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Atmospheric pressure gas chromatography quadrupole-time-of-flight mass spectrometry for simultaneous determination of fifteen organochlorine pesticides in soil and water

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ABSTRACT

In this study, the application of atmospheric pressure gas chromatography quadrupole-time-of-flight mass spectrometry (APGC-QTOF-MS) has been investigated for simultaneous determination of fifteen organochlorine pesticides in soil and water. Soft ionization of atmospheric pressure gas chromatography was evaluated by comparing with traditional more energetic electron impact ionization (EI). APGC-QTOF-MS showed a sensitivity enhancement by approximately 7–305 times. The QuEChERs (Quick, Easy, Cheap, Effective, Rugged, and Safe) method was used to pretreat the soil samples and solid phase extraction (SPE) cleanup was used for water samples. Precision, accuracy and stability experiments were undertaken to evaluate the feasibility of the method. The results showed that the mean recoveries for all the pesticides from the soil samples were 70.3–118.9% with 0.4–18.3% intra-day relative standard deviations (RSD) and 1.0–15.6% inter-day RSD at 10, 50 and 500 μg/L levels, while the mean recoveries of water samples were 70.0–118.0% with 1.1–17.8% intra-day RSD and 0.5–12.2% inter-day RSD at 0.1, 0.5 and 1.0 μg/L levels. Excellent linearity ($0.9931 \leq r^2 \leq 0.9999$) was obtained for each pesticides in the soil and water matrix calibration curves within the range of 0.01–1.0 mg/L. The limits of detection (LOD) for each of the 15 pesticides was less than 3.00 μg/L, while the limit of quantification (LOQ) was less than 9.99 μg/L in soil and water. Furthermore, the developed method was successfully applied to monitor the targeted pesticides in real soil and water samples.

1. Introduction

Organochlorine pesticides (OCPs) is an important group of environmental contaminants which were known to cause disorders in endocrine system of non-target organism [1,2]. Although many OCPs have been banned in most countries for almost several years, the residue of OCPs are still detected in most environment matrices [3,4]. Moreover, most of them exist in water and soil in ultra-trace level (from pg/L to ng/L) [5]. Therefore, it is of great significance to develop more reliable and sensitive methods for identification and quantification of OCPs at trace level to facilitate their risk assessment. OCPs are commonly determined using gas chromatography equipped with electron capture detector (GC-ECD) [6,7], which often leads to false positives due to interferences from sample matrix. Additionally, more selective methods have been developed by gas chromatography mass spectrometry in electron ionization mode (GC–MS–EI) [8] and using tandem mass spectrometry (GC–MS/MS) detection [9]. While MS detection provides high specificity, its sensitivity and precision is poorer in comparison to GC-ECD [10]. Atmospheric pressure gas chromatography (APGC) source is a alternative soft ionization technique to overcome sensitivity limitations of GC–MS–EI methods. APGC results in minimal fragmentation of the molecular ion and provides higher signal intensity compared to EI ionization [11,12]. While APGC has been successfully applied for analysis of dioxins [13], furans [14] and pesticides [15,16], there is limited research available on the application of APGC-QTOF-MS for the determination of OCPs. Therefore, it is necessary to assess the potential characteristic of APGC for improvement in sensitivity and selectivity for OCP analysis. APGC technique can be coupled to quadrupole-time-of-flight (QTOF) instrument to provide high sensitivity in full-spectrum-acquisition mode comparing with conventional scanning methods

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[9]. Time of flight mass spectrometry provides high resolution and fast scanning speed, for qualitative analysis of target analytes in complex matrices [17,18]. To the best of our knowledge, there are few research publications for quantification of OCPs in water and soil using atmospheric pressure gas chromatography quadrupole time-of-flight mass spectrometry [16]. In order to evaluate its performance, systematic study has been conducted by selecting 15 OCPs to identify their ionization behavior under atmospheric pressure conditions, as well as comparing the difference between EI and APGC ionization sources. In summary, a sensitive and effective method for the simultaneous determination of 15 OCPs in soil and water using APGC-Q-TOF-MS was developed, and the method was successfully applied to the analysis of some authentic environmental samples.

2. Materials and methods

2.1. Reagents and materials

Standard solutions of chlorothalonil (100 mg/L), α-chlordane (100 mg/L), β-chlordane (100 mg/L), *o*,*p*′-DDE (100 mg/L), *p*,*p*′-DDE (100 mg/L), *o*,*p*′-DDT (100 mg/L), *p*,*p*′-DDT (100 mg/L), *o*,*p*-DDD (100 mg/L), *p*,*p*-DDD (100 mg/L), α-endosulfan (100 mg/L), lindane (100 mg/L), aldrin (100 mg/L), endrin (100 mg/L), mirex (100 mg/L) were obtained from Agro-Environment Protection Institute, Ministry of Agriculture (Beijing, China). PCNB (20 mg/L) were purchased from National Institute of Metrology (Beijing, China). Analytical grade *n*-hexane and ethyl acetate for pesticide residue analysis were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China), acetone, methanol and dichloromethane (DCM) were obtained from Beijing chemical works (Beijing, China). Anhydrous magnesium sulfate ($MgSO_4$) was purchased from Xilong Chemical Co., Ltd. (Beijing,China) and sodium chloride (NaCl) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing,China). Chromatography grade n-hexane was purchased from Thermo Fisher Scientific Corporation (Shanghai, China). Ultra-pure water was obtained from a Milli-Q system (Bedford, MA, USA). Nylon syringe filters (0.22 μm; Tengda, Tianjin, China) were used to filter the concentrated extracts. C_{18} (40 μm), PSA (40 μm), GCB (40 μm), Florisil (40 μm) sorbents and PEP (Polarity Enhanced Polymer) SPE cartridge were purchased from Bonna-Agela Technologies (Tianjin, China).

