Research progress of pesticide residue chemical analysis technique

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Content

I. Importance

- Provide the basis for establishment of pesticides Maximum Residue Limits (MRLs)

pesticide MRLs ⟺ pesticide residue analysis method

4140 MRLs in China


GB

中华人民共和国国家标准

GB 2763—2016

代替 GB 2763—2014

食品安全国家标准

食品中农药最大残留限量

National food safety standard—

Maximum residue limits for pesticides in food

2016-12-18 发布　　2017-06-18 实施

中华人民共和国国家卫生和计划生育委员会
中华人民共和国农业部
国家食品药品监督管理总局　　发布

I. Importance

- Provide the basis for establishment of pesticides Maximum Residue Limits (MRLs)
- Analyze pesticide residues in food and environment sample to ensure the rational use of pesticides
- Provide method for routine monitoring of market to ensure the quality and safety of agricultural products

II. Residue analysis method

1

Chemical analysis technique:

Extraction

Purification

Detection

more accurate, chemical stability

2

Rapid test method:

- Enzyme inhibition
- immunoassay (RIA , ELISA, CLEIA, MB-ELISA, FLISA, FPIA)

3

Others bio-technique:

- Nano biotechnology
- Molecular imprinting technique
- microfluidics

high selectivity, easy preparation

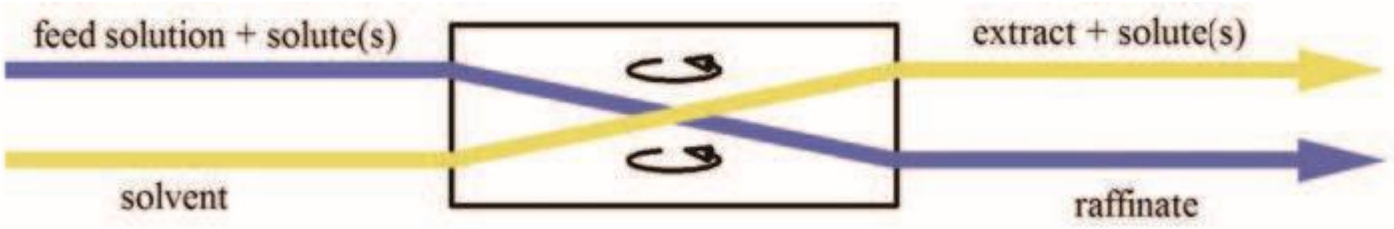
III. Chemical analysis methods

- **Pesticide residue analysis preparation procedure:**
  - Extraction and Purification
    - to extract the target in the sample
    - to remove the non-target




III. Chemical analysis methods

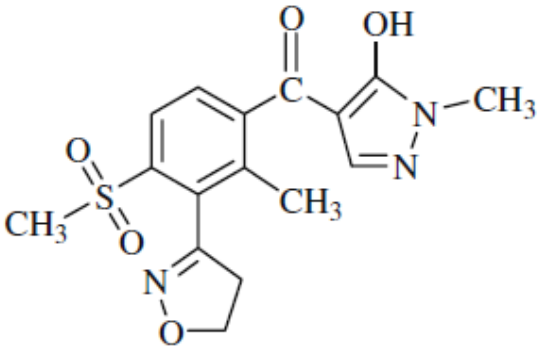
1. Liquid—Liquid Extraction



- **Liquid–liquid extraction (LLE) consists in transferring one (or more) solute(s) contained in a feed solution to another immiscible liquid (solvent).**
- **LLE is a classic method for the routine sample preparation due to its simplicity, robustness and efficiency.**

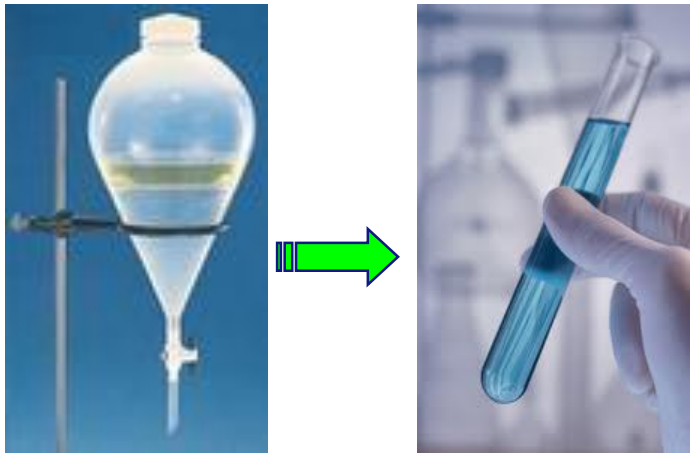
1. Liquid—Liquid Extraction

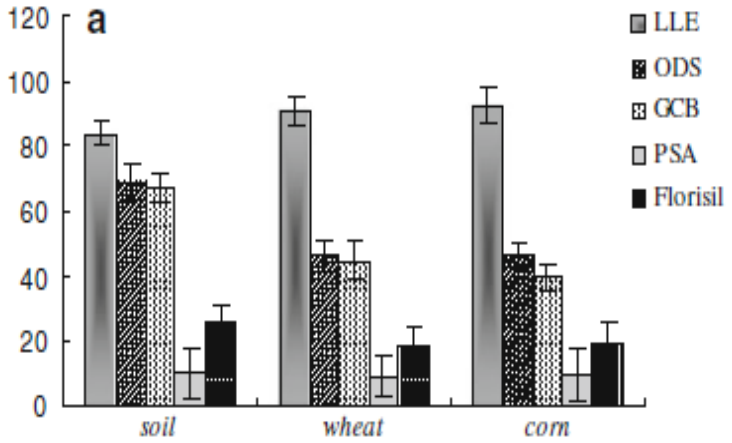
Determination of Oxazolone in different agricultural products and soil using LLE



difficulty：Strong polarity, difficult extraction, low recovery ;

Thin-Tube liquid Liquid Extraction Method ;
Adjust pH and select Purifying agent



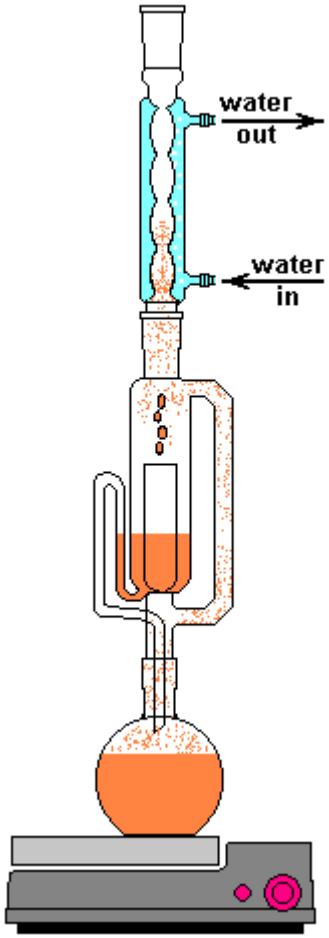


Good recovery and low solvent use

Analytical and Bioanalytical Chemistry 2011;400(9):3097-3107.

III. Chemical analysis methods

2. Soxhlet extractor method



- **good selectivity.**
- **Low use of solvent**
- **simple**
- **long time**

Determination of organochlorine pesticides in Ginseng for export

III. Chemical analysis methods

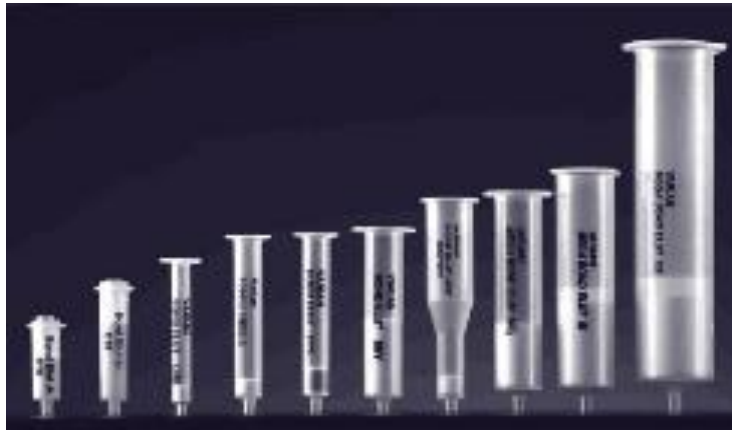
3. Microwave-assisted extraction(MAE)

