

Determination of Pesticide Residues in Drinking Water Using Automated Solid-Phase Extraction and GC-NPD

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Overview

The Thermo Scientific™ Dionex™ AutoTrace 280 Solid-Phase Extraction instrument automates all steps in the solid-phase extraction (SPE) process, including conditioning, loading, rinsing, and eluting. This system extracts organic pollutants from large-volume liquid samples ranging from 20 mL–4 L and requires only 10 minutes of operator intervention to complete a batch of six samples. This poster provides a complete workflow for organophosphorous pesticides using automated SPE and gas chromatography (GC) with nitrogen phosphorus detection (NPD). Methods for both are provided and can be used immediately by any environmental or food laboratory that would like to test for these compounds in water samples.

Introduction

Organophosphorous pesticides have been widely used to prevent and treat plant diseases and pests in agricultural products and as a result, excessive residual pesticide content is frequently reported in drinking and surface water sources. A number of these compounds are acutely toxic to human and animal life, making the detection of residual organophosphorous pesticides a growing concern. This work addresses the detection of trace amounts of organophosphorus pesticides in water and optimizes the conditions for solid-phase extraction (SPE) and chromatographic analysis using the Thermo Scientific™ Dionex™ AutoTrace 280 Solid-Phase Extraction instrument and the Thermo Scientific™ TRACE™ 1300 Series gas chromatograph with a nitrogen-phosphorus detector (NPD). Eight different types of organophosphorus pesticide residues were detected in drinking water. The results show that this method achieves rapid, simple extraction with small quantities of solvent. In addition, the method has high sensitivity to the eight types of organophosphorus pesticides, a high recovery rate and good linear range.

Methods

Sample Preparation

500 mL of tap water from the Thermo Scientific Beijing Laboratory was used for the samples. Methanol and NaCl were added to reduce the solubility of the organophosphorous pesticides in water. This enables greater retention during the extraction process and higher recovery of the target analytes. These samples were then spiked with 50 µL of 10 µg/mL mixed standard solution containing eight organophosphorous pesticides (Dichlorvos, Demeton, Phorate, Disulfoton, Dimethoate, Methyl Parathion, Malathion, and Parathion). The sample was purified on a 6 mL SPE cartridge and eluted with ethyl acetate and dichloromethane. The collected liquid was concentrated to 1 mL by nitrogen stream and analyzed using gas chromatography.

SPE Conditions

Six spiked tap water samples were processed automatically on the Dionex AutoTrace 280 Solid-Phase Extraction instrument according to the method below.

| Step | Extraction Procedure | Flow Rate |
|------|--|-------------|
| 1 | Activate extraction cartridge with 5.0 mL methanol into the solvent waste channel | 15.0 mL/min |
| 2 | Activate extraction cartridge with 5.0 mL ethyl acetate into the solvent waste channel | 15.0 mL/min |
| 3 | Activate extraction cartridge with 5.0 mL dichloromethane into solvent waste channel | 15.0 mL/min |
| 4 | Activate extraction cartridge with 5.0 mL ethyl acetate into solvent waste channel | 15.0 mL/min |
| 5 | Activate extraction cartridge with 5.0 mL methanol into solvent waste channel | 15.0 mL/min |
| 6 | Activate extraction cartridge with 5.0 mL water into solvent waste channel | 15.0 mL/min |
| 7 | Load a 550.0 mL of sample onto the extraction cartridge | 10.0 mL/min |
| 8 | Rinse the extraction cartridge with 5.0 mL of water into the waste channel | 10.0 mL/min |
| 9 | Dry the small extraction cartridge with nitrogen for a period of 10 min | 15.0 mL/min |
| 10 | Elute 4.0 mL fraction from the extraction cartridge with ethyl acetate in the sample collection tube | 3.0 mL/min |
| 11 | Elute 4.0 mL fraction from the extraction cartridge with ethyl acetate in the sample collection tube | 3.0 mL/min |
| 12 | Elute 2.0 mL fraction from the extraction cartridge with dichloromethane in the sample collection tube | 3.0 mL/min |

