentrations in the logarithmic scales, providing a good linear regression equation $y = 0.1769x + 1.9782$ with a square of linear fitting correlation coefficient $R^2 = 0.985$. The response range of this method was found to be about 5 orders of magnitude, 0.01 ppb–100 ppb. The limit of detection of dimethoate was calculated to be $8.76 \times 10^{-11}$ g mL$^{-1}$ using the following equation based on measurements of a series of dimethoate-spiked samples: $LOD = c3\sigma/S$,[33] where $c$ is the dimethoate concentration in the orange juice

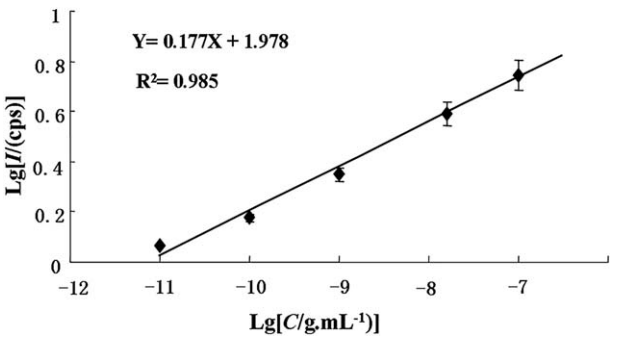


**Fig. 6** The relationship between the signal response of the fragment ion (at *m*/*z* 199) and the concentrations of dimethoate solution in the logarithmic scales. The error bar for each datum is obtained by six individual measurements, and the square of the linear fitting correlation coefficient $R^2$ is 0.985.

sample, $\sigma$ is the standard deviation of all the measurements ($n = 20$) performed on the blank sample, and $S$ is the mean value of the 20 signals measured.

These results can be comparable to the results from DAPCI-MS (LOD = $1.2 \times 10^{-11}$ g mL$^{-1}$).[32] Although the LOD value is a little higher compared to the result obtained by matrix solid-phase dispersion (MSPD) followed by LC-MS (ref. 2) analysis (LOD = $0.01 \times 10^{-12}$ g mL$^{-1}$),[6] the MSPD and chromatograph separation procedure required prior to the residue determination make the whole analysis laborious and time-consuming. However, the analysis for each sample by the TDCI-MS can be completed within 30 seconds in this study. The maximum residue limits (MRLs) for fruits set by the European Union (EU) range from 0.01 mg kg$^{-1}$ (acetamiprid in raspberry) to 2.0 mg kg$^{-1}$ (malathion in orange) (Commission Directive 2007/11/EC; Council Directive 88/298/EEC). The calculated LOD in this study was at least five orders of magnitude lower than the established MRLs for fruits. Such an LOD is able to meet the needs of the detection of trace dimethoate (concentration: $10^{-11}$ g mL$^{-1}$) in complex matrices, implying that the method developed here is suitable for quantification of specified pesticides in fruit juices.

### Recovery efficiency and standard deviation

To test the precision of the method, different recovery studies were carried out using the dimethoate-free juice samples, in which the presence of pesticides was examined to make sure that the matrix does not contain the studied analytes. Several fresh orange juice aliquots were spiked at three concentration levels (0.1, 1.0, and 10 ng mL$^{-1}$) with the working standard solution. Six measurements were performed to obtain the dimethoate concentration in the orange juice samples spiked with different amounts of dimethoate. The concentrations of dimethoate were derived by fitting the acquired intensities to the calibration curve of dimethoate shown in Fig. 6. The corresponding values are shown in Table 1. The recovery of dimethoate (0.1–10.0 ng mL$^{-1}$) ranged from 94.3% to 102.8%. The relative standard deviation (RSD) for six measurements on the same sample for the run-to-run study was in the range 3.12–5.34%, and interday RSD ($n = 6$) values were between 5.78–10.02%. These results confirmed the absence of memory effects during our experiments, demonstrating the precision of the reported method and the potential of the proposed approach for quantitative purposes.

### Validation of the method for rapid actual sample analyses

To validate the reliability of the developed method, a total of 5 different kinds of market-purchased orange products were directly crushed into viscous juice samples for quantitative analysis within a few minutes, without washing or any pretreatment. Note that these selected orange samples are one of the five most common varieties in Southeast China. A similar procedure was used to prepare the juice samples with spiked dimethoate at different levels as described above. With the use of the working curve specifically made for analysis of actual juice products, dimethoate was rapidly quantified using TDCI-MS. As shown in Table 2, significant amounts of dimethoate were determined in 4 out of 5 samples. Positive orange juice samples contained dimethoate at levels 0.00051–0.00229 mg kg$^{-1}$, which are much lower than the MRLs (at 0.02 mg kg$^{-1}$) set by the European Union (EU). The blind test results were in good agreement with the quantitative analysis data obtained using the DAPCI-MS method. In order to confirm these measured values, various amounts of dimethoate were added into the practical samples according to the measured dimethoate levels. For example, an amount of 1.0 ng mL$^{-1}$ dimethoate was added into the samples containing dimethoate at less than 1.0 ng mL$^{-1}$, while an amount of 10.0 ng mL$^{-1}$ dimethoate was added