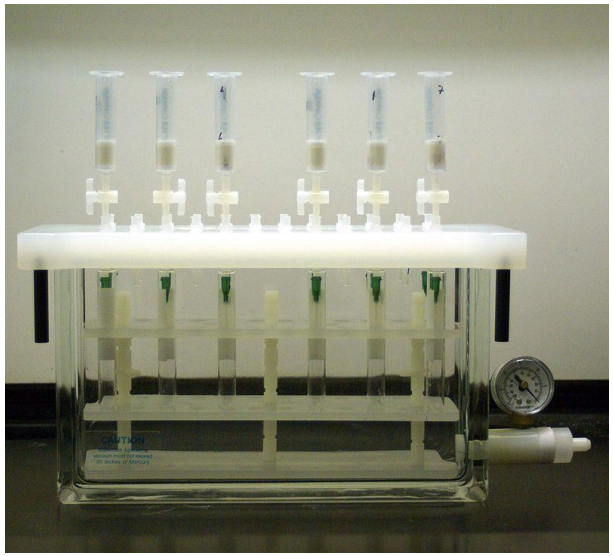
- **MAE was applied for the first time for the extraction of organic pollutants in 1986.**
- **High temperature or microwaves are believed to accelerate the extraction procedure and enhance the recoveries of analytes.**

III. Chemical analysis methods

4. Solid phase extraction（SPE）

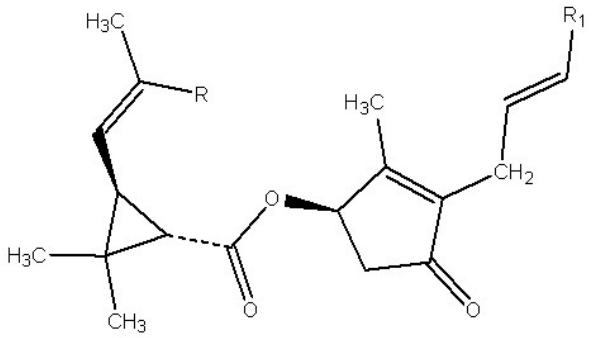
- **Time of invention: 1978**
- **Extraction Steps:**
  - adsorbent activation, sample, washing, elution
- **Fillers:**
  - silica gel, adsorption resin, C8, C18, nitrile, phenyl, amino and other special fillers



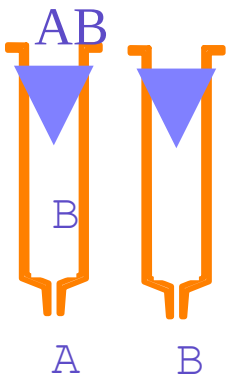


III. Chemical analysis methods

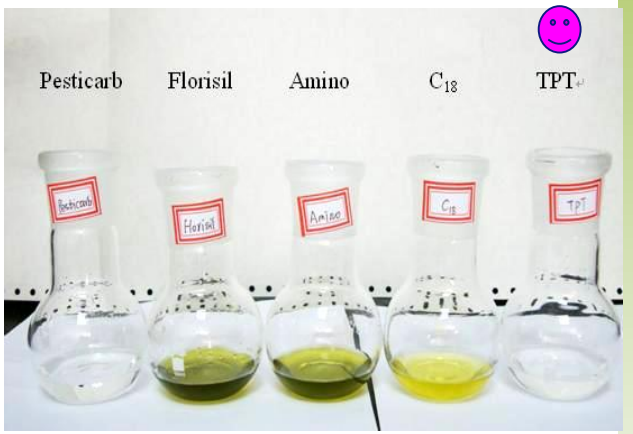
Determination of 6 kinds of natural pyrethrin insecticides in different tea using SPE



(C_I) Cinern-I:	R= CH_3,	R_1= CH_3
(J_I) Jasmolin-I:	R= CH_3,	R_1= C_2H_5
(P_I) Pyrethrin-I:	R= CH_3,	R_1= $CHCH_2$
(C_{II}) Cinern-II:	R= CO_2CH_3,	R_1= CH_3
(J_{II}) Jasmolin-II:	R= CO_2CH_3,	R_1= C_2H_5
(P_{II}) Pyrethrin-II:	R= CO_2CH_3,	R_1= $CHCH_2$



TPT

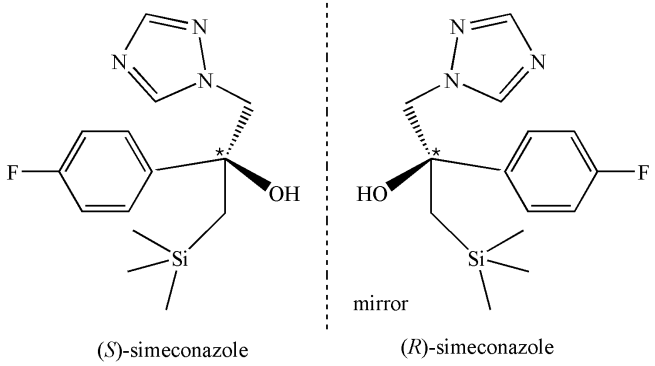


Yongquan Zheng et al. Analytica Chimica Acta 678 (2010) 56–62

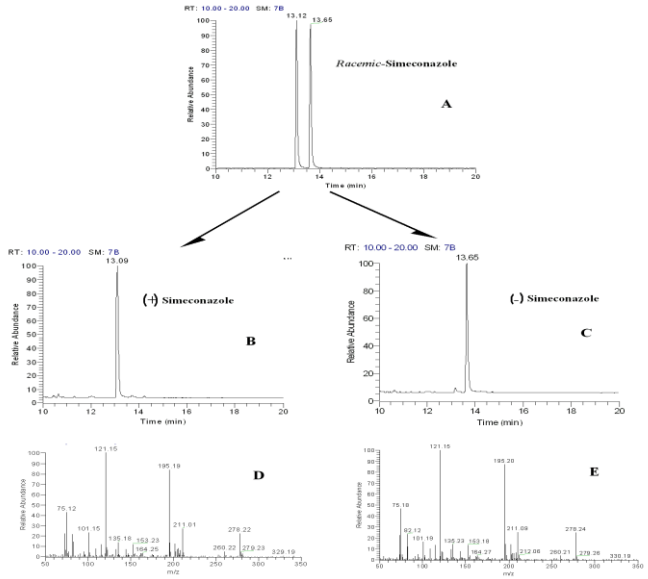
- **Advantages: simple, fast, good reproducibility**

III. Chemical analysis methods

Determination of flusilazole and Phenylethylenediole in different tea using SPE



GCB/PSA complex SPE



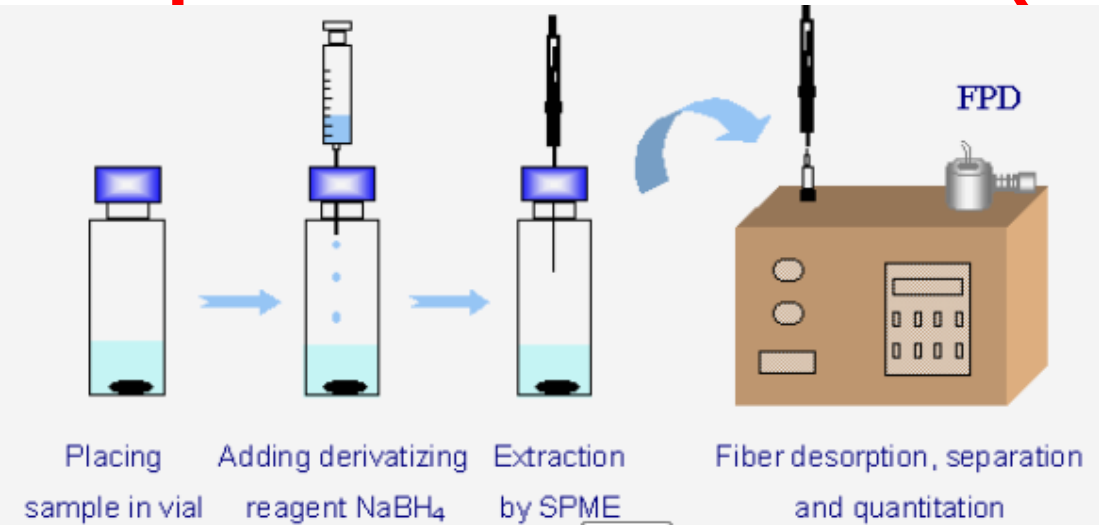
- **Good recovery**
- **Efficient purification**

Analytica Chimica Acta
2011, 702: 127–135

Analytical and Bioanalytical Chemistry
2012;404(6-7):2017-2031.