GC-NPD Conditions

The analysis was performed using a Thermo Scientific™ TRACE™ 1310 Gas Chromatography with an SSL injector and a Thermo Scientific™ AI/AS 1310 Series autosampler. The system configuration and method parameters are listed in the table below.

| Parameter | Settings |
|--------------------------------|--|
| Chromatography Column | TG-1701 MS, 30 m, 0.25 mm, 0.25 µm |
| Oven Temperature Program | 80 °C (1 min), 20 °C/min to 250 °C (0 min), 5 °C/min |
| Detector Type and Conditions | Instant Connect NPD: 300 °C Air: 60 mL/min Hydrogen: 2.3 mL/min Make-up gas: Nitrogen 15 mL/min |
| Carrier Gas Type and Flow Rate | Nitrogen, constant current mode Flow Rate: 1 mL/min |
| Injection Method and Volume | Splitless, for 1 min, injector temperature 250 °C; sample volume: 1 mL |

Results

Optimization of SPE Conditions

Chinese Method GB5749-2006 “Hygiene Standards for Domestic Drinking Water” requires that residual amounts of eight types of organophosphorus pesticide in drinking water be monitored. Therefore, the retention capacities and elution efficiencies of various SPE columns when extracting these organophosphorus pesticides was investigated. SPE columns tested included silicon, Waters Oasis® HLB, Agela Cleanert PEP, Agela Cleanert S C18 and Agela Cleanert C8. The test results showed that the Cleanert PEP column offered the best retention capacity.

In a separate experiment, the elution efficiencies of solvents including methanol, ethyl acetate, dichloromethane and n-hexane prepared in different proportions on the organophosphorus pesticides retained on the Agela PEP SPE column were tested. The test results showed that carrying out elution with ethyl acetate/ethyl acetate/dichloromethane (4 mL/4 mL/2 mL) produced the highest elution efficiency with the smallest quantity of solvent. The boiling points of Demeton and Phorate were low, the solubility in water was quite high, and the recovery rate produced by the direct use of SPE was not ideal. However, adding NaCl to the water increased the recovery rate and allows SPE to be used for this method.

Extraction efficiencies were tested by adding 2, 5 and 10 g of NaCl to the water. The recovery rate was highest when adding 5 g NaCl to the water. Figure 1 shows the effect of adding different amounts of NaCl on Phorate recovery rates. Another reason for low Demeton recovery rates is the low boiling point, which makes it degrade easily during testing. Large quantities of Demeton are lost easily during the concentration process. Therefore, lowering the nitrogen blowing temperature to 30 °C during the concentration process and reducing the flow rate to prevent rapid degradation are recommended.

Figure 1. The effect of the quantity of NaCl added on recovery rates.

