CHINESE JOURNAL OF ANALYTICAL CHEMISTRY
Volume 38, Issue 4, April 2010
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Chin J Anal Chem, 2010, 38(4), 453–457.

RESEARCH PAPER

Rapid Determination of Dimethoate in Nanoliter of Juice Using Surface Desorption Atmospheric Pressure Chemical Ionization Mass Spectrometry

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Abstract: A rapid analytical method based on nanoliter-level sampling technique and surface desorption atmospheric pressure chemical ionization mass spectrometry (SDAPCI-MS) has been developed for the determination of trace dimethoate in juices without any sample preparation. The nanoliter-level juices were sampled by a home-made sampler equipped with a stainless steel sampling probe. The minimum sampling volume was suggested to be 0.11 nL. Based on the experimental results, the linear correlation between dimethoate signal and concentration was significant in the range of 0.001–10.0 mg kg^{-1} with the correlation coefficient (R) of 0.988. The recoveries were in the range of 80.5%–120.6%, and the detection limit of dimethoate was determined to be 1.2×10^{-11} mg kg^{-1}.

Key Words: Nanoliter-level sampling; Surface desorption atmospheric pressure chemical ionization; Mass spectrometry; Dimethoate; Juice

1 Introduction

Organophosphorus pesticides are a group of effective insecticides, which have been widely used for decades. However, organophosphorus pesticide residues in food have aroused great concern in recent years due to their potential hazards to human health. Consequently, it is worldwide increasingly important to monitor organophosphorus pesticide residues in food[1–5]. Nowadays, the analytical methods including liquid chromatography-mass spectrometry[6], gas chromatography-mass spectrometry[7,8], liquid-liquid micro-extraction chromatography[9], and so on, are commonly used for the determination of pesticide residues, providing precise quantitative measurements of pesticides in food samples. However, the separation-based methods have suffered from problems such as complicated procedures of sample preparation, application of organic solvents, and time consumption[4,9]. Mass spectrometry is considered as one of the most promising methods for the detection of pesticide residues in food[10] because of its high performance in sensitivity, accuracy, and selectivity. Therefore, the development of rapid analytical method based on mass spectrometry for the determination of trace pesticides in food without sample preparation is a practical need of high priority.

Low-volume sampling (such as nanoliter and picoliter) is of great significance in reducing sample consumption, especially for the biological samples that are difficult to be obtained. For example, a minimal blood sample volume (e.g., subnano liters) is highly desirable to minimize the potential damage in blood test. At present, the picoliter-level sample can be successfully handled using microfluidic technique[11]. However, the method reported[11] is not yet applicable for the analysis of raw samples with complex matrices. Without sample pretreatment, nanoliters of the heterogeneous samples (e.g., fruit juice, soup,

Received 28 January 2010; accepted 3 April 2010
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This work was supported by the Ministry of Science and Technology of China (No. 2008IM040400) and the Department of Education of Jiangxi Province of China (No. GJJ10504).

DOI: 10.1016/S1872-2040(09)60033-5

and porridge) are difficult to be directly introduced using microfluidic devices. In this study, a home-made nanoliter-level sampling device has been designed and prepared in the lab. Then, the sampling device is further combined with surface desorption atmospheric pressure chemical ionization mass spectrometry (SDAPCI-MS) that is characterized with the capability to analyze substances in a complicated matrix[12–18], and it is used for the fast detection of trace dimethoate in nanoliter juice sample. The experimental results demonstrated that the analytical method developed here is a promising tool for the rapid detection of pesticide residues in complex samples, with subnano liters sample volume.

2 Experimental

2.1 Instrumentation and reagents

A home-made nanoliter level sampler is composed of a sampling needle and a scalable enclosure (Fig.1a). A stainless steel needle (15.0 cm, length) was used as the basic material for the sampling probe. Its front end was soaked into 1.0 M HCl solution for half an hour till its diameter was decreased to micrometer level, and then it was washed with distilled water and methanol, successively. The prepared tip is very transmutative and need to be prevented from any collision with hard surfaces such as stainless steel. Therefore, an adjustable enclosure, made of PTFE material, was used to facilitate sampling and to protect the sampling needle. The sampling needle was positioned about 1–2 mm out of the shell for sampling of the juice, and the sample volume can be adjusted according to the depth of the needle dipped into the juice samples. The needle loaded with juice sample was placed directly on the SDAPCI source for analysis.

The SDAPCI ion source was home-made, which was coupled to an LTQ-XL linear ion trap mass spectrometer (Finnigan, San Jose, CA) equipped with Xcalibur data- processing system.

