

# Coupled LC-GC for the Analysis of Pesticide in Food

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**Key Words:** LC-GC, SPE, large volume injection, pesticide, food

## 1. Introduction

Analysis of pesticide residues in food is not so easy to do because various foods contain complex matrix. Recently several reports have been described that on-line LC-GC system is useful for the analysis of complex samples such as pesticide residues in food. The high sample capacity and wide range of separation performance of LC can be utilized in selective cleanup of sample and GC has high separation efficiency. However, coupling of LC to GC is not a trivial matter because the introduction of a large amount of LC fraction into a GC column requires the use of special techniques to separate the solvent from the sample. One of the subject for coupling LC with GC is a technique of eliminating water which is contained in LC fraction. Another subject is a technique of transferring analytes to GC.

The purpose of this study is coupling reversed-phase HPLC with GC for attaining automated analysis of pesticide residues in food. An interface equipped with a SPE cartridge is developed for coupling LC with GC. Finally, the performance of this LC-(SPE)-GC system has been evaluated by inspecting the data with analyzing chlorpyrifos in ginger.

## 2. Experiment

The system is shown in the following. With adding water to the LC fraction, the diluted fraction is loaded on the SPE cartridge. The analyte is adsorbed on the SPE. The cartridge was dried with nitrogen gas. The analyte is eluted from the the SPE cartridge with 20  $\mu$ L of hexane by syringe pump and the eluate is directly injected into a GC injector via a needle. The GC injector consists of a PTV injector equipped with a stomach shaped insert. The stomach shaped insert makes it possible to accept all of the injected eluate from the SPE cartridge.

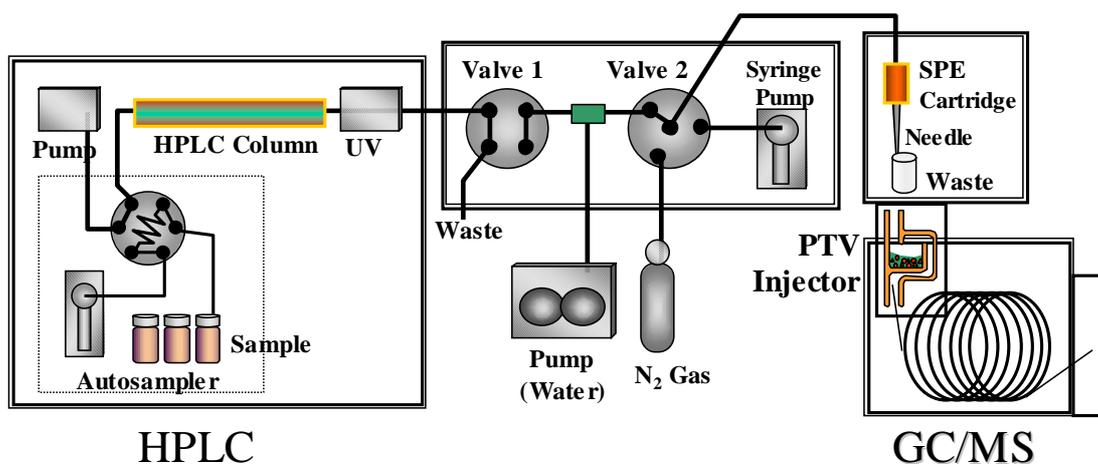


Fig. Schematic flow diagram of LC-GC system.

## LC-GC System Conditions

HPLC (MIDAS;Spark, Agilent 1100)		Interface Injector (LaviStoma; EMINET)	
Injection:	100 $\mu$ L, Sample loop	Insert:	Stomach Type Insert
Column:	3.0 mm i.d. $\times$ 100 mm Inertsil ODS-3	Solvent Vent:	10 sec, Purge flow 150 mL/min
Solvents:	A: Acetonitrile/Water (50/50) B: Acetonitrile	Splitless:	3 min
	Flow rate 0.5 mL/min	Inj. Temp.:	70°C(3min)-120°C/min-220°C/min (3min) -50°C/min-260°C(10min)
Detector:	UV 210 nm	GC/MS (QP-5050A; Shimadzu)	
Interface SPE (LGI-S100)		Column:	0.25 mm i.d. $\times$ 30 m, 0.25 $\mu$ m Inert Cap 5MS/Sil
SPE:	2 mm i.d. $\times$ 10 mm C18	Oven:	70°C(3min)-20°C/min-280°C(4min)
Diluting:	Water 0.4 mL/min	Carr. gas:	He, 1 mL/min
Purge:	N <sub>2</sub> gas, 0.5 min	MS:	SCAN;50-550 m/z
Elution:	Hexane, 20 $\mu$ L		

### Sample preparation

20 g portions of homogenized ginger were extracted with 70 mL of acetonitrile. The extract solution was adjusted to 100 mL with water.

