Title: (Capitalize the first letter of each key word)	Coupled LC-GC Interface Using a SPE Technique and a Large Volume Injection Technique with a Spiral Insert
Abstract: (Your abstract must use Normal style and must fit in this space), Times New Roman Font, 12 point	A new interface using a solid phase extraction (SPE) technique and a large volume injection technique has been developed for coupling of reverse-phase liquid chromatography (LC) with capillary gas chromatography (GC). The system is shown in the following. With adding water to a LC fraction, the diluted fraction is loaded on a SPE cartridge. By this means, the analyte is adsorbed on the SPE. After the cartridge was dried with nitrogen gas, the analyte is eluted from the SPE cartridge with a solvent that can be injected into GC. The eluate is directly injected into a GC injection port via a needle that is fitted with the SPE cartridge. Next, the analyte is transferred to an analytical column of GC by a large volume injection technique. The GC injector consists of a PTV injector equipped with a spiral insert in the shape of a stomach. The purpose of this study is to decide optimum conditions of the volume of water adding to the LC fraction in order to make an analyte adsorb on the SPE cartridge and the volume of eluate in order to elute the analyte from the SPE cartridge. And then, the precision of this LC-(SPE)-GC system has been evaluated under these optimum conditions. Coupling of reverse-phase LC with GC has been accomplished by a new interface using the SPE technique to change the LC fraction eluent into small amount of solvent that can be injected into GC and the stable large volume injection system with spiral insert.

Coupled LC-GC Interface Using a SPE Technique and a Large Volume Injection Technique with a Spiral Insert

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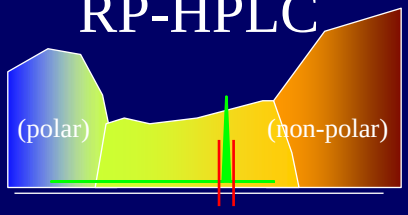
Abstract

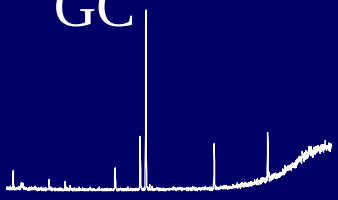
- A new interface /using a solid phase extraction (SPE) technique /and a large volume injection technique /has been developed/ for coupling of reverse-phase liquid chromatography (LC)/ with capillary gas chromatography (GC).

LC-GC System

RP-HPLC



GC



Selective cleanup of sample by LC!

High separation efficiency by GC!

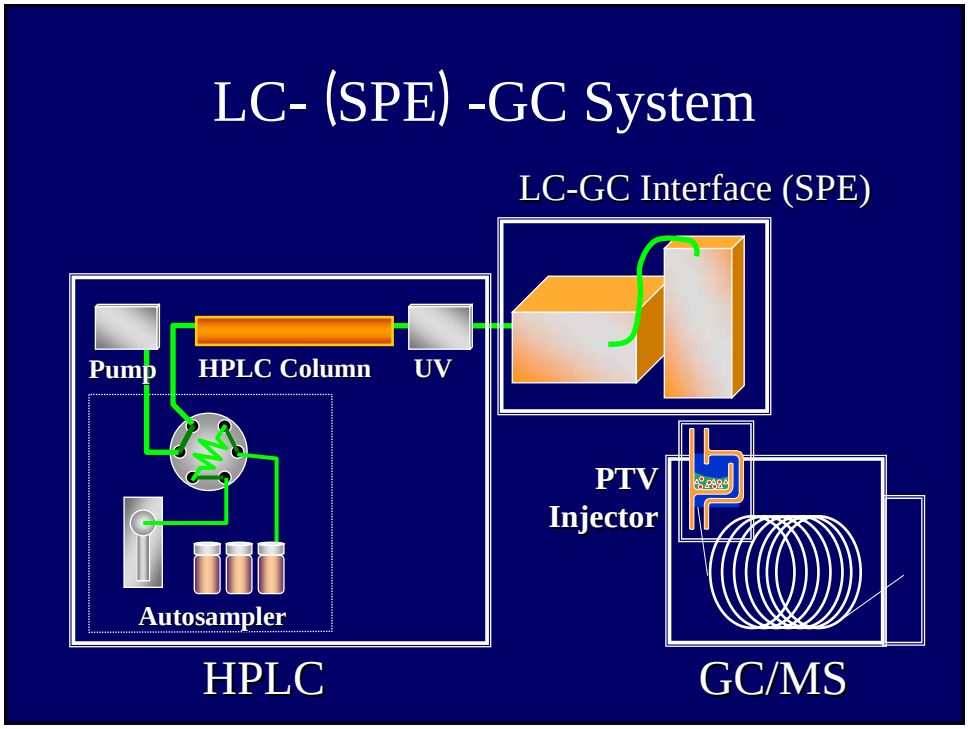
High sample capacity and wide range of separation performance of LC can be utilized in the selective cleanup of sample. Analysis is done by GC with high separation efficiency.