**Table 1** Recovery and precision for dimethoate measurements

| Spiking levels (ng mL$^{-1}$) | Detected levels (ng mL$^{-1}$) | | RSD (%) ($n = 6$) | | Recovery (%) |
|---|---|---|---|---|---|
| | Detected values | Mean values | Intraday | Interday | |
| 0.1 | 0.0989, 0.0876, 0.0983, 0.0934, 0.0984, 0.0891 | 0.0943 | 5.34 | 10.02 | 94.3 |
| 1.0 | 1.0643, 0.9786, 0.9751, 1.0589, 1.0913, 1.0039 | 1.0287 | 4.87 | 8.13 | 102.8 |
| 10.0 | 10.079, 9.876, 10.064, 9.890, 9.698, 9.254 | 9.810 | 3.12 | 5.78 | 97.9 |

**Table 2** Quantitative detection of dimethoate in actual orange juice samples

| Code | Measured dimethoate (ng mL$^{-1}$) | Mean value of dimethoate measured (ng mL$^{-1}$) | Amount of dimethoate added (ng mL$^{-1}$) | Total amount of dimethoate found after standard addition (ng mL$^{-1}$) | Recovery (%) |
|---|---|---|---|---|---|
| 1 | 0.98, 0.91, 0.87, 0.84, 0.95, 0.97 | 0.92 | 1.0 | 1.79 | 93.2 |
| 2 | No detection | No detection | 1.0 | 0.94 | 94.0 |
| 3 | 0.46, 0.49, 0.56, 0.48, 0.51, 0.55 | 0.48 | 1.0 | 1.35 | 91.2 |
| 4 | 1.09, 0.94, 1.03, 1.07, 0.98, 1.07 | 1.02 | 10.0 | 10.46 | 94.9 |
| 5 | 2.38, 2.23, 2.19, 2.36, 2.29, 2.34 | 2.28 | 10.0 | 11.80 | 96.1 |

to the samples containing dimethoate between 1.0 ng $mL^{-1}$ and 10.0 ng $mL^{-1}$. The recoveries were in the range of 91.2–96.1% (Table 2), demonstrating the robustness of this method for the detection of dimethoate in actual juice samples. The method has been validated for the quantitative detection of dimethoate in various commercial orange products. Further, the relatively good recovery (91.2–96.1%) derived from the standard addition measurements implies that the calibration curve shown in Fig. 6 can be applied to the detection of dimethoate in various types of viscous orange juice samples, although their matrixes might not be the same due to their different maturity, types, producing area, *etc.* The data showed that TDCI-MS is surprisingly useful for obtaining quantitative information about trace amounts of complex viscous analytes such as dimethoate in the matrices of fruit juice samples.

## Conclusions

A minimal thermal dissociation atmospheric chemical ionization (TDCI) source was successfully coupled to LTQ-MS for rapid detection of pesticide residues in highly viscous juice samples using ionic liquids, without any sample pretreatment and aid of high-voltage. Orange juices are types of heterogeneous liquid samples of high viscosities. Fast detection of trace compounds such as pesticide residues in fruit juices is highly desirable, but there are many challenges due to the complexity of the samples. As demonstrated in this study, the analytes present in the viscous orange juice samples were sensitively and rapidly sampled using the ionic liquid, instead of organic solvents or electric field used by other ambient ionizations. The RSD for the 6 measurements was in the range of about 3.1–10.0%. The limit of detection for dimethoate ($8.76 \times 10^{-11}$ g $mL^{-1}$) is much lower than the MRLs for fruits ($0.01–2.0 \times 10^{-6}$ g $mL^{-1}$) set by the EU. Using the 1-butyl-3-methylimidazolium bromide solution, a total of 5 different kinds of viscous juice samples were quantitatively analyzed by tandem mass spectrometry using the miniature TDCI source, without any pretreatment. The analysis speed has improved, and the analysis of 3 types of samples was completed within 1 min. These demonstrate that the method developed here can be used for quantification of trace pesticides in viscous fruit juice samples without chemical contamination and high voltage damage, providing a simple and "green" method for high-throughput food analysis with a high degree of safety. Due to the independent heater device applied in the TDCI source, it has a significant advantage for nonvolatile compound analysis.

However, there are still some limitations for this method. Firstly, the use of ionic liquids for generation of reagent ions could contaminate the ion source easily. Secondly, the high voltage damage could not be completely avoided since the high repelling potential was still used for improving the intensity of the ion signal in this work, although the repelling potential has been demonstrated to be not directly related to the generation of analyte ions. Finally, the relatively high proton affinity of ionic liquids influence hinder the method from general use to a certain extent.

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