III. Chemical analysis methods

5. Solid phase micro-extraction(SPME)



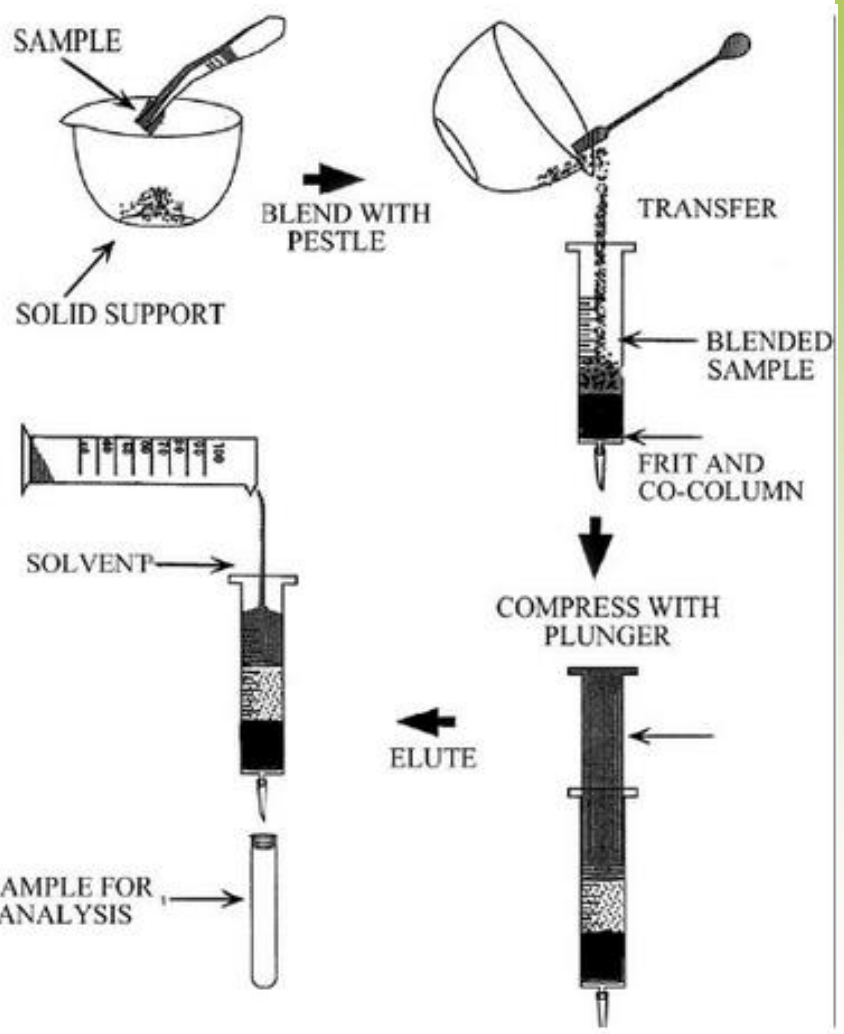
- **Similar to the SPE, SPME is based on the partition equilibrium of analytes between the sample and the stationary phase.**
- **Greatly reducing the consumption of organic solvent and complicated procedures, SPME proves to be a valuable alternative analytical method to many traditional procedures.**

III. Chemical analysis methods

6. Matrix solid phase dispersion(MSPD)

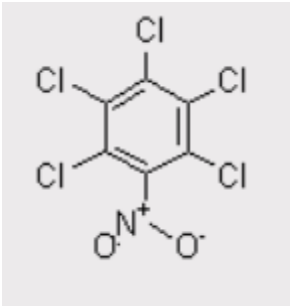
- **In contrast to the common SPE methods, MSPD combines the extraction and clean-up procedure into a single step.**

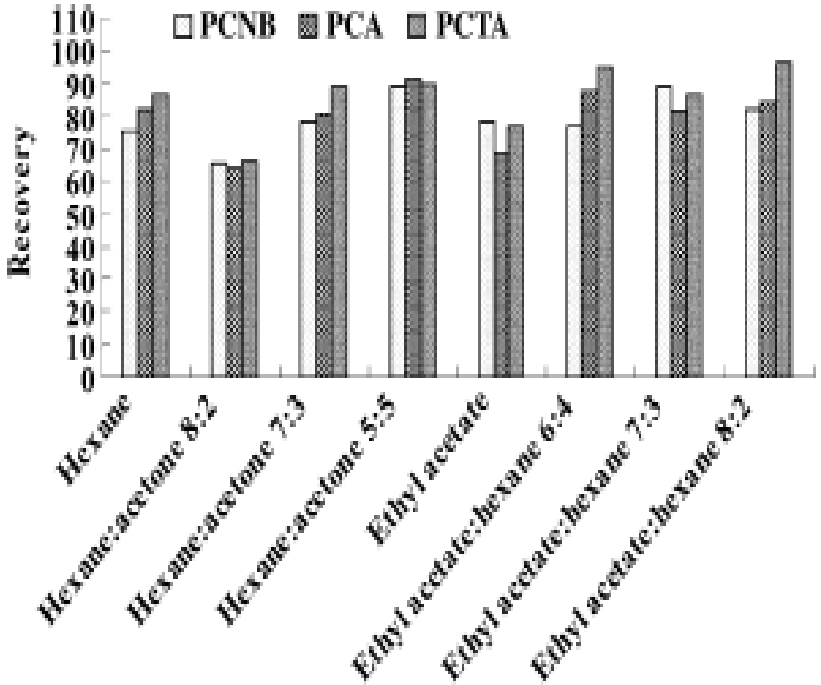
- **Generally, the MSPD method consists of the following steps:**
  - sample homogenization,
  - cellular disruption,
  - extraction,
  - the clean-up by adsorbents.



6. Matrix solid phase dispersion(MSPD)

Pentachloronitrobenzene and its metabolites residue analysis method in ginseng



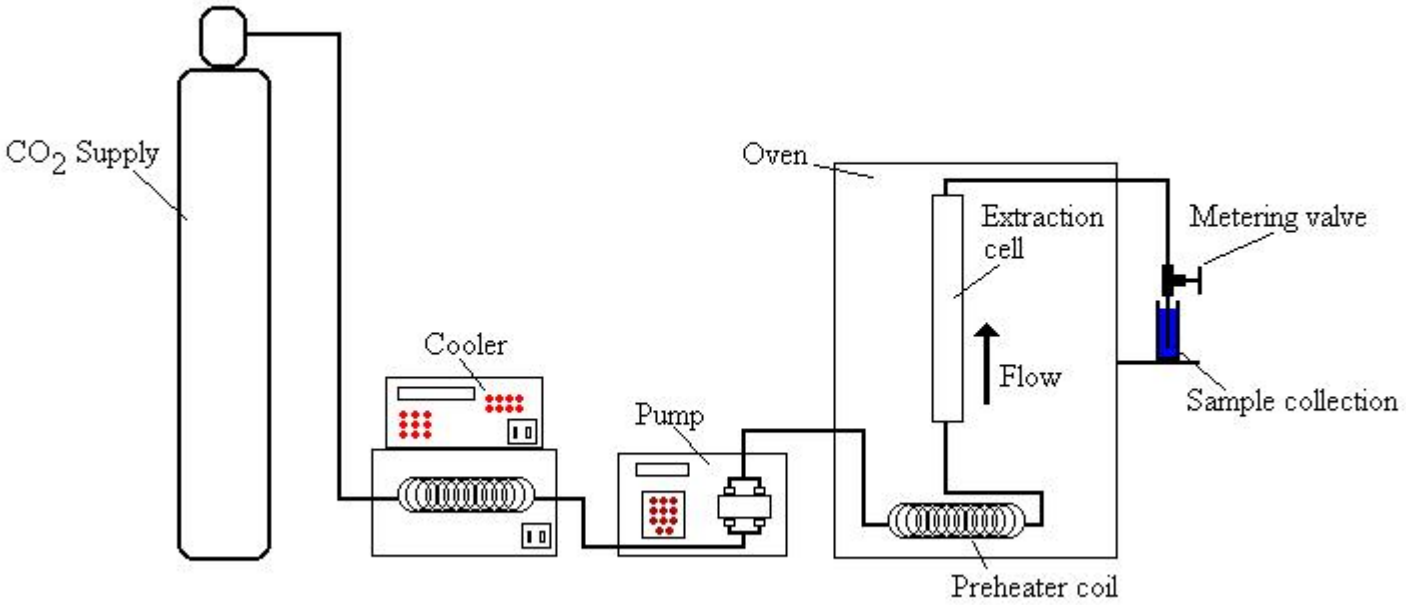


Reduced solvent use by 90%

Chromatographia 2009;69(9-10):1113-1117

III. Chemical analysis methods

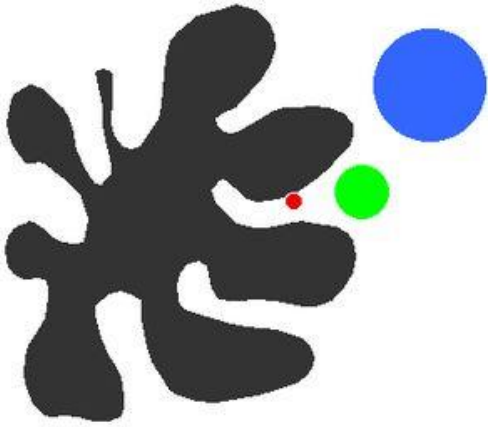
7. Supercritical fluid extraction (SFE)



