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# Determination of 57 Pesticide Residues in Chinese Herbal Medicines Using Online Gel Permeation Chromatography-Gas Chromatography-Mass Spectrometry

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Determination of 57 kinds of organochlorine, organophosphorus and pyrethroid pesticides using online gel permeation chromatography (GPC) purification and gas chromatography-mass spectrometry (GC-MS) in eight kinds of traditional Chinese herbal medicine were studied. Simultaneous full scan and selective ion monitoring mode for GC-MS was used for qualitative and quantitative analysis. The correlation coefficients were higher than 0.99, Limits of detection (LODs) for 57 pesticide residues were between 0.0003 and 0.006 mg/kg, the limit of quantification (LOQ) were between the range of 0.001-0.02 mg/kg. The recoveries of 57 kinds of pesticides were between 80.86 and 112.26 %, the relative standard deviations were between 2.84 and 8.57 %.

**Keywords: Chinese herbal medicine, Pesticide, Gel permeation Chromatography, Gas chromatography, Mass spectrometry.**

## INTRODUCTION

*Aucklandiae lappa*, *Paris polyphylla smith var. (French)*, *Polygonum multiflorum*, *Poria*, *Pistacia chinensis*, *forsythia suspensa*, *Flos lonicerae* and *Panax notoginseng* are authentic Chinese herbal medicines in Yunnan Province and they have a wide range of applications and market prospects. The contaminations of variety of pesticide residues such as organochlorine, organophosphorus and pyrethroid pesticides may be introduced during the cultivation and transportation of these Chinese herbal medicines. In order to ensure medicine safety and to meet market requirements, it is imperative to establish some rapidly and accurately analytical methods for simultaneous detection of multiple pesticide residues in Chinese herbal medicines.

Solid phase extraction (SPE) purification and gas chromatography (GC) determination have been mostly used in the detection of pesticide residues in Chinese herbal medicine[1]. Compared with traditional method of solid phase extraction, gel permeation chromatography (GPC) purification has some advantages such as a high degree of automation and good reproducibility, which is suitable for the purification process of the determination of pesticide residues in complex matrix[1-5]. Gel permeation chromatography method can remove the oils, pigments, alkaloids and other polymers which may interfere with the target compounds in the sample matrix. So in recent years, the GPC purification method has been widely used in pesticide residue detection.

Gas chromatography-mass spectrometry (GC-MS) is an accuratly quantitative and qualitative determination method of the target component, which can avoid the false analysis and false-positive results caused by GC[6]. Gel permeation chromatography-gas chromatography-mass spectrometry (GPC-GC-MS) applies to the simultaneous detection of multiple pesticide residues of the agricultural products. In this article, the online GPC-GC-MS for measuring 57 pesticide residues in Chinese herbal medicines is proposed. The precision and accuracy were validated by eight different Chinese herbal medicines spiked with 0.1 mg/kg of residue.

## EXPERIMENTAL

Online gel permeation chromatography-gas chromatography/mass spectrometer (Shimadzu, Japan GPC-GC/MS QP 2010 Plus), equipped with electron impact (EI) ion source; High-speed centrifuge (Feige, Anke GL-20G-II); Nitrogen evaporator (Organomation Associates, Jnc OA-SYS, USA); Ultrasonic cleaning instrument (Branson 1210, USA); Solid phase extraction device (CNW, Germany); Pipette (200 µL, Eppendorf, Germany).

57 Kinds of pesticides and heptachlor epoxides were of purity = 95 % and purchased from the Laboratories of Dr. Ehrenstorfer (Augsburg Germany); acetonitrile, acetone, cyclohexane and toluene were of HPLC grade and purchased from Fisher Scientific; Anhydrous sodium sulfate were of analytical grade and purchased from Guangfu reagent Factory;

ENVI-carb graphitization solid phase extraction column (250 mg, 3 mL) were from Supelco.

Standard stock solutions of pesticides were prepared by weighing accurately 5 to 10 mg of each pesticide and dissolving in toluene and were stored in refrigerator at -18 °C. A mixed standard solution was prepared in acetone-cyclohexane (volume ratio 3:7) from the individual standard stock solutions.

**Chromatography condition**

**GPC condition:** A 150 × 2 mm gel penetration column (Shodex CLNpak EV-200) was used for separation of the analytes. The mobile phase was acetone and cyclohexane (volume ratio 3:7) and the flow rate of 1 mL/min was used. The column temperature was 40 °C. Detection was set at the wavelength of 210 nm.

