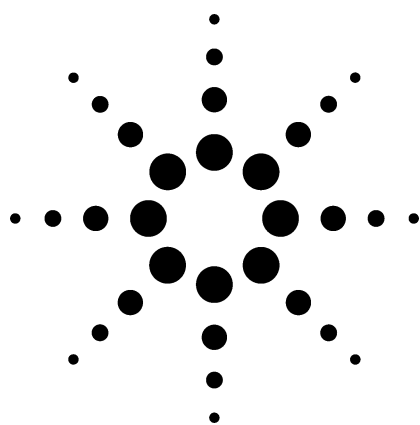




Analysis of Organophosphorus Pesticides with Agilent 6820 Gas Chromatograph/ Nitrogen Phosphorus Detector

Application

Environmental and Food Analysis

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Abstract

Fifteen of the most common and important organophosphorus pesticides (OPs) were studied using the Agilent 6820 gas chromatograph (GC) equipped with the new nitrogen-phosphorus detector (NPD). The 6820 GC-NPD demonstrated good linearity for concentrations of pesticides range from 1 to 500 ng/mL ($R^2 > 0.999$) for most compounds. All OPs produced high signal-to-noise ratios for splitless injections at 10 ng/mL (ppb) concentrations with the NPD detector. Instrumental limits of detection for most OPs studied were at low or sub-ppb concentrations. This suggests the 6820 GC with an NPD is well suited for OP pesticide residue determinations in foods, water, or other samples.

Introduction

Synthetic organic pesticides are widely used in modern agriculture to protect crops and improve production. The “green revolutions” of many countries are obtained through the application of these compounds. There are increasing concerns over

food safety and the identities and residual concentrations of pesticides due to their stability, inappropriate or illegal usage. In China, organophosphorus pesticides (OPs) account for 70% of the total amount of the pesticides used [1]. Maximum residue levels (MRLs) have been set up for 27 OPs in different kinds of food, and analytical methods have been developed for their analysis [2]. The China National standard method GB/T 5009.145-2003 is a method for the determination of 16 organophosphorus and 4 carbamate pesticides by GC-NPDs [3]. In this application note, the Agilent 6820 GC equipped with an NPD is employed to determine 15 of the most common OPs of concern.

Experimental

The experiments were carried out on an Agilent 6820 GC with split/splitless inlet and NPD. De-activated liners for splitless injection (p/n 5183-4696) were used to improve the inertness of the system; the septa were Agilent green septa (p/n 5183-4759). Cerity Networked Data System (NDS) for Chemical QA/QC software was used for instrument control, data collection, and data processing. The sample was introduced manually with a 10- μ L syringe (p/n 5182-3428). All target compounds were dissolved in acetone. The experimental conditions are listed in Table 1. All flows were set using the Veriflow-500 digital flowmeter (p/n HVF-500-2).



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Table 1. Instrumental Parameters

Software	Cerity NDS for chemical QA/QC
Inlet	Split/Splitless inlet
Inlet temperature	250 °C
Injection mode	Splitless
Injection volume	1 µL
Purge time	0.75 min
Column	HP-5ms, 30 m × 0.32 mm × 0.25 µm (p/n 19091S-413)
Carrier gas	He, head pressure: 12 psi, 2.5 mL/min at 60 °C.
Oven temperature	60 °C for 1 min, to 200 °C at 10 °C/min, to 250 °C at 5 °C/min, 5 min hold.
Detector	NPD at 325 °C with white rubidium bead (p/n G1534-60570)
Detector gases	H ₂ : 3 mL/min; Air: 60 mL/min; makeup N ₂ : 10 mL/min

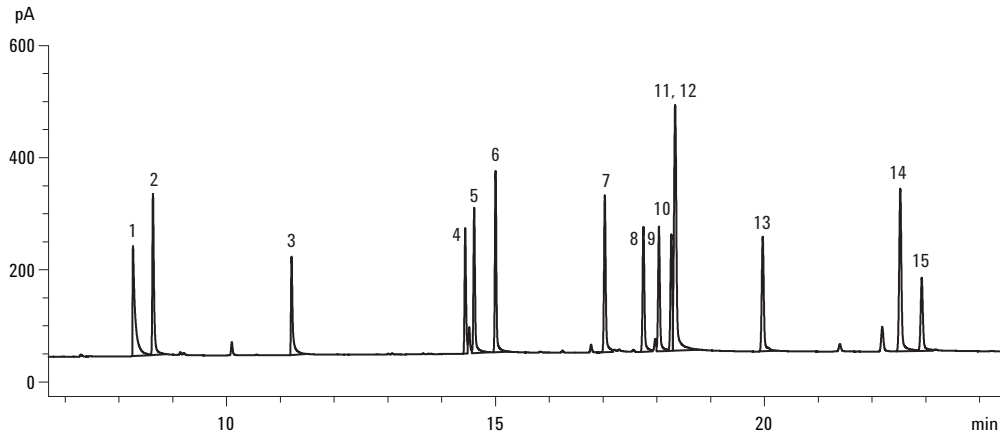
by 1-µL injections of standards at 1, 10, 50, 100, and 500 ng/mL concentrations were linear with $R^2 > 0.999$ for most compounds. The calibration curve for dichlorvos, a typical OP, is shown in Figure 2.