- **Compared to the traditional solvent extraction, SFE can offer cleaner extracts with lower solvent consumption, less extraction time, and potentially more efficient and selective extraction from complex matrices.**

III. Chemical analysis methods

8. Gel permeation chromatography(GPC)

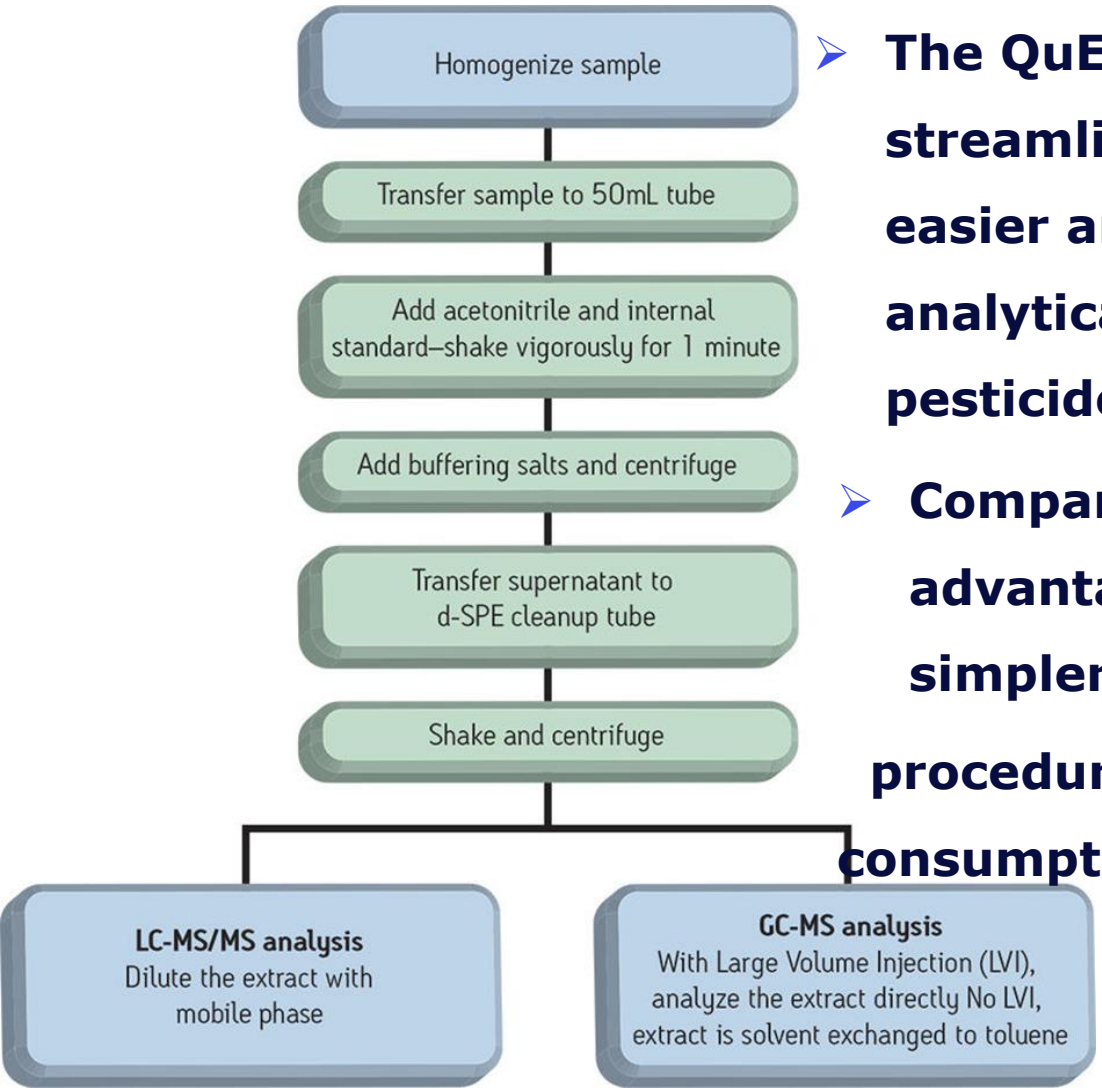


- The separation mechanism of GPC is based on the molecular size . Large molecules elute from the gel, followed by smaller molecules.

- GPC is generally recommended for the clean-up of extracts obtained from biological samples.
- It is not easy to separate for the same size of the mixture

III. Chemical analysis methods

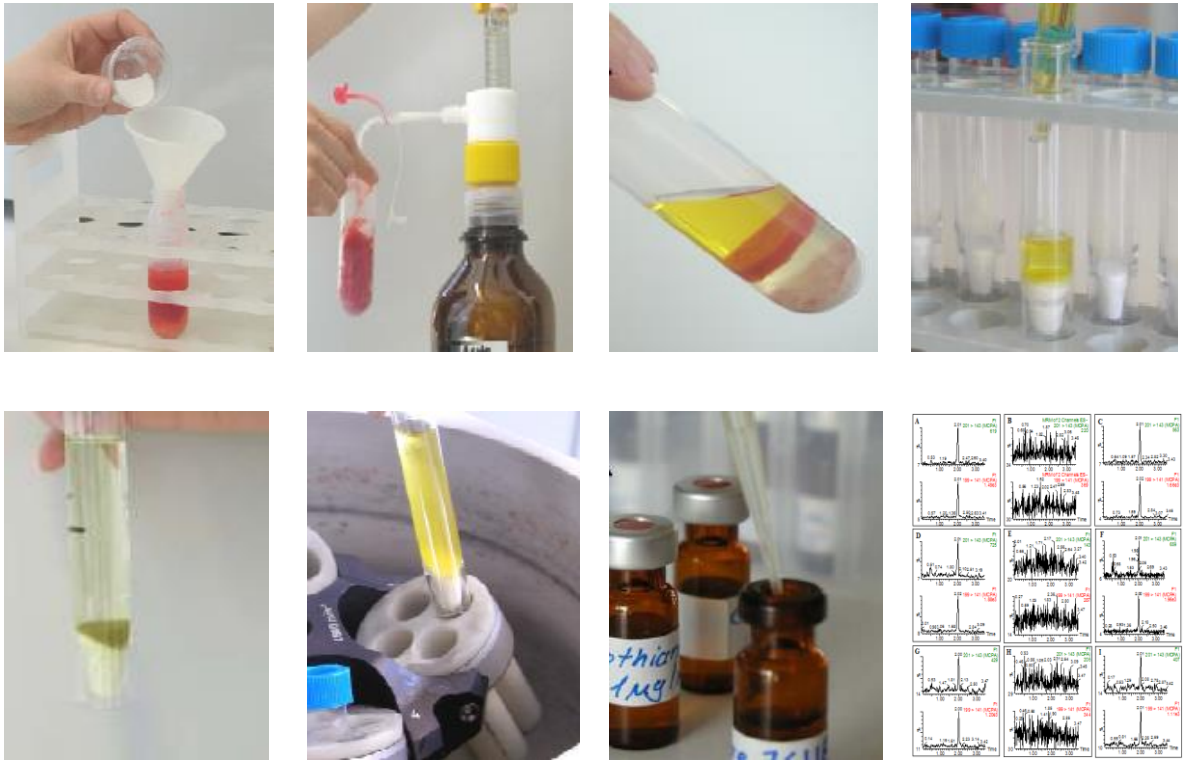
9. QuEChERS Quick, Easy, Cheap, Effective, Rugged, and Safe