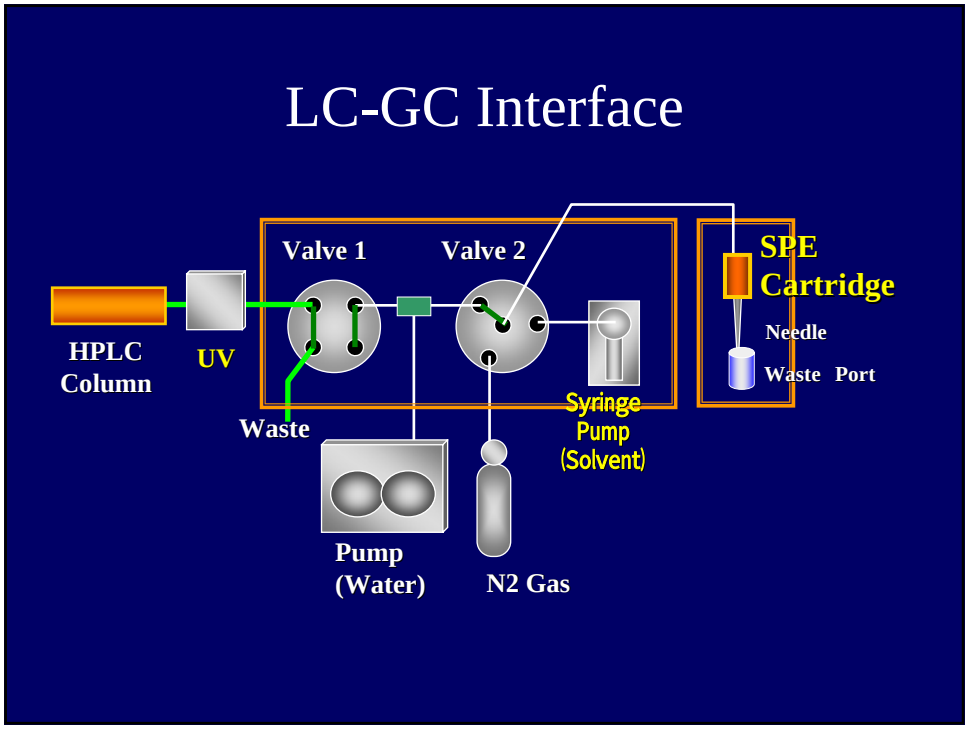
The problem at issue

- Volume of LC fraction is 0.3 to 1 mL. It is hard to inject all of this large volume eluate into GC.
- The LC fraction contains large volume of water or polar solvent. This is no good for GC analysis.

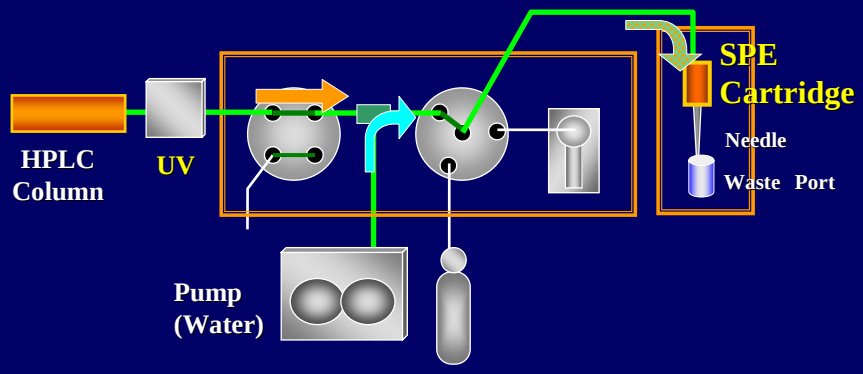
SAIKA solution

- We have used SPE technique as the interface between LC and GC. Then we can transfer large volume solvent of LC fraction into small volume of solvent to be injected to GC.
- We have developed new Large Volume Injector with spiral insert and this has shown stable performance.


LC- (SPE) -GC System
LC-GC Interface (SPE)
Pump
HPLC Column
UV
Autosampler
PTV
Injector
HPLC
GC/MS


LC-GC Interface
Valve 1
Valve 2
SPE
Cartridge
Needle
Waste Port
HPLC
Column
UV
Waste
Syringe
Pump
(Solvent)
Pump
(Water)
N2 Gas

Diluting & Concentrating

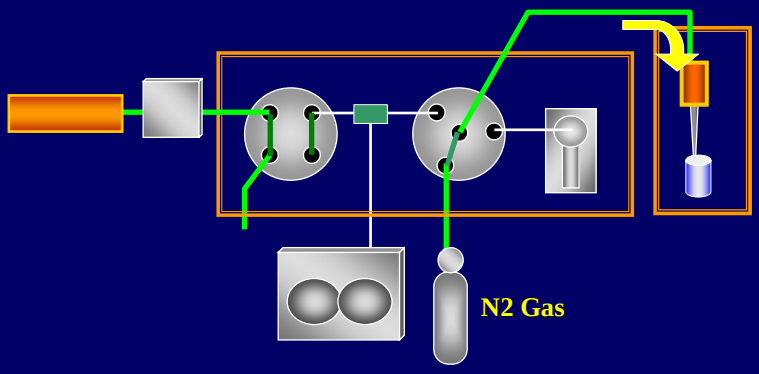


With adding water to the LC fraction, the diluted fraction is loaded on the SPE cartridge.

The target compound is adsorbed on the SPE.

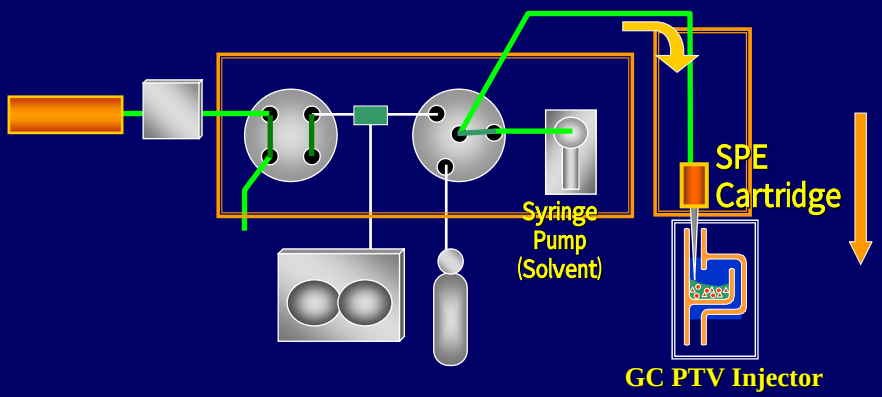
Dilution & Concentration

Drying



The SPE cartridge, the tube and the valve are dried by flowing nitrogen gas.

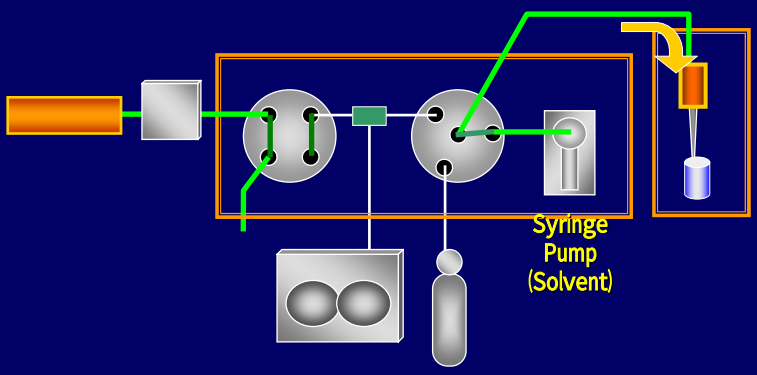
Elution & Injection



The target compound is eluted from the SPE with a solvent and the eluate is directly injected into GC injector via the injection needle.