Then 1 mL of the extract was cleaned up through an C18 cartridge (50 mg) for avoiding HPLC column from deteriorating, and adjusted to 2 mL with 70% acetonitrile-water for LC-(SPE)-GC/MS analysis.

### 3. Result and Discussion

The performance of the system was investigated with respect to the LC-(SPE)-GC process by a ginger spiked with 0.1  $\mu$ g/g of chlorpyrifos. Chlorpyrifos elute around 8.2min. The fraction eluting from 7.8 to 8.6 min was transferred to the SPE interface. The excellent chromatography obtained can be observed in Fig. 2. The cleaning achieved with the LC process is highly satisfactory.

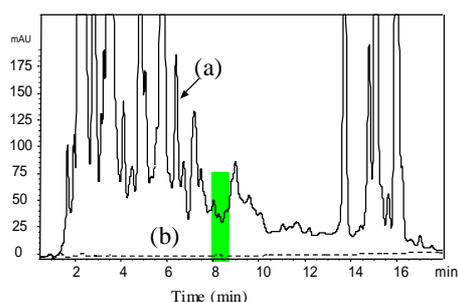


Fig.2 HPLC chromatogram of a ginger spiked with 0.1  $\mu$ g/g of chlorpyrifos (a) and a standard solution of it (b). Marked fraction transferred to the SPE cartridge.

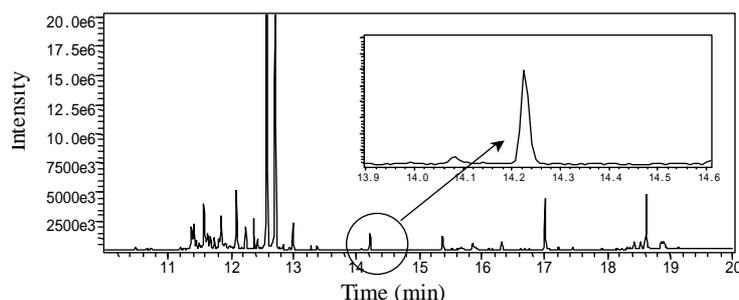


Fig.3 GC/MS-SCAN chromatogram of the LC-(SPE)-GC/MS analysis of a ginger spiked with 0.1  $\mu$ g/g of chlorpyrifos.

### 4. Conclusion

Coupling of LC with GC has been accomplished by a new SPE interface and a PTV injector equipped with a stomach shaped insert. The LC-(SPE)-GC system provides very high efficiency and selectivity performance, and then allows automated analysis of pesticide residues in food.

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The purpose of this study is coupling reversed-phase HPLC with GC for attaining automated analysis of pesticide residues in food. An interface equipped with a SPE cartridge is developed for coupling LC with GC. The system is shown in the following. With adding water to the LC fraction, the diluted fraction is loaded on the SPE cartridge. The analyte is adsorbed on the SPE. The cartridge was dried with nitrogen gas. The analyte is eluted from the SPE cartridge with 20  $\mu$ L of hexane and the eluate is directly injected into a GC injector via a needle. The GC injector consists of a PTV injector equipped with a spiral insert. The spiral insert makes it possible to accept all of the injected eluate from the SPE cartridge.

Finally, the performance of this LC-(SPE)-GC system has been evaluated by inspecting the data with analyzing chlorpyrifos in spinach.

## Experimental

### HPLC (MIDAS;Spark, Agilent 1100)

Injection: 100  $\mu$ L, Sample loop  
Column: 2.1 mm i.d.  $\times$  100 mm  
Inertsil ODS-3

Solvents: A: Acetonitrile/water (50/50)  
B: Acetonitrile  
flow rate 0.5 mL/min

Detector: UV 210 nm

### Interface SPE

SPE: 2 mm i.d.  $\times$  10 mm C18  
Diluting: water 0.4 mL/min  
Purge: N<sub>2</sub> gas, 1 min  
Elution: Hexane, 20  $\mu$ L

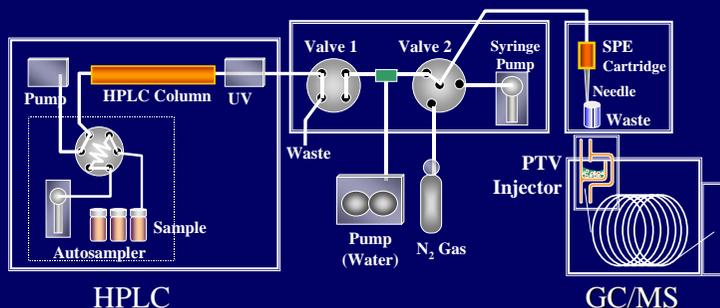
### Interface Injector (LVI-S200; EMINET)