- **The QuEChERS method is a streamlined approach that makes it easier and less expensive for analytical chemists to examine pesticide residues in food.**
- **Compared to the classic LLE, the advantages of QuEChERS are simpler and less time-consuming procedure, and lower organic solvent consumption.**

Research on the QuEChERS method of MCPA

Innovation: formic acid clean-up the protective agent and improved the recovery rate



Greatest advantage : fast, only 30 minutes is needed for treatment and analysis ;

Journal of AOAC international 2010,93(3):1013-1019

Residue analysis method of spirotetramat and its metabolites in agricultural products

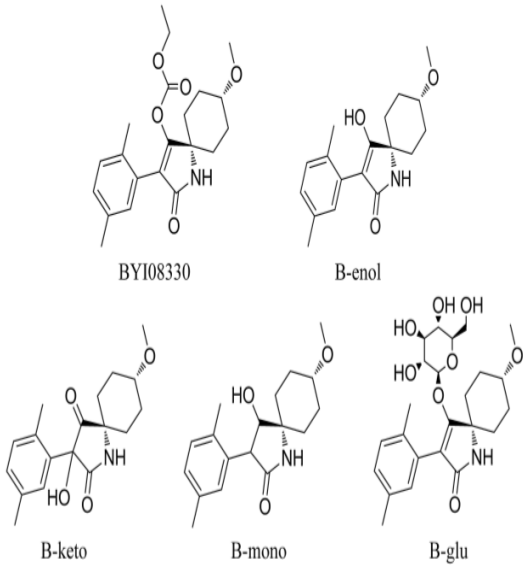


Fig. 1. Chemical structures of spirotetramat (BYI08330) and its four metabolites.

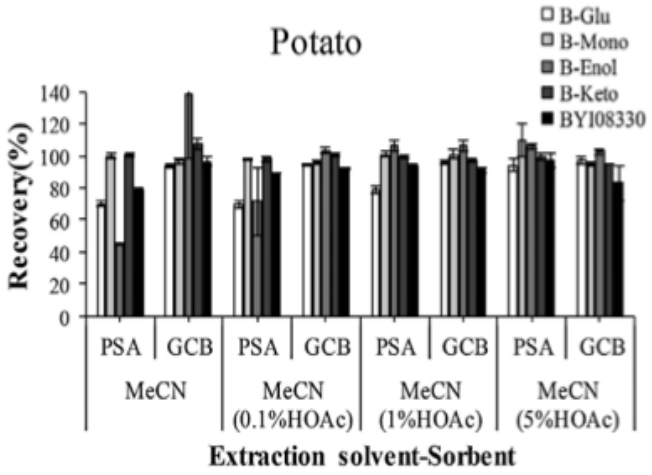
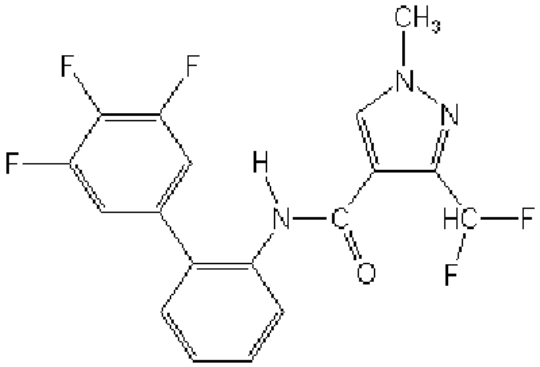


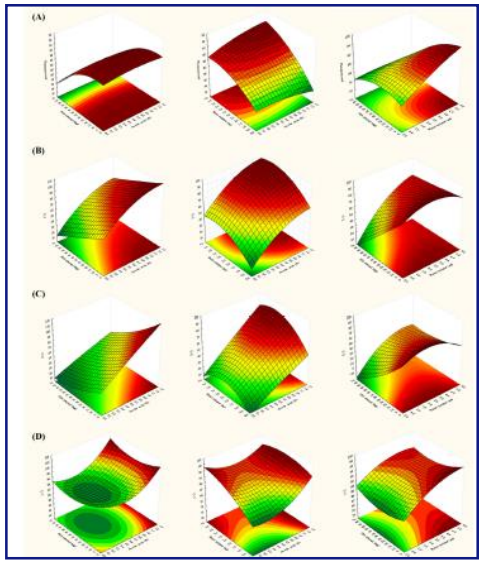
Fig. 3. Effect of different kinds of sorbents and MeCN containing varying contents of HOAc for targeted compounds in different plant matrix at 100 μg/kg level ($n = 3$).

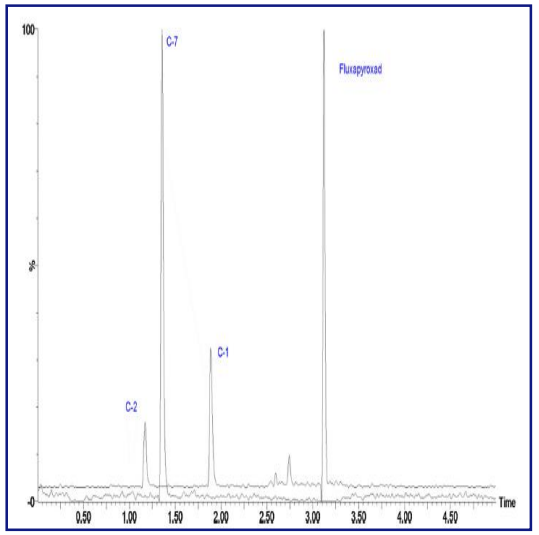
For the complex matrix which contains 6 kinds of fruits and vegetables, the solvent extraction efficiency was systematically evaluated, the best purifying and dispersing system (GCB and PSA) was selected

Journal of Chromatography A 2013, 1299, 71-77

Residue analysis method of fluxapyroxad and its metabolites in environment







This research applied Chemometric methods to optimize the pretreatment analysis method of QuEChERS, and its result shows that MeCN/acetic acid ratio (+) water volume(+) and PSA amount (-) are the most important factors which affects the pretreatment analysis method.

Journal of Chromatography A 2014, 1358, 46-51

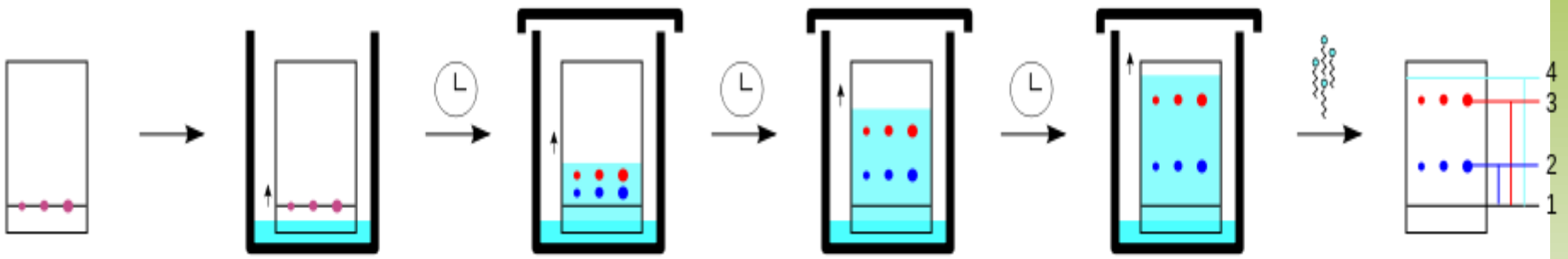
IV. Detection methods

- **Pesticide residue analysis preparation procedure:**
  - Extraction and Purification
    - to extract the target in the sample
    - to remove the non-target
  - **Detection**
    - to select the appropriate method for qualitative and quantitative analysis of pesticide residues in the tested sample




4. Detection methods

1. Thin-layer chromatography(TLC)



Rough, inaccurate

- **Thin-layer chromatography is most effective for the low-cost analysis of samples requiring minimal sample clean-up, or where thin-layer chromatography allows a reduction in the number of sample preparation steps**

4. Detection methods

2. GC & HPLC

- **Some detectors of GC are sensitive only to specific types of substances, such as Electron capture detector （ECD）, Flame photometric detector （FPD）, Nitrogen–phosphorus detector（NPD）.**

- **High performance liquid chromatography is a traditional detection method, can be separated and detected strong polarity, molecular weight of ionic pesticides.**