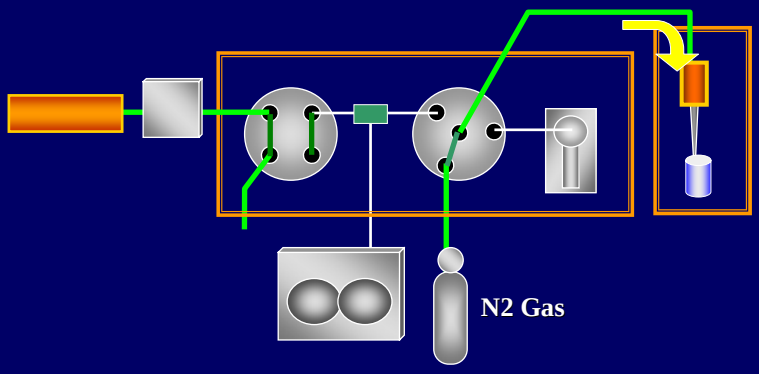
Elution & Injection

Cleaning



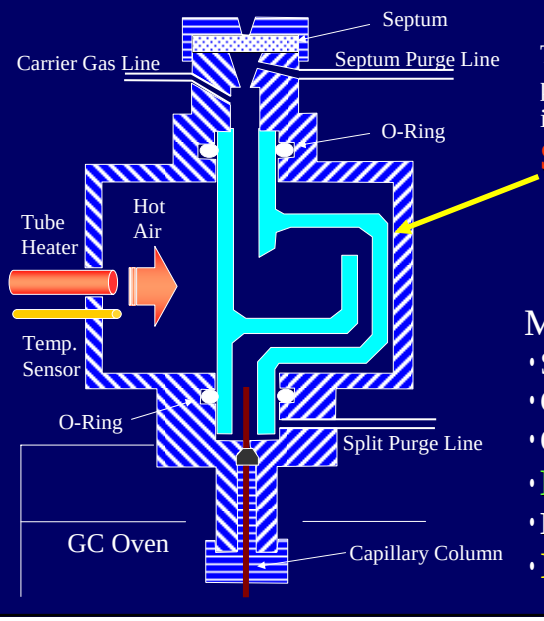
The SPE cartridge and tube are cleaned with a solvent.

Drying



The SPE cartridge, tube and valve are dried with flowing nitrogen gas again.