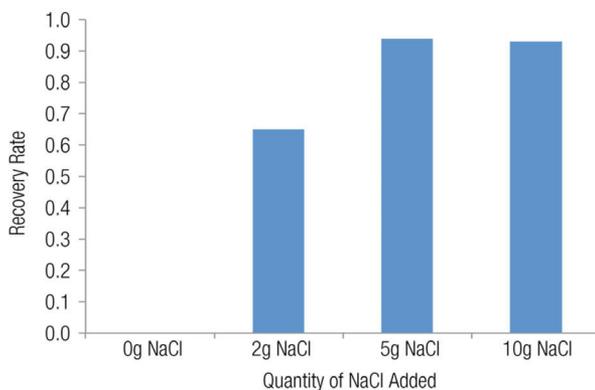


Figure 2. Blank tap water sample chromatogram

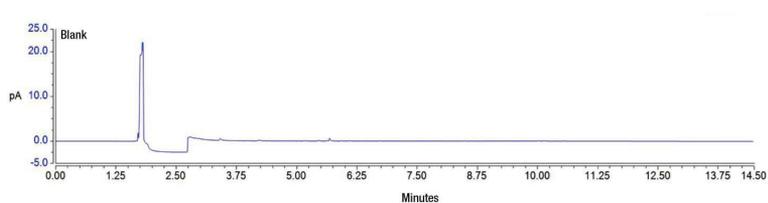
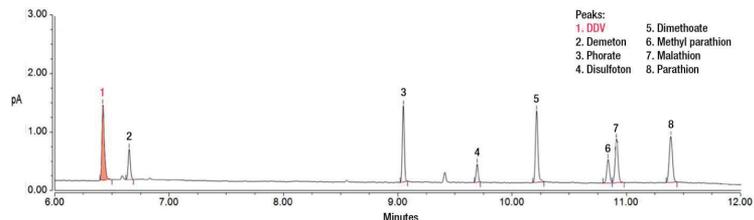


Figure 3. Spiked tap water sample chromatogram*



Method Performance

A mixed standard solution was added to the water samples (spiked concentrations: 0.2, 0.4 and 1 µg/L) to investigate the spike recovery rates of the eight pesticides. The test results showed that spike recovery rates for each component are between 83% and 100% and are in compliance with routine analysis detection requirements. At the same time, water samples were spiked with 0.2 µg/L, 0.4 µg/L, and 2.0 µg/L and analyzed six times in parallel. The average RSD value was between 2.4% and 8.7%, in compliance with stability requirements. The detection limit for each component was calculated using three times the signal-to-noise ratio. The detection limits for each component were 0.02–0.1 µg/L as demonstrated in Table 1 below.



Dionex AutoTrace 280 Solid-Phase Extraction Instrument



TRACE 1310 GC with NPD

Chromatograms and Method Performance

This method compared an unspiked tap water sample to a sample spiked with eight organophosphorus compounds. Both types of samples were run through the entire extraction and analytical procedure as outlined. Figure 2 is the chromatogram for the unspiked tap water blank. As observed, no residual organophosphorus pesticides are present. Figure 3 is the chromatogram for the spiked tap water samples. Each compound is separated according to the expected retention time and the chromatogram provides identifiable, well-resolved peaks for each of the pesticides.

Table 1. Detection Limits and RSDs for Spiked Samples

| Compound | Spiked sample 0.2 µg/L Recovery rate/% | Spiked sample 0.4 µg/L Recovery rate/% | Spiked sample 1.0 µg/L Recovery rate/% | Detection limit/µg/L | RSD/% (n=6) |
|------------------|---|---|---|----------------------|----------------|
| Dichlorvos | 93.2 | 88.4 | 98.6 | 0.01 | 4.1 |
| Demeton | 88.3 | 88.5 | 90.7 | 0.05 | 8.7 |
| Phorate | 98.7 | 91.5 | 95.4 | 0.05 | 6.3 |
| Disulfoton | 95.3 | 89.8 | 95.7 | 0.01 | 7.3 |
| Dimethoate | 88.5 | 89.3 | 99.8 | 0.01 | 2.4 |
| Methyl parathion | 94.0 | 90.9 | 89.3 | 0.05 | 3.8 |
| Malathion | 90.5 | 88.8 | 90.1 | 0.01 | 4.4 |
| Parathion | 93.2 | 95.7 | 96.4 | 0.01 | 3.5 |

Conclusion

- The Dionex AutoTrace 280 Solid-Phase Extraction instrument provides a means to accomplish an efficient, reproducible, and automated extraction for organophosphorus pesticides in environmental waters.
- Use of the TRACE 1310 Gas Chromatograph with NPD provides low detection limits for eight key organophosphorous compounds (0.02-1.0 µg/L) and the excellent recovery ranges (83-100%) at three different spiked concentrations.
- The extraction and analytical methods presented this work meet the requirements of the Chinese EPA Method and can be used by other regulatory agencies for compliance monitoring of organophosphorus compounds in water samples.

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