4. Detection methods

3. GC-MS & HPLC-MS

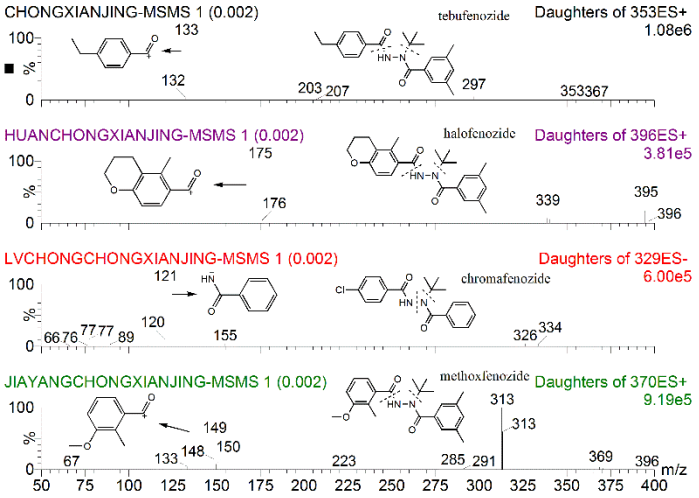
- **Coupled chromatography - MS systems are popular in chemical analysis.**

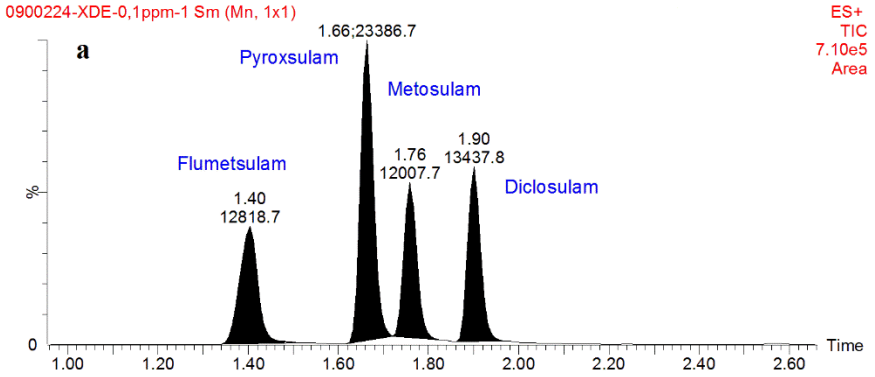
→ powerful

- **While GC or LC separates mixtures with multiple components, mass spectrometry provides structural identity of the individual components with high molecular specificity and detection sensitivity.**

→ Easy
Efficient

Research on Multi-residue analysis of diacylhydrazine insecticides and triazolopyrimidine herbicides



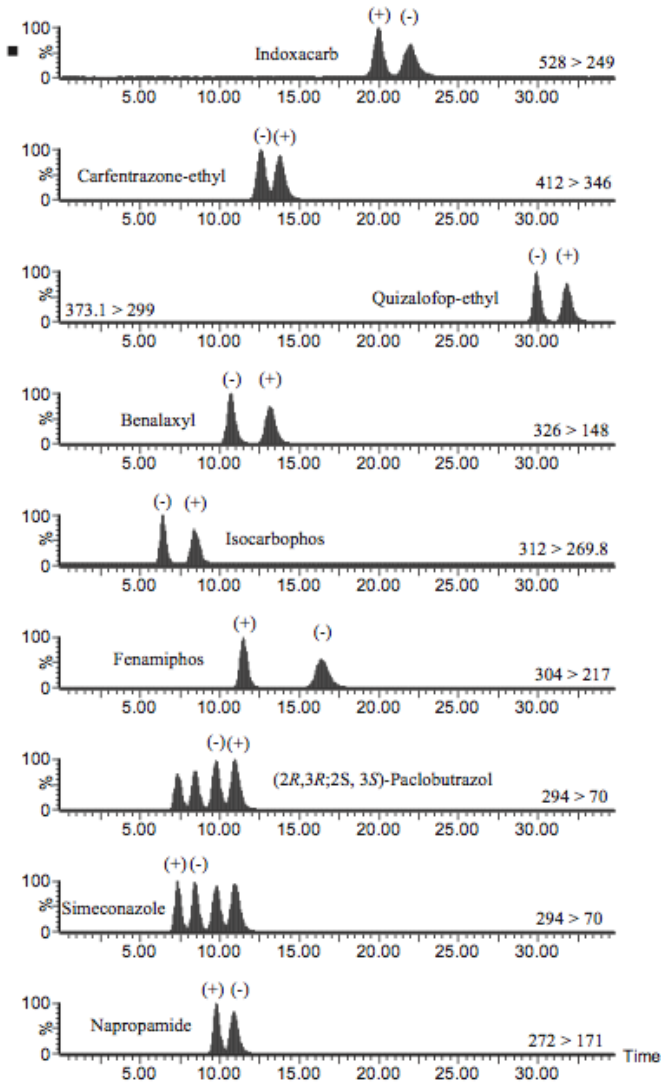


Studying on multi-residue analytical methods for pesticides with similar chemical structures and systemically research on theirs fragmentation process of mass spectrometry.

1）*Analytical and Bioanalytical Chemistry* 2011;399(7):2539-2547.

2）*Analytical and Bioanalytical Chemistry* 2011;401(3):1051-1058. .

Residue analysis methods of 9 chiral pesticides in environment using LC-MS/MS



18 enantiomers were simultaneously isolated and detected

chiral column：Chiralcel AD-RH

Mobile phase: acetonitrile/ammonium acetate aqueous solution= 55/45

Flow velocity：0.45mL/min

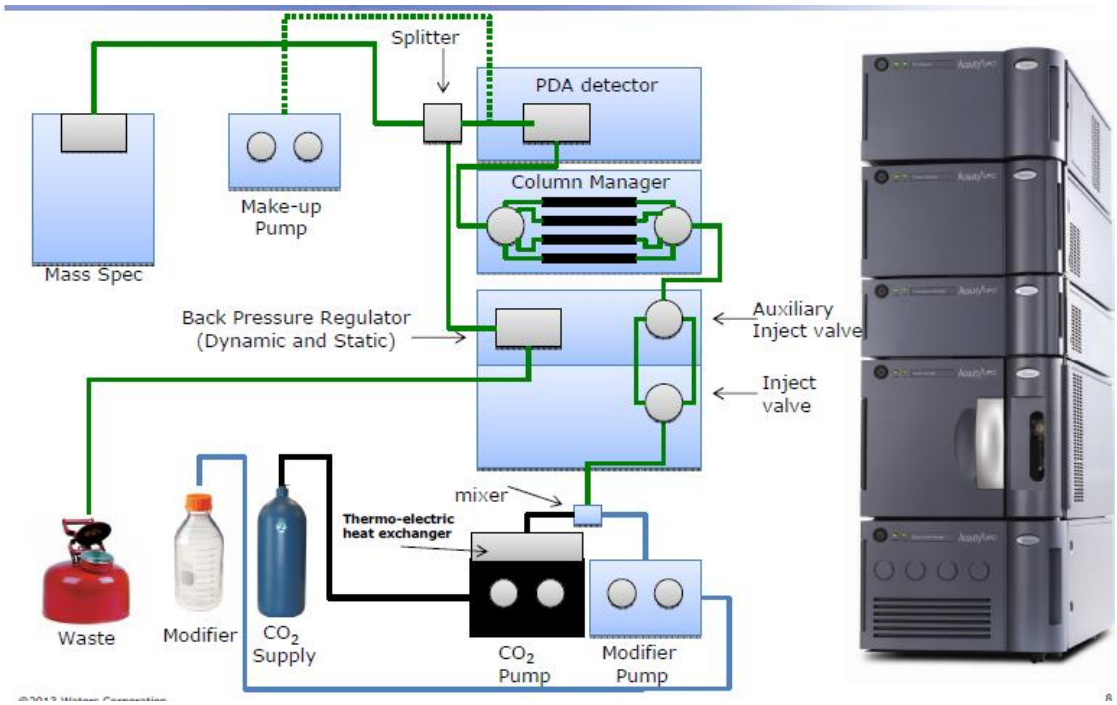
Column temperature： 25°C

After repeated screening on Chiral immobilization and the condition of dispersive purification，the residue analysis methods of 9 chiral pesticides in environment using LC-MS/MS were successfully established.

Journal of Hazardous Materials , 2013, 250:9-18.