2.2. Instrument

Analysis of the pesticides were performed by an Agilent 7890A GC system (Agilent Technologies, Santa Clara, CA) equipped with a 7693 autosampler (CTC Analytics, Zwingen, Switzerland) coupled to a Q-TOF (Xevo G2-S, Waters Corporation, Manchester, UK), operating in APGC mode. A HP-5MS (Agilent Technologies) analytical column of 30 m × 0.250 mm inner diameter and 0.25 μm of film thickness was used. The temperature program for the gas chromatography was as follows: initial temperature, 80 °C held for 1 min, increased temperature ramp by 20 °C min^{-1} to 200 °C and held for 1 min, then increased ramp by 5 °C min^{-1} to 300 °C and held for 2 min,the total time was 30 min. Helium was used as carrier gas at 2.0 mL/min. API positive polarity and resolution mode were selected for MS ionization. The Xevo G2-S QTOF was operated at a scan time of 0.2 s and the mass range was considered as *m*/*z* 50–650. For mass spectrometry (MS^E, where *E* represents collision energy), two acquisition functions were used in applying different collision energies: a low energy (4 eV) function and a high energy function which in the case of a collision energy ramp (20–40 eV). The corona voltage was 2.2 KV, the cone gas was set at 150 l/h and the source temperature was 150 °C.

2.3. Sample treatment

2.3.1. Soil

For soil samples, 5 g homogenized samples were weighed in a 50 mL polypropylene centrifuge tube and spiked at three different levels with the mixture of eight OCPs and then 5 mL ultra-pure water was added. The tubes were allowed to sit aside for 30 min to distribute the pesticide uniformly. Afterwards, 10 mL mixture of hexane and acetone (9:1,v/v) was added. The sample tubes were oscillated for 10 min. Afterwards, 1 g NaCl was added to the sample tubes. The sample tubes were vortexed for 5 min at relative centrifugal force (RCF) 2811 × *g*, then centrifuged for 5 min. Then 1.5 mL upper layer solvent was transferred into a 2 mL centrifuge tube that contained an amount of cleaning agent (40 mg Florisil and 150 mg $MgSO_4$). Then 2 mL centrifuge tubes were vortexed for 1 min and centrifuged for 5 min at RCF 2400 × *g*. Through 0.22 μm nylon syringe filter and filtered into an autosampler vial for APGC-Q-TOF-MS injection.

2.3.2. Water

Water samples (200 mL) were prepared at three concentration levels by adding specific amount of mixed standard solutions of fifteen OCPs. Before loading samples, a PEP SPE cartridge was activated by 5 mL methanol, and following by 5 mL ultra-pure water. After activation, 200 mL water samples were passed through a PEP SPE cartridge at a flow rate of 4 mL/min and were dried under a vacuum (0.2 MPa) for 25 min to remove retained water. The retained analytes were eluted by 20 mL *n*-hexane and acetone (9:1, v/v). The eluate was then evaporated to dryness by using a rotary evaporator (36 °C, 0.09 MPa). The analytes were redissolved in 2 mL hexane and filtered using a 0.22 μm Nylon syringe filter for APGC-Q-TOF injection.

2.4. Method validation

The validation of the method was evaluated in terms of linearity, limits of detection, and recovery (Table 1). Standard stock solution (2 mg L^{-1}) of the mixture of the fifteen organochlorine pesticides was prepared in chromatography grade *n*-hexane. Serial dilutions were performed to prepare the pure solvent standards 0.01, 0.05, 0.1, 0.2, 0.5, 1 mg L^{-1}) with *n*-hexane. Correspondingly, matrix-matched standard solution were prepared (0.01, 0.02, 0.05, 0.1, 0.2, 0.5 mg L^{-1}) by adding the concentrated blank sample extract (soil and water) to each serially diluted standard solution. The matrix-induced signal suppression/enhancement (SSE) was determined by slope ratio of matrix-matched calibration curve/pure solvent calibration curve.

The matrix-dependent LOQ and LOD of the method were determined by the corresponding chromatogram of the lowest calibration standard used in the matrix-matched calibration. The LOQs of the fifteen organochlorine pesticides were established based on the lowest concentration with a signal-to-noise ratio of 10:1, whereas the LODs were established as the lowest concentration with a signal-to-noise ratio of 3:1.

The recovery of soil and the water samples were conducted to investigate the accuracy, precision and feasibility of the method. The experiments were conducted by analyzing five replicates (intra-day precision) on three different days (inter-day precision) to evaluate the repeatability of the method. For soil samples, five replicates of the spiked samples at three levels (10, 50, 500 μg/kg of each organochlorine pesticides) were prepared on three different days. For water samples, five replicates of the spiked samples at three levels (0.1, 0.5, 1 μg/L of each organochlorine pesticides) were prepared on three different days. The extraction and sample cleanup procedure for the target OCPs are discussed in Section 2.3. The stability of the method for determination of OCPs was deter-