**GC/MS condition:** 5 m × 0.53 mm inert silica capillary and 5 m × 0.25 mm × 0.25 μm DB-5MS pre-column and 25 m × 0.25 mm × 0.25 μm DB-5MS analysis column were used as gas chromatography column. The initial column temperature was 82 °C and was kept for 5 min, then it was heated up to 300 °C with the velocity of 8 °C/min and was hold for 5.75 min. The carrier gas was helium (purity ≥ 99.999 %) and the flow rate of 1.75 mL/min was used.

The EI ion source temperature was 230 °C and the interface temperature was 280 °C in mass spectrometry detection. The scan time was 6.8-32.4 min of group A and 7.1-34.7 min of group B. Ion monitoring mode was selected and all ions of pesticides were detected in accordance with the order of peak.

**Sample extraction and purification:** To prepare each sample, 5.000 g of a previously homogenized herbal material was transferred into a 50 mL centrifuge tube. Then, 10 mL acetonitrile and 100 μL internal standard solution were added to each sample using an adjustable volume solvent dispenser. The centrifuge tubes were capped before vortex mixing for 1 min at maximum speed. To separate phases, samples were centrifuged for 3 min under 4500 rpm. 2 mL aliquot of upper solution was moved for purification.

Anhydrous sodium sulfate with the height of 1 cm was added to the top of ENVI-carb extraction column. 5 mL acetone-toluene (volume ratio 3:1) solution was used to pre-leach the extraction column. When the liquid serface reaches the top of the anhydrous sodium sulfate, the aliquot of upper solution needed purification was rapidly added into the extraction column and was eluted with 8 mL acetone-toluene (volume ratio 3:1) solution. The effluent was collected with 10 mL colourimetric tube and was concentrated to about 0.5 mL by nitrogen evaporator in 40 °C water bath. 2 mL acetone-cyclohexane (volume ratio 3:7) solution was added for solvent exchange and then wad dried under nitrogen blowing in 40 °C water bath. Last, it was dissolved by acetone-cyclohexane (volume ratio 3:7) solution and set the volume to 1mL and was detected by online gel permeation chromatography-gas chromatography-mass spectrometry.

## RESULTS AND DISCUSSION

**Selection of extraction solvent:** Some Chinese herbal medicines (*e.g.*, gentian) contain a lot of pigment and there have large quantities of pesticides needed simultaneous determination, so the extraction solvents of samples require a higher choice for the polarity difference. Acetone-hexane (1:2), acetone-acetonitrile (1:2), acetonitrile, acetonitrile-water (4:1) were selected as the extraction solvents in this experiment. It was found that the recoveries can meet the requirements while *n*-hexane-acetone, acetonitrile-acetone and acetonitrile were used as the extraction solvent. A low recovery was achieved while acetonitrile-water was used as extraction solvent and purification steps and difficulty were increased because more water-soluble substances were extracted. Compared to acetonitrile, more impurities were extracted while acetone-hexane and acetone-acetonitrile were used as the extraction solvent. Acetonitrile was selected as extraction solvent in this experiment because the followed purification steps are relatively simple, matrix interference is small and the recovery is ideal.

**Selection of solid-phase extraction condition:** Several solid phase extraction columns such as ENVI-carb column, ENVI-carb + $NH_2$ column, ENVI-carb + PSA column and ENVI-carb + C18 column were compared in this experiment. The recoveries of 11 kinds of representative pesticides in gentian were studied and the results shown in Fig. 1. From the experimental results, it can be seen that the recovery of the ENVI-carb solid phase extraction column is ideal and the operation is simple. Several solutions such as acetone-toluene (3:1), acetone-hexane (1:2), acetone-ethyl acetate-hexane (1:2:1) and acetonitrile-toluene (3:1) were used as elution solvent. The results indicate that the recovery of acetone-toluene (3:1) among these four eluent solvents is the best.