IV. Detection methods

4. Ultra Performance Convergence Chromatography (UPCC)



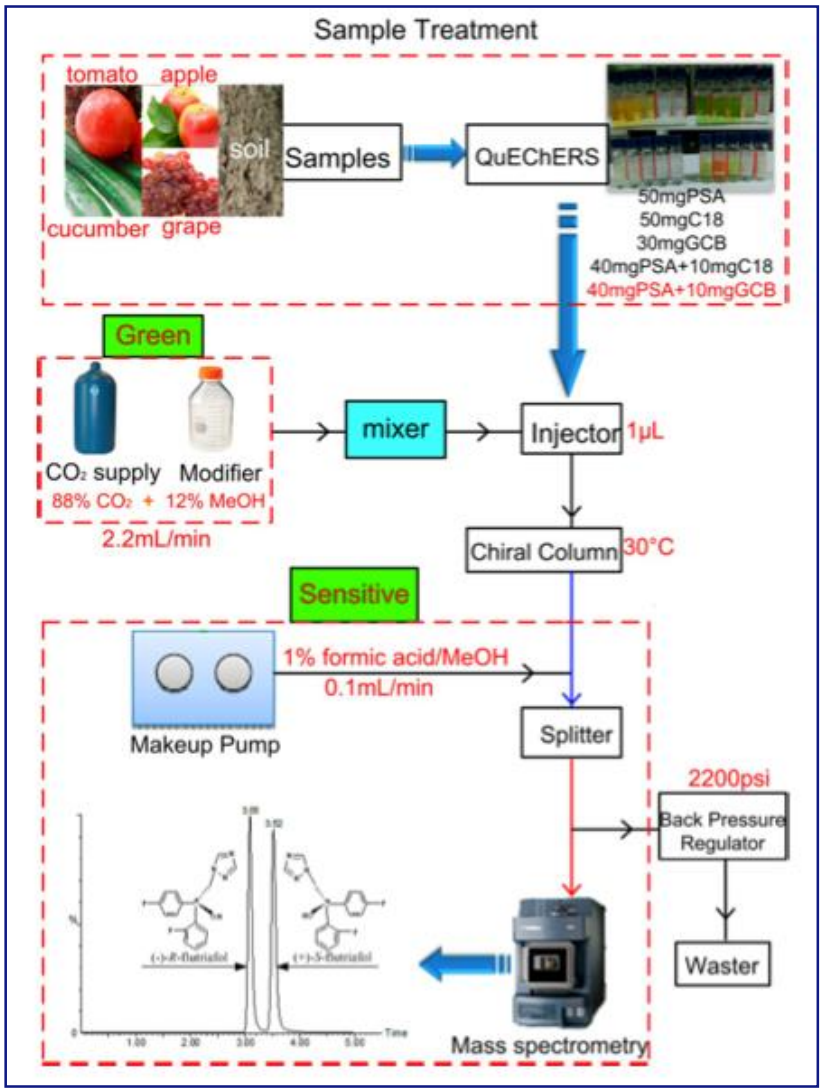
➢UPCC combined UPLC with SFC, it has more advantages than LC and GC.

➢High Separation efficiency

Acquity UPC²™

Using carbon dioxide as the mobile phase

Determine Flutriafol Enantiomers in agricultural products



The green and quick residue analysis method using chiral analytical combined with UPCC–MS/MS to determine triazole chiral fungicides was successfully developed .

The organic solvent and time were 13% and 20%, respectively of the original amount.

Journal of Agricultural and Food Chemistry 2014, 62, 11457-11464

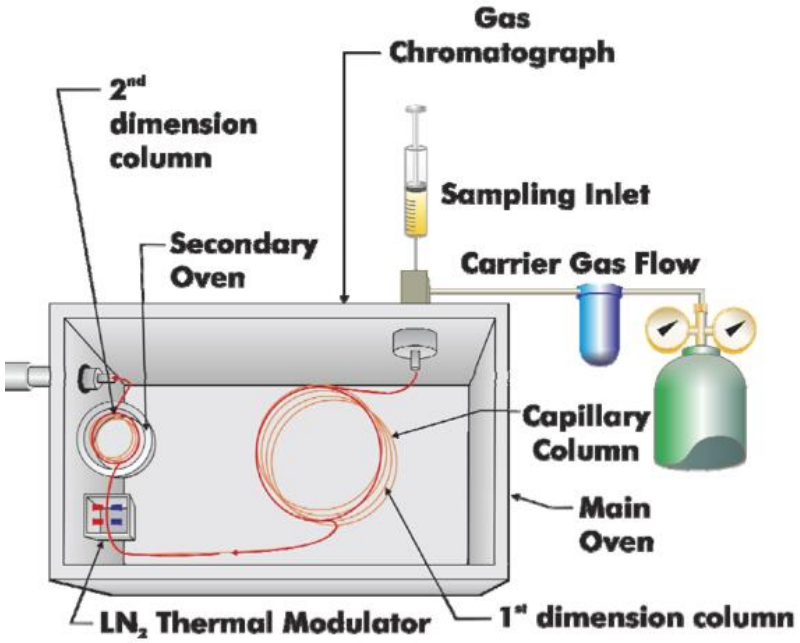
IV. Detection methods

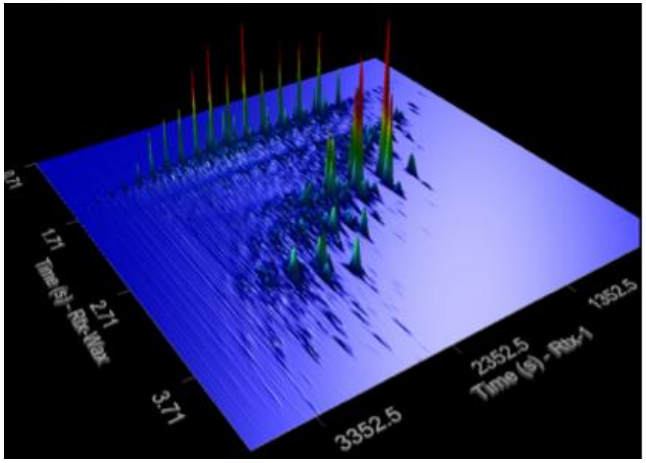
5. GC GC-TOFMS

- The capability of component separation and detection sensitivity was improved.
- The GC * GC-TOFMS had a sensitivity 10-82 times higher, and separation ability higher compared to that of GC-MS

Acta Tobacaria Sinica, 2007,13(1), 20-24.

- Two-dimensional structure spectra containing structural information can be provided

