SHIMADZU
Excellence in Science

Gas Chromatograph-Mass Spectrometry / AOC™-6000 Plus, GCMS-QP2020 NX

Application News

# Analysis of Organophosphorus Pesticides in Drinking Water using SPME-GCMS

Minhye Lee
Shimadzu Scientific Korea

## User Benefits

- The inspection items of Organophosphorus pesticides (Diazinon, Parathion, Phenitrothion, Phenthoate, and EPN) in water quality can be analyzed simultaneously.
- The automation of fiber conditioning, pretreatment, and sample injection of SPME is possible using AOC-6000 Plus.

## ■ Introduction

Organophosphorus pesticides (OPs) are a class of insecticides based on organophosphorus compounds. It is widely used to control insects on crops in the pesticide market. OPs disrupt the nervous system by ingestion and contact. These are a toxic substance that cause headaches, dizziness, nausea and convulsions. Because of the side effects of these OPs, in Korea, residual standards are also operated in the water quality environment field. In the past, solvent extraction was used as a pretreatment method for water quality testing, but this required excessive solvent use and complex extraction processes. Therefore, the simpler Solid Phase Micro Extraction (SPME)-Gas Chromatography-Mass Spectrometry (ES 05501.5) method has been revised and published by the National Institute of Environmental Research (NIER)[1].
This application news describes the suitability of OPs analysis using SPME automatic injection (AOC-6000 Plus) and GCMS-QP2020 NX for Diazinon, Parathion, Phenitrothion based on the Environmental Standards for drinking water pollution, and Phenthoate, EPN based on the Official test standards for environmental pollution.

## ■Analytical Conditions

The system configuration of SPME-GCMS for the analysis of OPs used Shimadzu AOC-6000 Plus and GCMS-QP2020 NX as shown in Fig 1. The SPME fiber and column used in the analysis were 100 µm PDMS fiber and SH-5 column (30 m x 0.25 mm I.D., df = 0.25 µm), respectively. The detailed analytical conditions are shown in Table 1.

Fig. 1 AOC™-6000 Plus + GCMS-QP2020 NX

Table 1. Analytical Conditions

| | |
|---|---|
| **AOC-6000 Plus** | |
| SPME fiber | : 100 µm PDMS |
| Incubation temp. | : 70 ˚C |
| Incubation time | : 5 min |
| Sample extract time | : 15 min |
| Sample desorb time | : 5 min |
| Agitation | : On |
| **GCMS-QP2020 NX** | |
| Analytical column | : SH-5 (30 m × 0.25 mm I.D., 0.25 µm) |
| Column temp. | : 70 ˚C (2 min) → 15 ˚C/min → 200 ˚C→ 10 ˚C/min → 250 ˚C (3 min) → 10 ˚C/min → 350 ˚C (5 min) |
| Gas flow | : 1.5 mL/min |
| Injection mode | : Split |
| Split ratio | : 5:1 |
| Injector temp. | : 250 ˚C |
| Ion source temp. | : 230 ˚C |
| Interface temp. | : 250 ˚C |
| Acquisition Mode | : SIM (m/z)<br>Diazinon: 179, 137,<br>Fenitrothion : 277, 125,<br>Parathion : 109, 97,<br>Phenthoate : 274, 125<br>EPN : 157, 141,<br>TPP (IS) : 326, 325 |

## ■ Standard solution

The standard mixture (Diazinon, Parathion, Pentate, EPN, and Penitrothion) at a concentration of 1,000 µg/mL was purchased from AccuStandard, and the internal standard (IS) was prepared at a concentration of 1,000 µg/mL using Triphenyl phosphate (TPP, 98 %) purchased from Sigma Aldrich.

## ■ Calibration curve and Chromatograms

For the preparation of calibration standard stock solutions, five mixed standard solutions were diluted with acetone to final concentrations of 0.1, 0.2, 0.5, 1, 2, 5 and 10 µg/mL, and the internal standard was diluted at a concentration of 1 µg/mL. To confirm the linearity of each component, 20 µL of each of the prepared mixed standard solutions and internal standard solutions put into a headspace vial containing 19.96 mL of water and then sealed them.

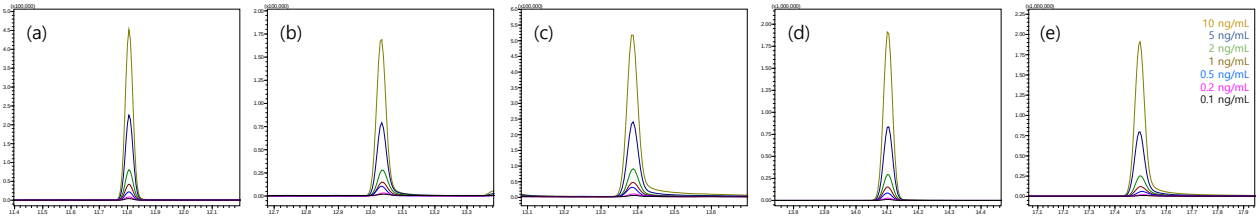


Fig. 2 Chromatograms by concentration of OPs (a) Diazinon, (b) Phenitrothion, (c) Parathion, (d) Phenthoate, (e) EPN