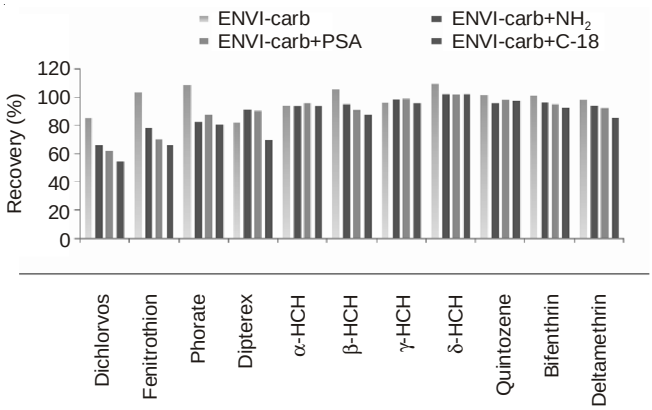


Fig. 1. Effect of different SPE columns on the recoveries of 11 pesticides

**Selection of groups and ion monitoring:** 57 Kinds of pesticides were scaned using GC/MS under the chromatography conditions and the scan mass spectra and retention time of each pesticide was achieved. The pesticides were divided into two groups (A and B, Table-1) according to the close retention time. Figs. 2 and 3 showed the selected ion chromatograms of two sets of pesticide A, B added to empty gentian samples. The mutual interference between the different pesticides, pesticides and matrix can be reduced by segment monitoring for each group of pesticides. Different matrix ion interference may exists in different samples, the characteristics ion of the analyst needed to be re-selected while the matrix ions affect the qualitative and quantitative detection.

**Linear relationship and limits of detection:** A series of standard working solutions were prepared according the

TABLE-1
RETENTION TIMES, LINEAR RANGES, LINEAR EQUATIONS, CORRELATION COEFFICIENTS ($r^2$), LIMITS OF DETECTION (LOD), LIMITS OF QUANTIFICATION (LOQ), AVERAGE RECOVERIES AND RELATIVE STANDARD DEVIATIONS (RSD) of EIGHT KINDS OF SAMPLES AT THE 10 × LOQ LEVEL FOR 57 PESTICIDES