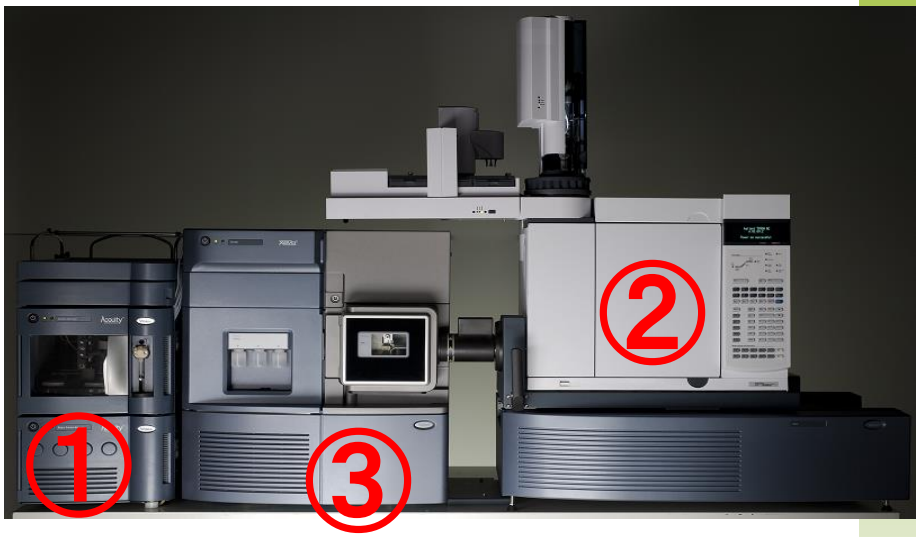




4. Detection methods

6. LC-APGC- QTOFMS

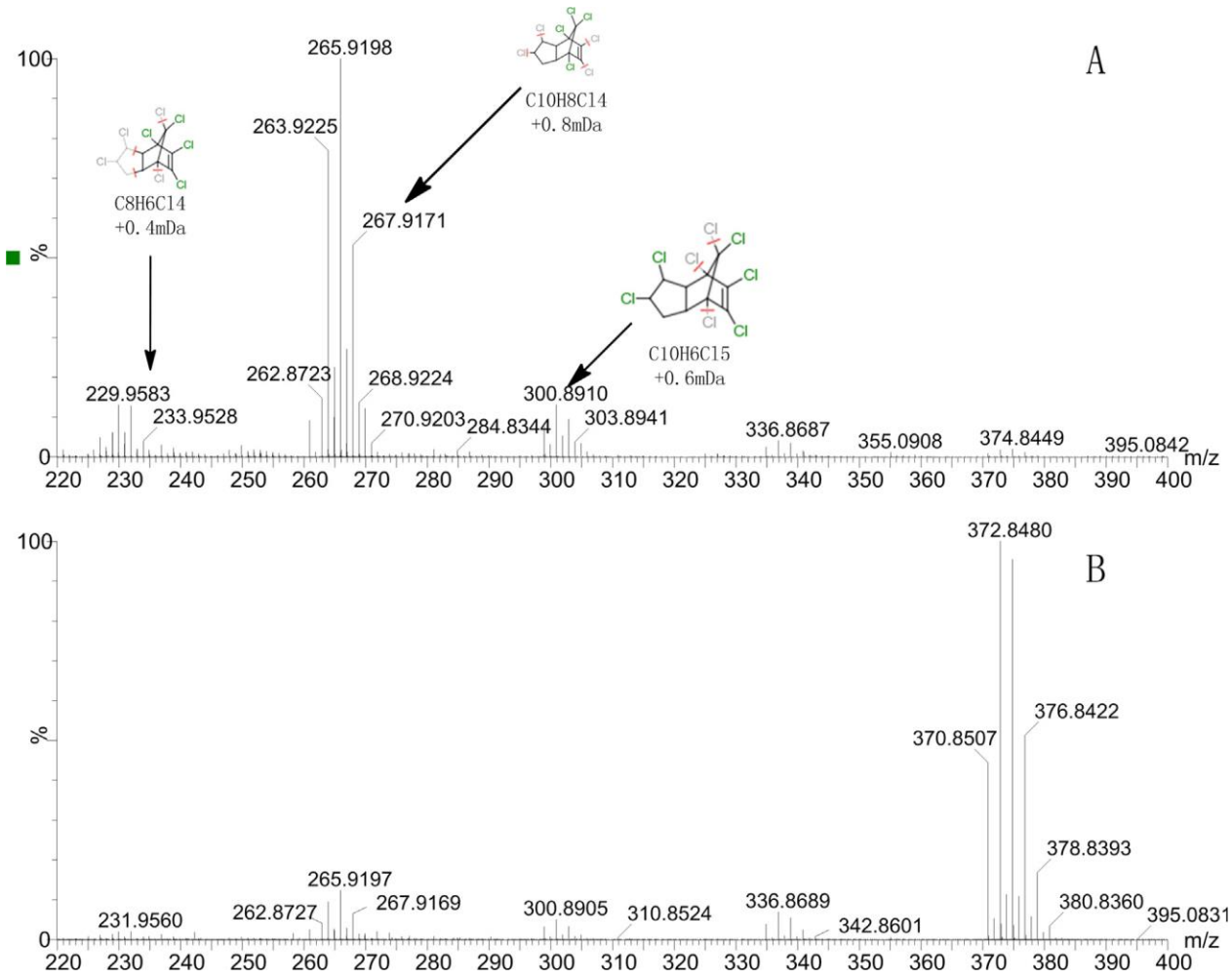
- A powerful complementary technique of traditional GC-MS and LC-MS
- Characteristics of traditional GC - MS : in electron ionization mode , molecular easy to thoroughly smash, lack of characteristic qualitative information.



UPLC①+APGC②+TOF-MS③

- High resolution quality, provide accurate mass, More accurate qualitative

APGC-QTOF for monitoring organochlorine pesticides



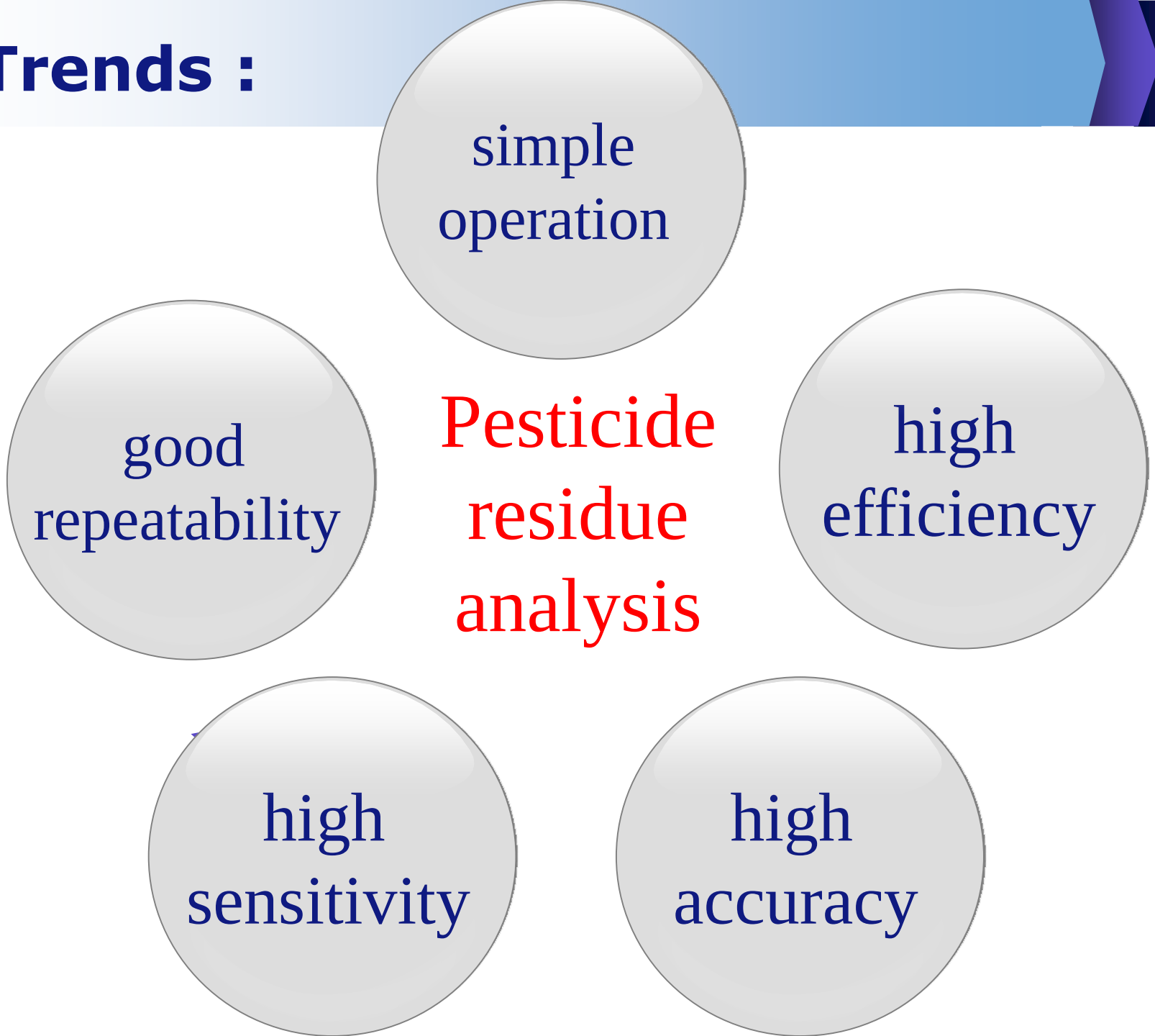
Most of OCPs exist in water and soil in ultra-trace level (from pg/L to ng/L).

APGC source is a alternative soft ionization technique to overcome sensitivity limitations of GC–MS methods.

APGC-QTOF-MS showed a sensitivity enhancement by approximately 7–305 times.

Journal of Chromatography A, 2016,1435:115-124.

Trends :


simple operation
good repeatability
Pesticide residue analysis
high efficiency
high sensitivity
high accuracy

Development tendency

- QuEChERS or modify QuEChERS method
- Traditional instrument technology will combine with biotechnology
- Because of the requirement for real-time and rapid detection of pesticide residues, the research on small portable pretreatment equipment and chromatography coupled to tandem mass spectrometry will be the trend of future development

Thank you very much