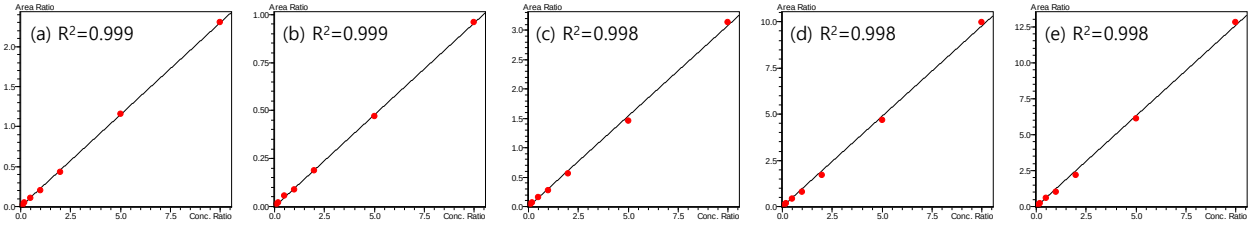


Fig. 3 Calibration curve of OPs (a) Diazinon, (b) Phenitrothion, (c) Parathion, (d) Phenthoate, (e) EPN

The concentration of the prepared standard solution is (0.1, 0.2, 0.5, 1, 2, 5, 10) ng/mL for each component, and the concentration of the internal standard solution is 1 ng/mL. The Chromatograms of the seven concentration levels for each compound are shown in Fig. 2. The calibration curves of all five components were found to show good linearity as shown in Fig. 3 ($R^2 \geq 0.998$).

## ■ MDL and LOQ

To obtain the method detection limit (MDL) and quantitative limit (LOQ), the sample of 0.5 ng/mL was measured seven times in series. MDL and LOQ were calculated by multiplying the standard deviation by 3.14 and 10, respectively. As a result, MDL were (0.03 to 0.06) ng/mL, and LOQ were (0.10 to 0.20) ng/mL (Table 2).

Table 2 MDL and LOQ of OPs (0.5 ng/mL, n=7)

| No. | Concentration (ng/mL) | | | | |
|---|---|---|---|---|---|
| | Diazinon | Phenitrothion | Parathion | Phenthoate | EPN |
| 1 | 0.46 | 0.51 | 0.48 | 0.4 | 0.41 |
| 2 | 0.47 | 0.51 | 0.47 | 0.41 | 0.47 |
| 3 | 0.45 | 0.5 | 0.46 | 0.4 | 0.45 |
| 4 | 0.46 | 0.49 | 0.46 | 0.39 | 0.45 |
| 5 | 0.46 | 0.47 | 0.45 | 0.39 | 0.45 |
| 6 | 0.47 | 0.51 | 0.47 | 0.41 | 0.46 |
| 7 | 0.44 | 0.5 | 0.46 | 0.38 | 0.43 |
| Average | 0.46 | 0.50 | 0.46 | 0.40 | 0.45 |
| MDL | 0.03 | 0.05 | 0.03 | 0.03 | 0.06 |
| LOQ | 0.11 | 0.15 | 0.10 | 0.11 | 0.20 |

## ■ Accuracy and Precision

Accuracy and precision were measured by preparing a standard solution (5 ng/mL) with a concentration of 10 times the quantitative limit. Four standard solutions at a concentration of 5 ng/mL were measured in series and calculated as the mean value and standard deviation. As shown in Table 3, the accuracy were (87.6 – 108.2) %, and the precision were (2.2 – 4.9) %.

Table 3 Accuracy and Precision of OPs (5 ng/mL, n=4)

| No. | Concentration (ng/mL) | | | | |
|---|---|---|---|---|---|
| | Diazinon | Phenitrothion | Parathion | Phenthoate | EPN |
| 1 | 4.74 | 4.84 | 4.57 | 4.32 | 4.57 |
| 2 | 4.95 | 4.83 | 4.58 | 4.56 | 4.84 |
| 3 | 4.60 | 4.70 | 4.79 | 4.04 | 4.58 |
| 4 | 4.98 | 5.07 | 4.73 | 4.32 | 4.83 |
| Average | 5.41 | 5.05 | 4.96 | 4.38 | 4.97 |
| Accuracy (%) | 108.2 | 101.0 | 99.2 | 87.6 | 99.4 |
| Precision (%) | 3.3 | 3.0 | 2.2 | 4.9 | 3.0 |

## ■ Conclusion

This application news is to analyze five types of OPs according to the Standard for Quality Test of Drinking Water. The suitability of the analysis was confirmed using Shimadzu AOC-6000 Plus and GCMS-QP2020 NX.
All components showed good linearity with the $R^2$ value of 0.998 or higher in the concentration (0.1-10) µg/mL range. MDL, LOQ, accuracy, and precision were excellent at (0.03 to 0.06) ng/mL, (0.10 to 0.20) ng/mL, (87.6 to 108.2), and (2.2 to 4.9), respectively, and were found to satisfy the method criteria.
Based on these results, it was confirmed that the use of AOC-6000 Plus and GCMS-QP2020 NX can automate fiber conditioning, pre-treatment and GC injection, making it more convenient to analyze and obtain excellent analysis results.

## ■ Reference

[1] National Institute of Environmental Research. 2022-36, Environmental Standards for drinking water pollution, Organophosphorus Pesticides-Solid Phase Microextraction (SPME)-Gas Chromatography-Mass Spectrometry (ES 05501.5).



09-SSK-018-EN First Edition: Sep. 2024

SHIMADZU
Shimadzu Corporation
www.shimadzu.com/an/

Shimadzu Scientific Korea
www.shimadzu.co.kr