Table 2. Retention Times of Target Pesticides

Peak number	Compound	Retention time
1	Methamidophos	8.26
2	Dichlorvos	8.63
3	Acephate	11.21
4	Monocrotophos	14.44
5	Phorate	14.60
6	Dimethoate	15.00
7	Parathion-methyl	17.03
8	Fenitrothion	17.75
9	Malathion	18.04
10	Fenthion	18.27
11	Parathion	18.34
12	Chlorpyrifos	18.34
13	Methidathion	19.97
14	Ethion	22.52
15	Triazophos	22.92

Results and Discussions

The separation of 15 OPs is illustrated in Figure 1. The compounds, except for chlorpyrifos and parathion, were well separated with the HP-5ms column. Peak identifications are listed in Table 2. Calibration curves constructed from data obtained

**Figure 1. Chromatogram of 15 OPs at 1-ppm using the NPD.**

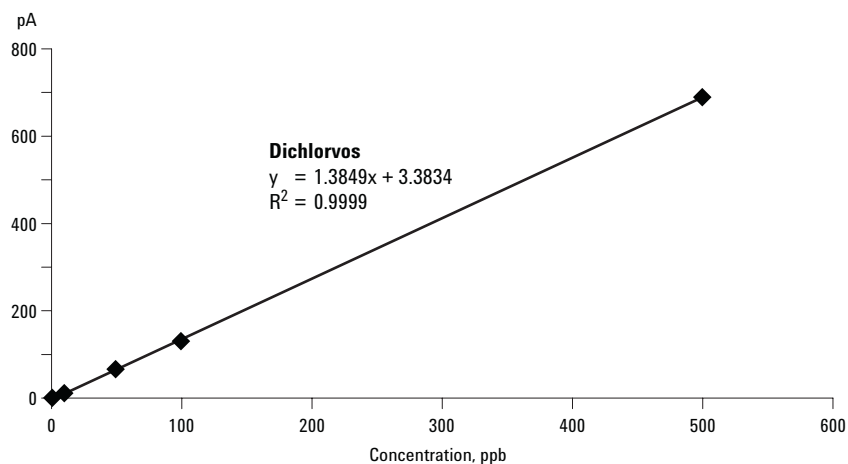


Figure 2. Calibration curve for dichlorvos, a typical OP.

Approximate Instrumental Limits of Detection

The chromatogram for 10-ppb pesticides using the NPD is shown in Figure 3. All compounds are easily quantitated. Acephate, with the lowest response factor, provided around a 30 ratio of signal to noise. In fact, most compounds at 1 ppb show good peaks except methamidophos, acephate, and monocrotophos. The limits of detection (LODs) are much lower than the maximum residue levels (MRLs) for the OPs.

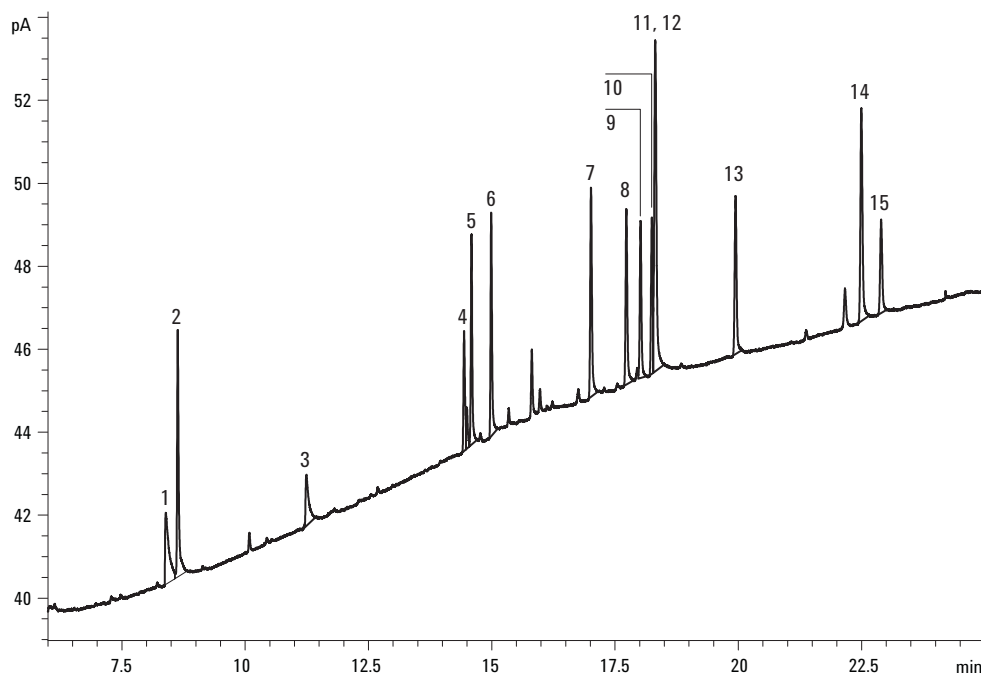


Figure 3. Chromatogram of 10-ppb OPs using the Agilent 6820 GC/NPD.

Sample Solvent Precautions

In some sample extraction procedures, organic solvents, containing elements with high electronegativity, (such as methylene chloride), may be used. However, these solvents may cause baseline shifts, change the detector sensitivity, shorten lifetime of the rubidium bead, or even make the detector unusable. This is true for all types and vendors of NPD [4]. If the final solution for injection consists of methylene chloride or chloroform, it is best to change the solvent to acetone or hexane.

Conclusion

The Agilent 6820 GC with NPD can be used for the sensitive and selective determination of OPs. The NPD detector provides good linearity for most of these compounds in the 1–500-ppb range.

References

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