Coupled LC-GC for the Analysis of Pesticide in Food

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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. 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 µL 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 stomach shaped insert. The stomach shaped 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 chlorpyriphos in spinach.

Experimental

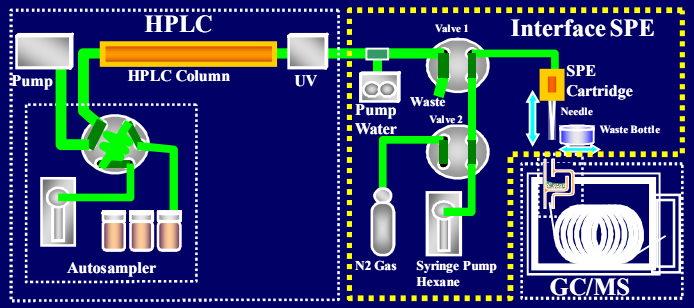
HPLC (MIDAS;Spark, Agilent 1100)
- Injection: 100 µL, Sample loop
- Column: 2.1 mm i.d. × 100 mm Inertsil ODS-3
- Solvents: A: Acetonitrile/water (50/50) B: Acetonitrile flow rate 0.5 mL/min
- Detector: UV 210 nm

Interface SPE
- SPE: 2 mm i.d. × 10 mm C18
- Diluting: water 0.4 mL/min
- Purge: N2 gas, 1 min
- Elution: Hexane, 20 µL

Interface Injector (LaviStoma; EMINET)
- Insert: Stomach Type 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)

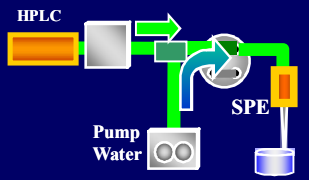
GC/MS (QP-5050A; Shimadzu)
- Column: 0.25 mm i.d. × 30 m Inert Cap 5MS/Sil
- Oven: 70°C(3min)-20°C/min-280°C(4min)
- Carr. gas: He, 1 mL/min
- MS: SCAN;50-550 mz, SIM;199, 314 mz

LC-(SPE)-GC system



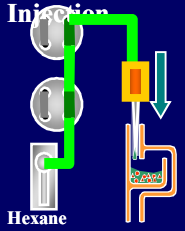
SPE Interface

Dilution & Concentration



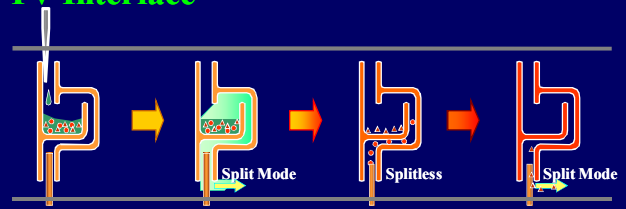
With adding water to the LC fraction, the diluted fraction is loaded on the SPE cartridge. The analyte is adsorbed on the SPE.

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



The injector is kept at a temperature lower than the boiling point of sample solvent.

While the evaporated sample solvent is exhausted, the sample is concentrated.

Target compounds are transferred to the column at an elevated temperature.

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.

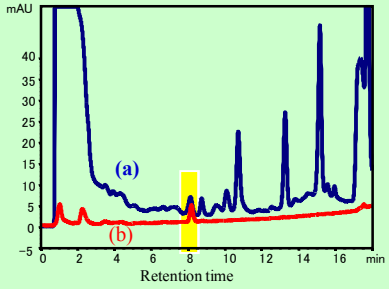


Fig. 1 HPLC chromatogram of a spinach spiked with 1 µg/g of chlorpyriphos (a) and a standard solution of it (b). Marked fraction transferred to the SPE interface.

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

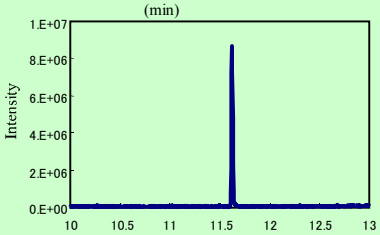


Fig. 2 GC/MS-SCAN chromatogram of the LC-(SPE)-GC/MS analysis of a spinach spiked with 1 µg/g of chlorpyriphos

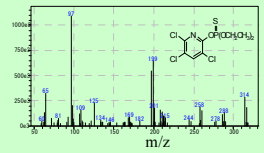


Fig. 3 MS spectrum of peak

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 µg/g of chlorpyriphos. 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 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.