Dimethoate (40% effective concentration) was commercially available in the market. A stock solution with a concentration of 1.0 g L^{-1} was prepared. Orange juice samples containing grains were bought from local supermarket. All the juice samples were directly used without any further pretreatment such as grain separation and extraction.

2.2 Experimental method

The SDAPCI ion source was used in positive ion mode with a mass range of 50–400 Da, discharge voltage of 3.5 kV, and ion transfer tube temperature of 200 °C. The angle α formed by the discharge needle and the MS inlet was 30°. The discharge tip was positioned at the same horizontal line with the MS inlet. To ensure that the trace sample on the cutting edge of sampler can be analyzed directly by SDAPCI (Fig.1b), the needle was placed vertically, and its height was adjusted carefully to the proper level. In the MS^2 experiment, the isolation window of precursor ion was set at 1.4 Da and the collision energy was 20%. Other parameters of MS were automatically optimized.

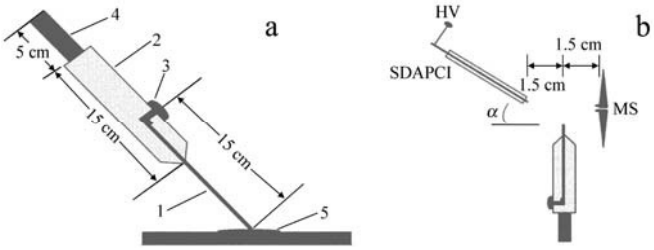

Fig.1 Schematic illustration of nano-SDAPCI-MS for rapid analysis of nanoliter of heterogeneous juice samples

a: Schematic illustration of a home-made nanoliter sampler. 1. Stainless steel needle of the sampler; 2.Teflon shell; 3. Adjustor for the needle of the sampler; 4. Teflon handle; 5. Sample with complex matrices; b: Schematic diagram of the SDAPCI source for rapid analysis of juice samples on the tip of the sampler

3 Results and discussion

3.1 Determination of sampling volume

To precisely determine the minimum sampling volume, a series of standard *L*-arginine aqueous solutions with concentrations of 1×10^{-7}, 1×10^{-8}, 1×10^{-9}, 1×10^{-10}, 1×10^{-11} and 1×10^{-12} g L^{-1} were analyzed using ESI-MS in positive ion mode. The product ion (*m/z* 116) of protonated *L*-arginine (*m/z* 175) was used for quantification. The signal intensity (y) of *m/z* 116 was plotted with the concentration (x) of *L*-arginine solutions, and the working curve was obtained. The correlation coefficient of the curve is 0.993, indicating a good relationship between x and y. Then, 5 mL of juice was spiked with *L*-arginine to make an arginine solution with a final concentration of 0.1 g L^{-1}. A small amount (1 mL) of spiked juice was injected into a dry bottle cap, and then the bulk liquid was carefully removed, through which a juice film containing *L*-arginine was obtained on the surface of the bottle cap. Subsequently, the sampling experiment was performed and repeated 20 times sampling, the device needle was rinsed twice with 2 mL of deionized water after each sampling to make a dilute arginine water solution. Then the arginine water solution was analyzed using ESI-MS by following the procedure used to make the working curve. The signal intensity of *L*-arginine fragment ion (*m/z* 116) was 96.4, which determined that the concentration of the arginine solution was 1.09×10^{-7} g L^{-1}. According to $V = m/c$ (c is the concentration of the solution, m is the mass of the solution), the total mass (m_1) of L-arginine solute sampled by 20 times was $m_1 = cV = 1.091\times10^{-7}$ g $L^{-1}\times2$ mL $= 2.182\times10^{-7}$ mg; then the total volume (V_1) of the *L*-arginine juice sampled by 20 times is $V_1 = m_1/c_1 = 2.182\times10^{-7}$ mg/(0.1 g L^{-1}) $= 2.182\times10^{-6}$ mL (c_1 is the arginine concentration in the juice solution, i.e., 0.1 g L^{-1}),

so the volume (V) of juice sampled by each time was $V = V_1/20 = 2.18\times10^{-6}$ mL/20 =1.09×10^{-7} mL, that is 0.11 nL.

Note that the sampling volume was heavily related with the diameter of the sampler tip, the thickness of the liquid sample and the viscosity of the sample. For a given sample, the sample volume could be smaller than nanoliters if a sampler with a diameter smaller than 80 μm was used.