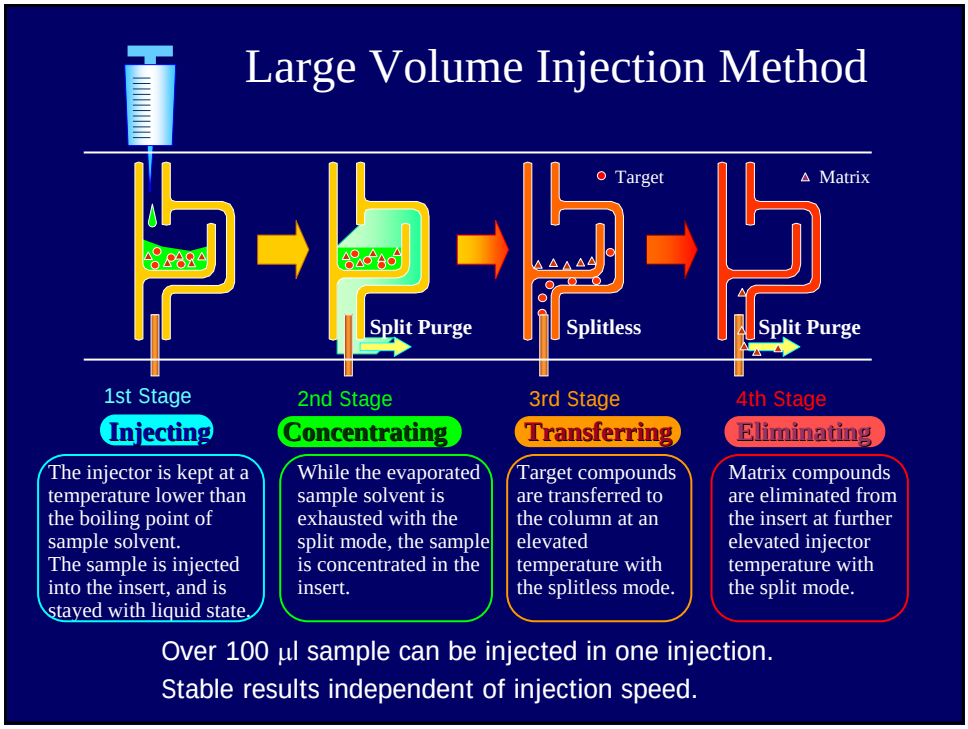
New PTV Injector for GC

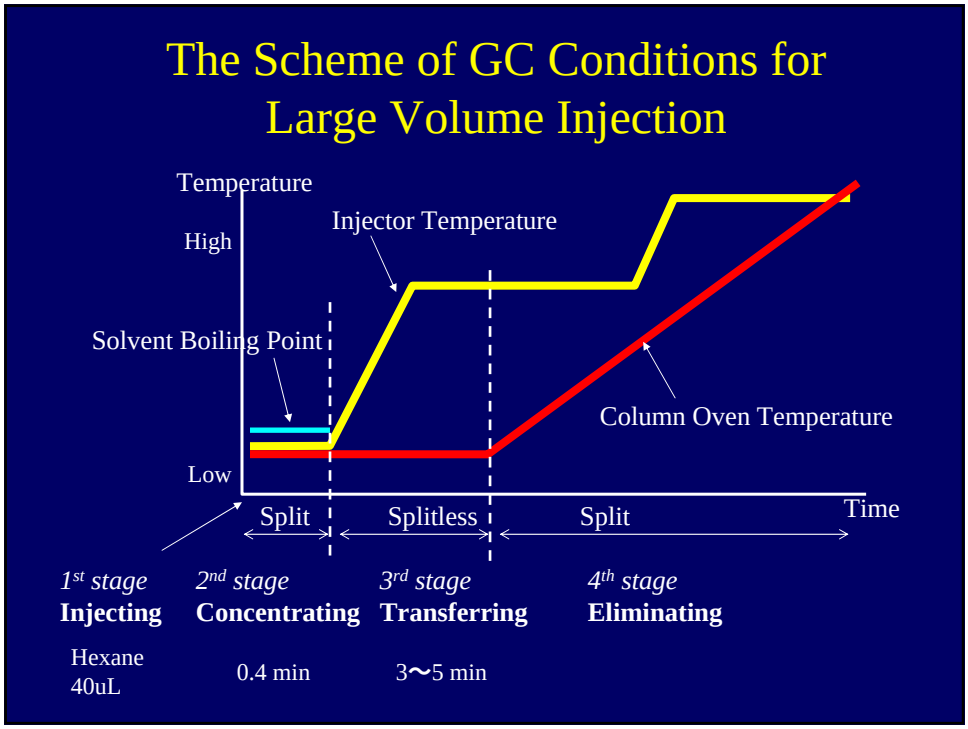


The injection system consisted of a programmed-temperature vaporizing injector with **Spiral Insert**.

Multi-Injector

- Split, Splitless Injection
- Cold Split, Cold Splitless
- On-column Injection
- **Large Volume Injection**
- **Derivatizating Injection**
- **Interface of On-Line GC**


Large Volume Injection Method
Target
Matrix
Split Purge
Splitless
Split Purge
1st Stage
Injecting
The injector is kept at a temperature lower than the boiling point of sample solvent. The sample is injected into the insert, and is stayed with liquid state.
2nd Stage
Concentrating
While the evaporated sample solvent is exhausted with the split mode, the sample is concentrated in the insert.
3rd Stage
Transferring
Target compounds are transferred to the column at an elevated temperature with the splitless mode.
4th Stage
Eliminating
Matrix compounds are eliminated from the insert at further elevated injector temperature with the split mode.
Over 100 μl sample can be injected in one injection.
Stable results independent of injection speed.


The Scheme of GC Conditions for Large Volume Injection
Temperature
High
Low
Injector Temperature
Solvent Boiling Point
Column Oven Temperature
Time
Split
Splitless
Split
1st stage
Injecting
2nd stage
Concentrating
3rd stage
Transferring
4th stage
Eliminating
Hexane 40uL
0.4 min
3〜5 min

Purpose of this work

- To decide optimum condition of the flow rate of adding water to the LC fraction in order to make an analyte adsorb on the SPE cartridge
- To decide optimum condition of the volume of eluate in order to elute the analyte from the SPE cartridge.
- Under these optimum conditions, the performance of this LC-(SPE)-GC system has been evaluated by inspecting the data with analyzing chlorpyrifos in foods.

LC-GC/MS Condition

HPLC (MIDAS;Spark, Agilent 1100)
Injection: 100 μL, Sample loop
Column: 3.0 mm i.d. ×100 mm Inertsil ODS-3
Solvents: A: Water
B: Acetonitrile
Flow rate 0.5 mL/min
Detector: UV 210 nm

Interface SPE (LGI-S100)
SPE Cartridge: 2 mm i.d.×10 mm C18
Fraction Time: 11:40-12:60 (80 sec.)
Diluting: Water 0.5 mL/min
Purge: N_2 gas, 1 min
Elution Solvent: 20%Acetone/Hexane
Elution Volume: 40 μL

Interface Injector (LVI-S200; EMINET)
Insert: Spiral Insert
Solvent Vent: 24 sec, Purge flow 150 mL/min
Splitless: 3 min
Inj. Temp.: 70°C-120°C/min-220°C/min (3min)-50°C/min-260°C(10min)

GC/MS (QP-5050A; Shimadzu)
Column: 0.25 mm i.d.×30 m, 0.25 μm Inert Cap 5MS/Sil
Oven: 70°C(3min)-20°C/min-180°C-10°C/min-230°C-20°C/min-300°C(3min)
Carr. gas: He, 1 mL/min
MS: SCAN;150-350 mz

Optimum condition of the flow rate of adding water

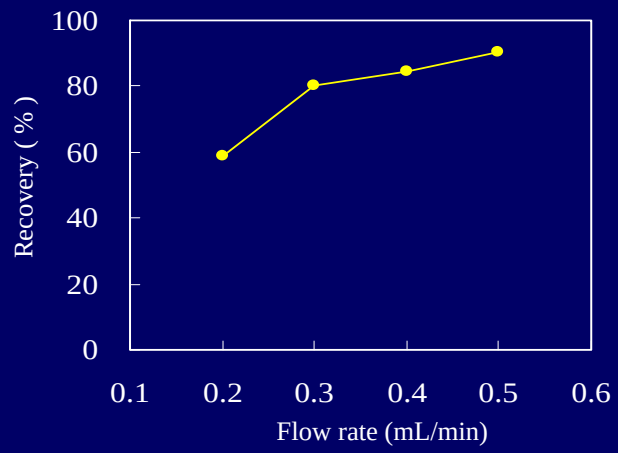


Fig. Relationship between the flow rate of adding water and the recovery ratio

Optimum condition of the elution volume

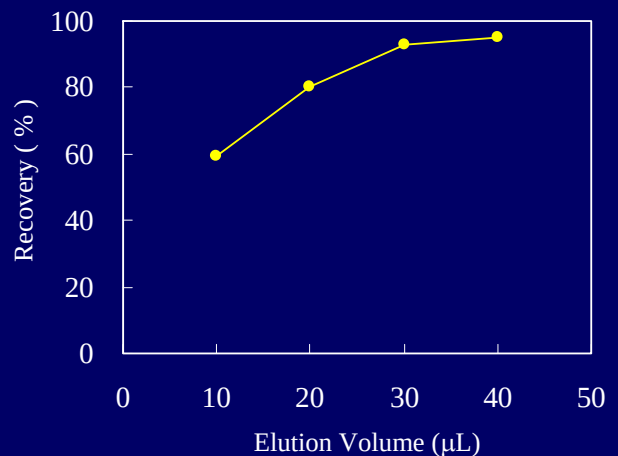


Fig. Relationship between elution volume and recovery

Sample Preparation for LC-GC analysis of pesticides in food

Sample 10g
- CH_3CN 20 mL

Homogenize

Filtration
- CH_3CN 20 mL

Filtrate
- Adj. to 50 mL with water

Extract solution

Take 1mL of extract solution (equal to the 0.2g of sample)
- 90% CH3CN/water 0.5 mL