Insert: Spiral Insert  
Solvent Vent: 10 sec, Purge flow 150 mL/min  
Splitless: 3 min  
Inj. Temp.: 70°C(3min)-120°C/min-220°C/min(3min)-50°C/min-260°C(10min)

### GC/MS (QP-5050A; Shimadzu)

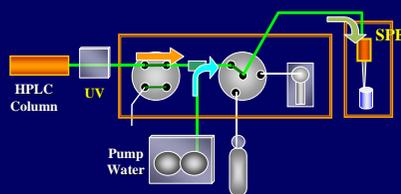
Column: 0.25 mm i.d.  $\times$  30 m Inert Cap 5MS/Sil  
Oven: 70°C(3min)-20°C/min-280°C(4min)  
Carr. gas: He, 1 mL/min  
MS: SCAN;50-550 m/z, SIM;199, 314 m/z

## LC-(SPE)-GC system



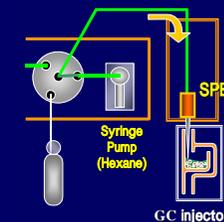
## SPE Interface

### Dilution & Concentration



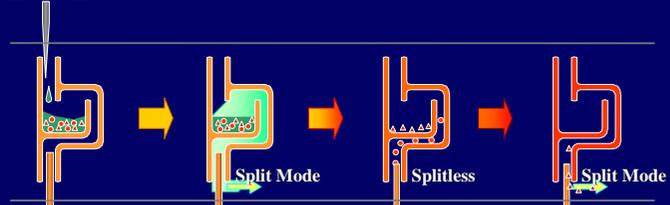
With adding water to the LC fraction, the diluted fraction is loaded on the SPE cartridge. The analyte is adsorbed on the SPE.

### Elution & Injection



The analyte is eluted from the SPE with hexane and the eluate is directly injected into a GC injector via a needle.

## PTV Interface



**1st Stage Injection**  
The injector is kept at a temperature lower than the boiling point of sample solvent.

**2nd Stage Concentration**  
While the evaporated sample solvent is exhausted, the sample is concentrated.

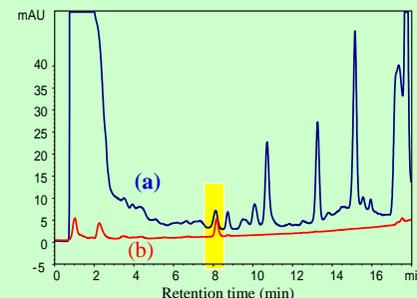
**3rd Stage Transfer**  
Target compounds are transferred to the column at an elevated temperature.

**4th Stage Elimination**  
Matrix compounds are eliminated from the insert at further elevated temperature.

## Application

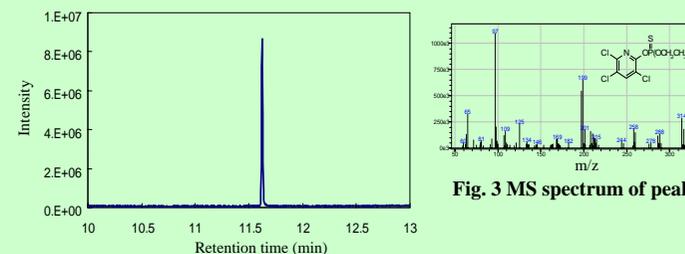
### Sample preparation

20 g portions of homogenized spinach were extracted with 70 mL of acetonitrile. The extract solution was adjusted to 100 mL with water. Then 1 mL of the extract was cleaned up through an C18 cartridge (50 mg) for avoiding HPLC column from deteriorating, and adjusted to 2 mL with 70% acetonitrile-water for LC-(SPE)-GC/MS analysis.



**Fig. 1 HPLC chromatogram of a spinach spiked with 1  $\mu$ g/g of chlorpyrifos (a) and a standard solution of it (b). Marked fraction transferred to the SPE interface.**

Chlorpyrifos elute around 8.2min. The fraction eluting from 7.8 to 8.6 min was transferred to the SPE interface.



**Fig. 3 MS spectrum of peak**

**Fig. 2 GC/MS-SCAN chromatogram of the LC-(SPE)-GC/MS analysis of a spinach spiked with 1  $\mu$ g/g of chlorpyrifos**

The excellent chromatography obtained can be observed in Fig. 2. The cleaning achieved with the LC process is highly satisfactory. The performance of the system was investigated with respect to the LC-(SPE)-GC process by a standard solution or a spinach spiked with 1  $\mu$ g/g of chlorpyrifos. The recovery was found to be higher than 98%. Reproducibility parameters (RSD) for the peak area was below 2%.

## Conclusion

Coupling of LC with GC has been accomplished by a new SPE interface and a PTV injector equipped with a spiral insert. The LC-(SPE)-GC system provides very high efficiency and selectivity performance, and then allows automated analysis of pesticide residues in food.