3.2 Dimethoate MS/MS analysis using SDAPCI

Trace analysis in complex matrix was usually completed by tandem mass spectrometry to exclude false positives[12,13]. Here, with the home-made sampler, dimethoate in juice was analyzed by tandem mass spectrometry. A strong signal (*m/z* 230), which corresponds to the molecular ion $[M + H]^+$ of dimethoate, was clearly observed in the positive ion detection mode using SDAPCI as shown in Fig.2a. The ion of *m/z* 230 was then selected for tandem mass spectrometry analysis. The major product ions were detected at *m/z* 199 and 182, which was ascribed to the ionic species generated by the loss of CH_3NH_2 and CH_3SH, respectively.

In MS^3, the fragment ions (*m/z* 199) could further cleavage CO, and $COSCH_2$ to produce the product ions of *m/z* 171 and 125, respectively. The positive ionic species of *m/z* 125 $[(CH_3O)_2P{=}S]^+$ observed in the MS^3 experiment was of high water affinity, resulting in a water cluster (*m/z* 143) via the ion/molecule reaction with water in the ion trap. This was consistent with the high relative humidity (60%) of the ambient air for the experiment. To cross-check the reliability of the experimental data, ESI-MS/MS experiment was also performed as a reference standard. It was found that the MS/MS spectrum of dimethoate in the SDAPCI-MS/MS spectrum was entirely in consistent with the ESI-MS/MS spectrum. Therefore, the successful detection of the signal at *m/z* 230, which generates characteristic fragments of *m/z* 199 (100%) and 182 in MS/MS experiments indicates that the real sample is contaminated by dimethoate.

3.3 Linear range and limit of detection

A series of standard solutions of dimethoate with concentrations of 0.10, 1.0, 10.0, 100, and 1000 mg kg^{-1} were prepared as the stock solution. A total of 100 μL of the standard solution of dimethoate was added to 10 mL of Nongfuguoyuan® (dimethoate-free commercial products) to prepare the contaminated juice samples with dimethoate concentrations of 0.0010, 0.010, 0.10, 1.0 and 10.0 mg kg^{-1}. All the samples were then analyzed using the SDAPCI-MS by following the procedure described in Section 2.2. The MS/MS signals of *m/z* 199 were obtained after subtracting the background spectrum. The mean values of six measurements and the relative standard deviation (RSD) were 6166 (19.1%), 7512 (25.7%), 8359 (14.0%), 9030 (9.0%) and 10817 (26.9%), respectively, for five individual juice samples. In the range of 0.0010–10.0 mg kg^{-1}, the signal intensities linearly responded to the analyte concentrations in the logarithmic scales as shown in Fig.2b, providing a linear regression equation of $Y = 0.056X + 3.972$, with a correlation coefficient $R = 0.988$.

The signal intensity of a blank sample was 1156.5 ($S/N \geq 3$, $n = 20$). The value of three times of the standard deviations for a blank sample was 1109.4. According to the formula[19] of $x = (y + 3\sigma - a)/b$ (σ is the standard deviation of blank sample, y is the corresponding static signal intensity of the blank sample, a is the intercept of the working curves, b is the slope of the working curve), $\log x = [\log(y + 3\sigma) - a']/b'$ (a' is the intercept of the experimental work curve, b' is the slope of the working curve in this experiment). The limit of detection of dimethoate was calculated to be 1.2×10^{-11} mg kg^{-1} in this method. The detection limit was surprisingly low. Probably, the stainless steel probe has high affinity of dimethoate, enriching the dimethoate on the surface of the sample probe. However, this needs further experimental studies.

3.4 Real sample analysis

The method developed here was applied to determine five types of commercial fruit juice samples. Before the addition of authentic dimethoate, no dimethoate was detected from the commercial product samples tested. Therefore, 50 μL of