SPE C18 30mg (cleanup)

Effluent
- Adj. to 2 mL with water

Sample solution


Spinach

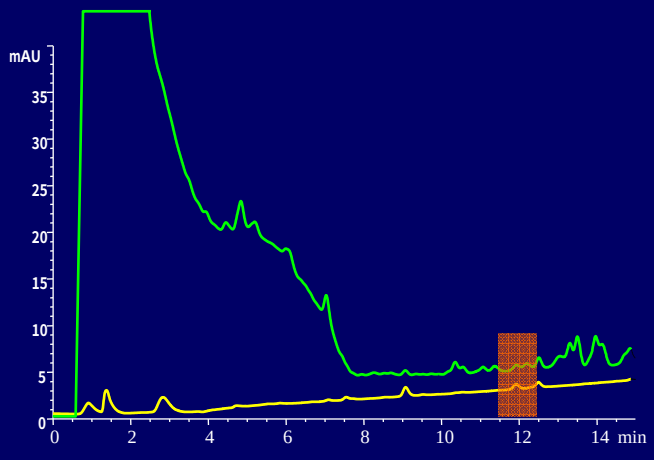

Green Pepper


Carrot


Green Onion

10 g portions of homogenized spinach were extracted with 40 mL of acetonitrile. The extract solution was adjusted to 50 mL with water.
Then 1 mL of the extract was cleaned up through an C18 cartridge (30 mg) for avoiding HPLC column from deteriorating, and adjusted to 2 mL with water for LC-(SPE)-GC/MS analysis.

LC-UV Chromatogram (Spinach)



Time (min)

Fig. HPLC chromatogram of a spinach spiked with 0.1 μg/g of chlorpyrifos (a) and a standard solution of it (b). Marked fraction transferred to the SPE cartridge.

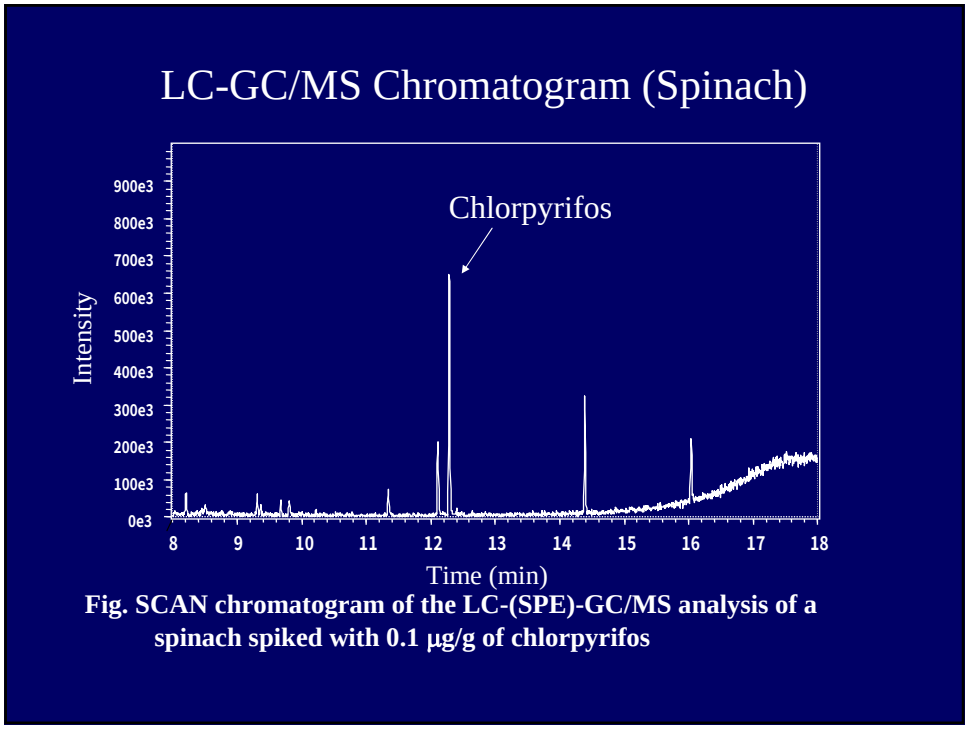


Fig. SCAN chromatogram of the LC-(SPE)-GC/MS analysis of a spinach spiked with 0.1 μg/g of chlorpyrifos

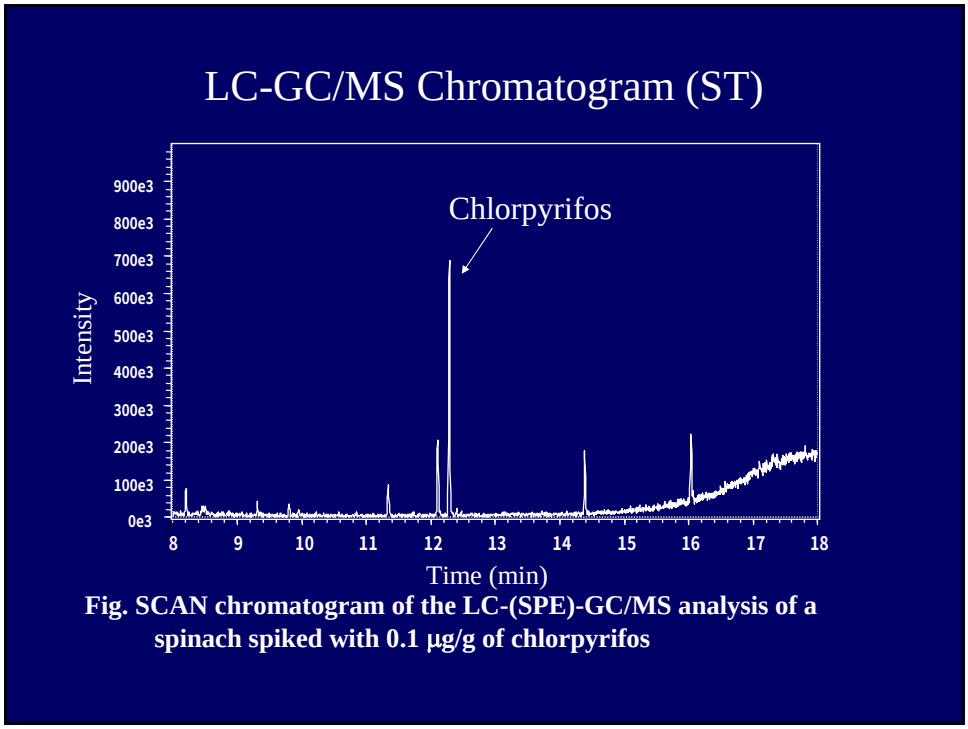


Fig. SCAN chromatogram of the LC-(SPE)-GC/MS analysis of a spinach spiked with 0.1 μg/g of chlorpyrifos

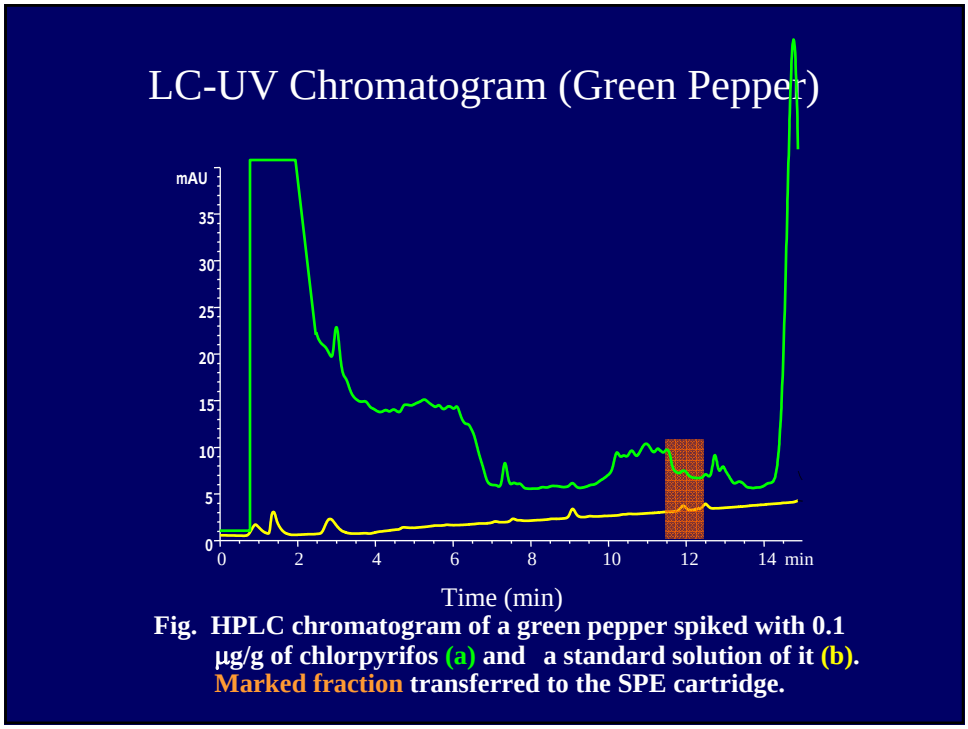


Fig. HPLC chromatogram of a green pepper spiked with 0.1 µg/g of chlorpyrifos (a) and a standard solution of it (b). Marked fraction transferred to the SPE cartridge.

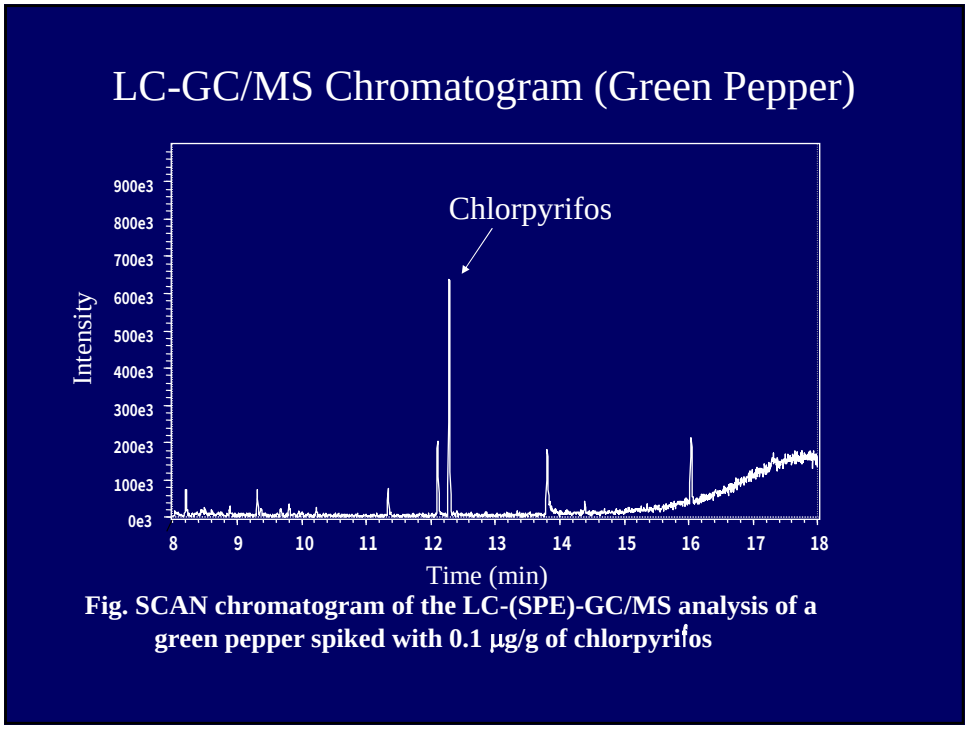


Fig. SCAN chromatogram of the LC-(SPE)-GC/MS analysis of a green pepper spiked with 0.1 µg/g of chlorpyrifos