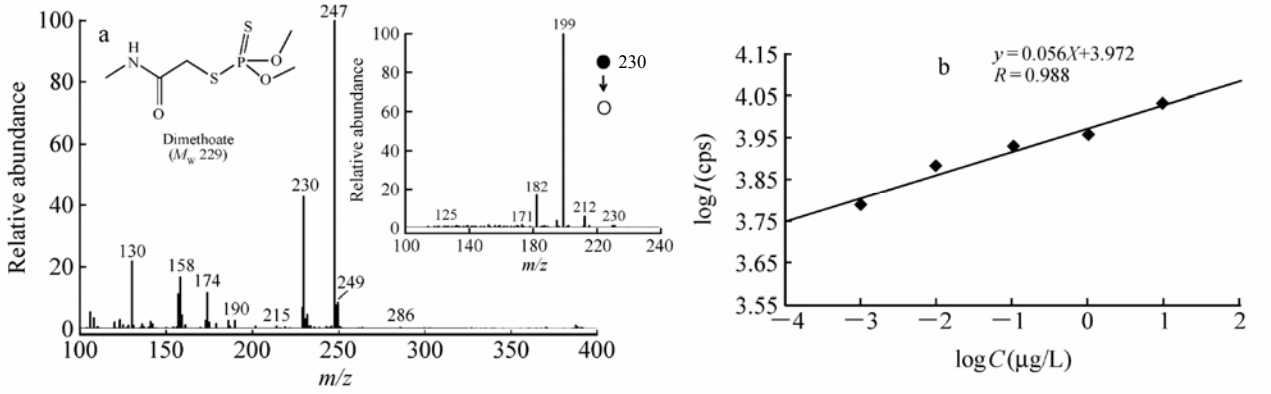

Fig.2 SDAPCI mass spectra of dimethoate in juice samples (a) and calibration curve of dimethoate (b), the inset shows the characteristic fragments obtained in the MS/MS spectrum.

dimethoate standard solution (50 mg kg^{-1}) was added into the 5 kinds of fruit juice (10 mL of each), respectively, to make five juice solutions spiked with dimethoate (0.25 mg kg^{-1}). Besides the dimethoate signal at *m/z* 230, a large number of peaks with high-level intensities were also observed in the MS spectrum (Fig.3) measured by SDAPCI-MS. The main reason was that there were more pulps and granular ingredients in the real juice samples. These grassy spectra also confirmed that the samples contained complex matrices, which imposed rapid determination of dimethoate impossible by using ordinary analytical methods. With the method developed here, a single sample measurement was completed within 20 s, and no more than 2 min was required to perform 6 measurements. Therefore, the analysis speed has been significantly improved.

To obtain the recovery of this method, 50 μL of standard dimethoate solution (50.0 mg kg^{-1}) was added into nine juice samples (10 mL of each), respectively. Then 100 μL of water was added to three of them. As the references, 100 μL of dimethoate (10.0 mg kg^{-1}) was added to another three samples while 100 μL of dimethoate (50.0 mg kg^{-1}) was added to the rest. The dimethoate concentration in the samples was found to be 0.21 mg kg^{-1} (n = 6) by using the nano-SDAPCI-MS. The recoveries were calculated to be 95.3%, 80.5%, 110.9%, 91.5%, 106.7% and 120.6%, respectively (Table 1). Accordingly, the RSDs of 6 kinds of fruit juice spiked with dimethoate were in the range of 8.4%–17.2%. The RSD values varied in a relatively large range, probably, because the sample was introduced manually, which added instability in sample loading and in holding of the sample probe (such as shaking). Obviously, this problem can be resolved by using an automatic sampling system, and it results in better analytical performance.

In conclusion, the experimental results reported here have shown that the nano-SDAPCI-MS method has several advantages such as high sensitivity, high speed sampling, easy operation, and low sample consumption for rapid analysis of complex samples. Our preliminary studies demonstrate that the nano-SDAPCI-MS can be a promising tool for rapid detection of trace analytes in complex biological samples, with minimal sample consumption such as subnanoliters.

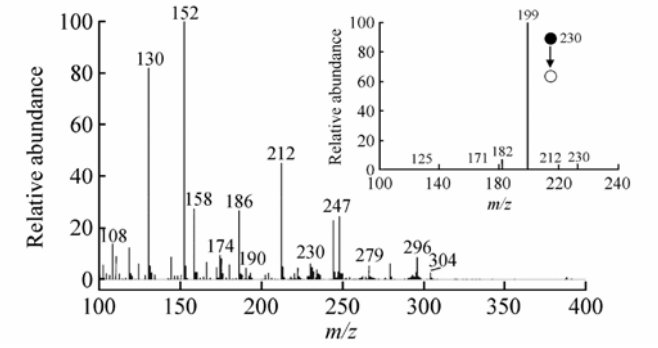

Fig.3 Mass spectra of dimethoate in juice samples recorded using SDAPCI-MS, Inset shows characteristic fragments of ions of *m/z* 230

Table 1 Recoveries for rapid analysis of real juice samples

Sample code	Amounts spiked (mg kg^{-1})	Amounts found (mg kg^{-1})	Recovery (%)	RSD (%)
1	0.10	0.31	95.3	8.4
2	0.10	0.29	80.5	10.2
3	0.10	0.32	110.9	17.2
4	0.50	0.67	91.5	11.4
5	0.50	0.74	106.7	10.3
6	0.50	0.81	120.6	15.2

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