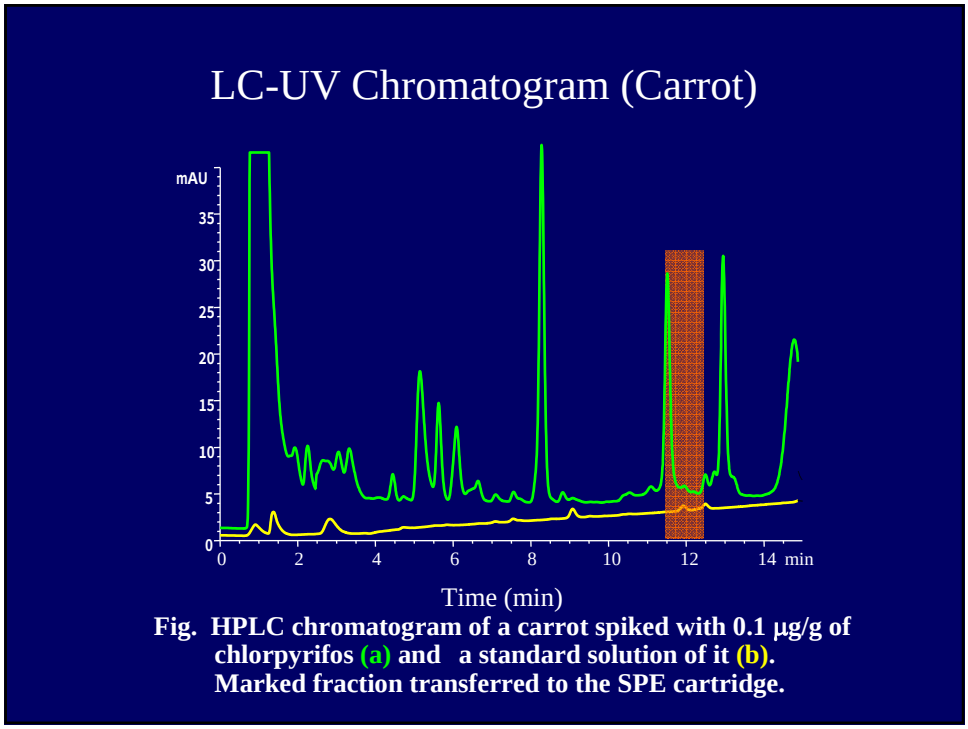


Fig. HPLC chromatogram of a carrot spiked with 0.1 μg/g of chlorpyrifos (a) and a standard solution of it (b). Marked fraction transferred to the SPE cartridge.

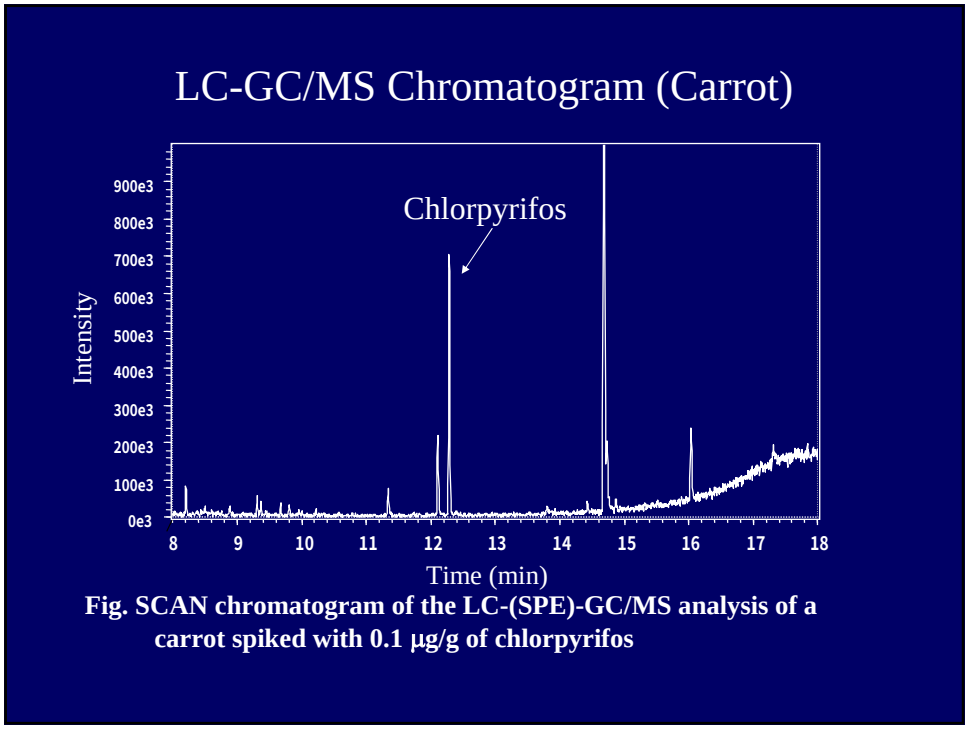


Fig. SCAN chromatogram of the LC-(SPE)-GC/MS analysis of a carrot spiked with 0.1 μg/g of chlorpyrifos

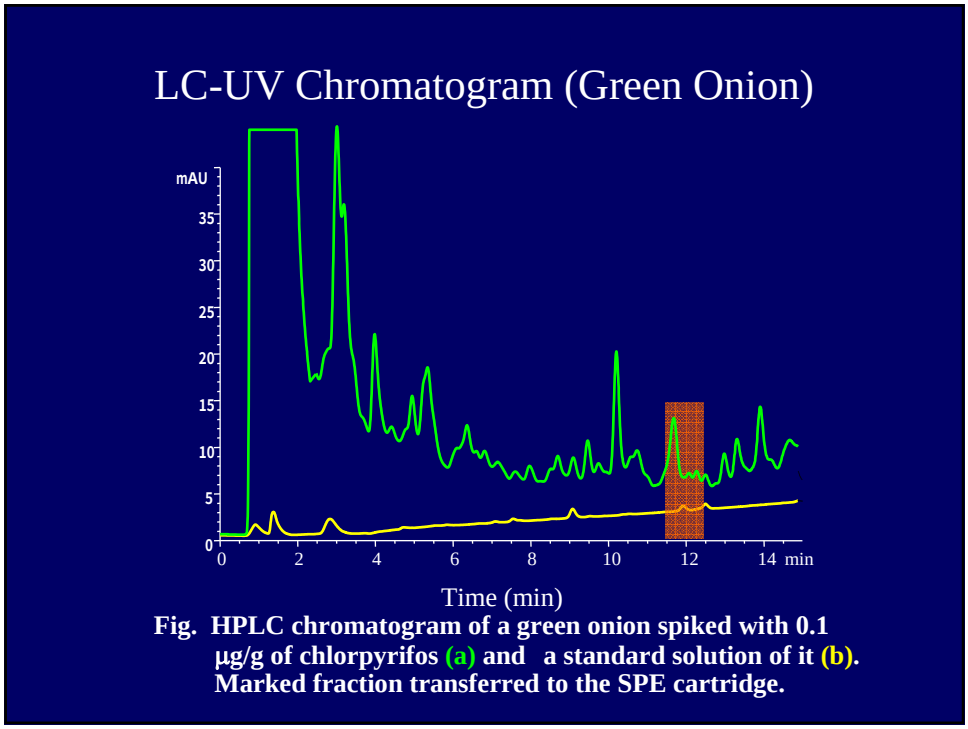


Fig. HPLC chromatogram of a green onion spiked with 0.1 µg/g of chlorpyrifos (a) and a standard solution of it (b). Marked fraction transferred to the SPE cartridge.

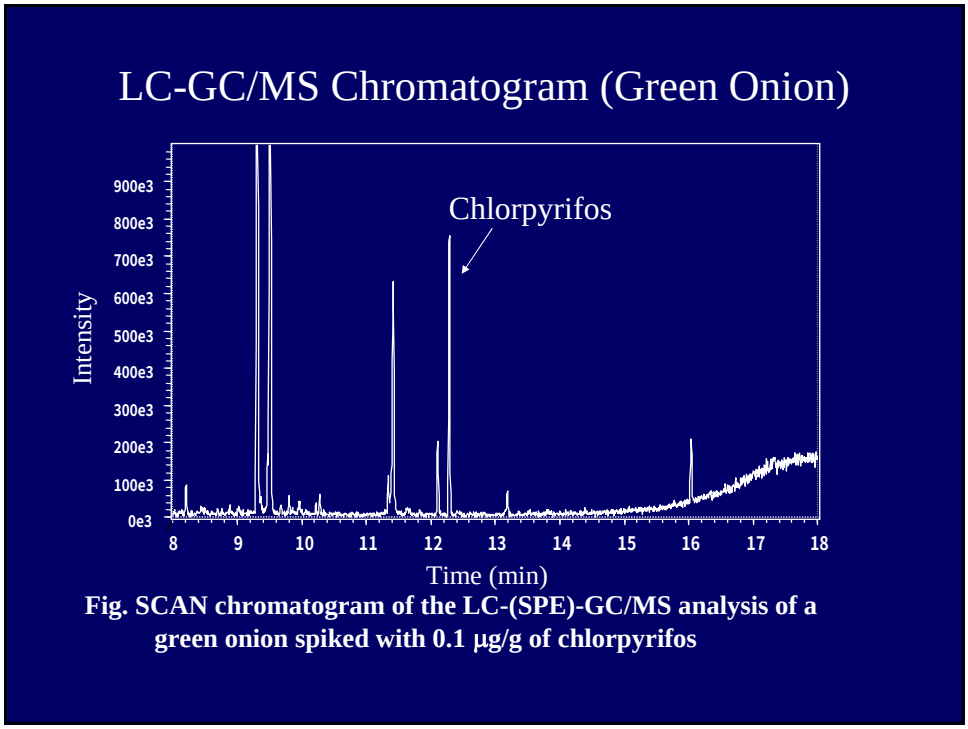


Fig. SCAN chromatogram of the LC-(SPE)-GC/MS analysis of a green onion spiked with 0.1 µg/g of chlorpyrifos

Conclusions

- **Coupling of reverse-phase LC with GC has been accomplished by a new interface using SPE technique and a large volume injector with spiral insert.**
- **The SPE technique can transfer the LC fraction eluent into small amount of solvent that can be injected into GC.**
- **The spiral insert makes it possible to accept all of the injected eluate from the SPE cartridge.**
- **The LC-(SPE)-GC system we have developed provides the pesticide residues analysis with very high efficiency and selectivity performance, and then allows automated analysis of pesticide residues in food.**

Thank you for your kind attention !!

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LC-GC/MS SIM Chromatogram (Green Onion)

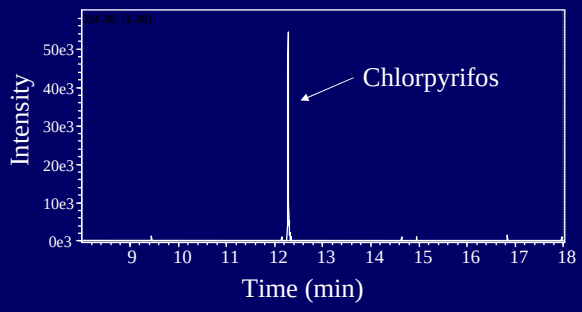

Fig. Ion chromatogram of the LC-(SPE)-GC/MS analysis of a green onion spiked with 0.1 μg/g of chlorpyriphos

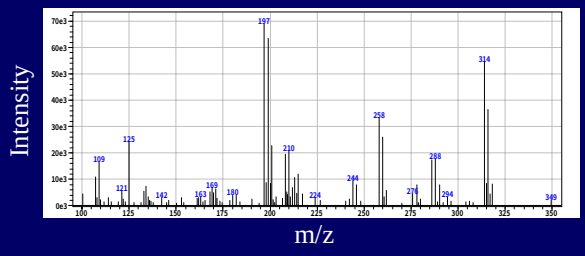

Fig. Mss spectrum of the peak