| No. | Pesticide | $t_R$ (min) | Linear range (mg/L) | Linear equation | $r^2$ | LOD[1)] (mg/kg) | LOQ[2)] (mg/kg) | Recovery[3)] (%) | RSD[4)] (%) |
|---|---|---|---|---|---|---|---|---|---|
| IS | Heptachlor-epoxide | 19.612 | | | | | | | |
| | | | | Group A | | | | | |
| 1 | Methamidophos | 7.826 | 0.0020-0.4 | $Y = 0.1468X - 6.1763\times10^{-2}$ | 0.9974 | 0.0006 | 0.002 | 99.92 | 8.40 |
| 2 | Dichlorvos | 8.086 | 0.0020-0.4 | $Y = 1.2436X - 9.1472 \times 10^{-2}$ | 0.9928 | 0.0006 | 0.002 | 81.82 | 6.78 |
| 3 | Carbaryl | 11.992 | 0.0020-0.4 | $Y = 1.6742X - 0.1345$ | 0.9996 | 0.0006 | 0.002 | 84.04 | 6.94 |
| 4 | Omethoate | 13.082 | 0.0050-1.0 | $Y = 1.3479X - 0.1352$ | 0.9972 | 0.0015 | 0.005 | 90.47 | 3.42 |
| 5 | Monocrotophos | 14.318 | 0.0050-1.0 | $Y = 6.0367X - 0.4764$ | 0.9998 | 0.0015 | 0.005 | 100.49 | 3.71 |
| 6 | Alpha-HCH | 14.768 | 0.0020-0.4 | $Y = 0.4126X + 4.4311 \times 10^{-2}$ | 0.9912 | 0.0006 | 0.002 | 99.93 | 6.45 |
| 7 | Beta-HCH | 15.413 | 0.0010-0.2 | $Y = 0.8162X + 2.1342 \times 10^{-2}$ | 0.9911 | 0.0003 | 0.001 | 105.33 | 7.39 |
| 8 | Lindane | 15.680 | 0.0020-0.4 | $Y = 1.1427X + 1.8763 \times 10^{-2}$ | 0.9932 | 0.0006 | 0.002 | 98.28 | 4.52 |
| 9 | Delta-HCH | 16.413 | 0.0020-0.4 | $Y = 1.0358X + 3.7652 \times 10^{-2}$ | 0.9942 | 0.0006 | 0.002 | 103.74 | 5.45 |
| 10 | Phosphamidon | 16.946 | 0.0020-0.4 | $Y = 1.6758X - 0.2136$ | 0.9916 | 0.0006 | 0.002 | 90.79 | 6.74 |
| 11 | Parathion-methyl | 17.364 | 0.0050-1.0 | $Y = 1.2147X - 3.1254 \times 10^{-2}$ | 0.9927 | 0.0015 | 0.005 | 83.63 | 4.69 |
| 12 | Fenitrothion | 18.015 | 0.0020-0.4 | $Y = 0.3728X - 1.2956 \times 10^{-2}$ | 0.9992 | 0.0006 | 0.002 | 104.31 | 5.26 |
| 13 | Chlorpyrifos | 18.431 | 0.0020-0.4 | $Y = 1.5216X + 0.1268 \times 10^{-2}$ | 0.9966 | 0.0006 | 0.002 | 106.69 | 7.88 |
| 14 | Parathion-ethyl | 18.635 | 0.0020-0.4 | $Y = 0.2461X - 3.2159 \times 10^{-2}$ | 0.9994 | 0.0006 | 0.002 | 92.28 | 6.66 |
| 15 | Isocarbophos | 18.744 | 0.0050-1.0 | $Y = 0.3614X + 1.2863 \times 10^{-2}$ | 0.9926 | 0.0015 | 0.005 | 80.86 | 3.19 |
| 16 | Profenofos | 20.936 | 0.0050-1.0 | $Y = 0.1696X + 1.6041 \times 10^{-2}$ | 0.9943 | 0.0015 | 0.005 | 104.94 | 3.27 |
| 17 | Triazophos | 22.440 | 0.0020-0.4 | $Y = 2.0123X + 0.5329 \times 10^{-2}$ | 0.9952 | 0.0006 | 0.002 | 107.59 | 5.76 |
| 18 | Propargite-1 | 23.384 | 0.0050-1.0 | $Y = 0.1325X - 0.0463 \times 10^{-2}$ | 0.9964 | 0.0015 | 0.005 | 88.18 | 4.01 |
| 19 | Propargite-1 | 23.421 | 0.0050-1.0 | $Y = 0.1431X + 0.0346 \times 10^{-2}$ | 0.9989 | 0.0015 | 0.005 | 97.05 | 5.08 |
| 20 | Phosmet | 24.197 | 0.0050-1.0 | $Y = 1.3532X + 0.1102$ | 0.9948 | 0.0015 | 0.005 | 104.58 | 3.61 |
| 21 | Fenpropathrin | 24.420 | 0.0050-1.0 | $Y = 0.1672X + 0.2148 \times 10^{-2}$ | 0.9917 | 0.0015 | 0.005 | 90.34 | 4.47 |
| 22 | Cyhalothrin | 25.525 | 0.0050-1.0 | $Y = 0.2874X - 0.1673 \times 10^{-2}$ | 0.9976 | 0.0015 | 0.005 | 102.63 | 5.02 |
| 23 | Cypermethrin-1 | 28.695 | 0.0050-1.0 | $Y = 0.3027X - 0.2752 \times 10^{-2}$ | 0.9921 | 0.0015 | 0.005 | 101.66 | 4.77 |
| 24 | Cypermethrin-2 | 28.932 | 0.0050-1.0 | $Y = 0.2341X - 0.6368 \times 10^{-2}$ | 0.9977 | 0.0015 | 0.005 | 101.24 | 5.42 |
| 25 | Cypermethrin-3 | 29.065 | 0.0050-1.0 | $Y = 0.3041X + 0.1104 \times 10^{-2}$ | 0.9939 | 0.0015 | 0.005 | 97.97 | 4.67 |
| 26 | Cypermethrin-4 | 29.167 | 0.0050-1.0 | $Y = 0.1703X - 1.1085 \times 10^{-2}$ | 0.9983 | 0.0015 | 0.005 | 94.75 | 5.03 |
| 27 | Fenvalerate-1 | 31.099 | 0.0025-0.5 | $Y = 0.5102X - 2.0187 \times 10^{-2}$ | 0.9978 | 0.00075 | 0.0025 | 104.44 | 3.90 |
| 28 | Fenvalerate-2 | 31.730 | 0.0025-0.5 | $Y = 0.2274X - 1.0341 \times 10^{-2}$ | 0.9974 | 0.00075 | 0.0025 | 103.87 | 6.09 |
| | | | | Group B | | | | | |
| 29 | Dipterex | 8.089 | 0.0050-1.0 | $Y = 0.2306X-1.0743 \times 10^{-2}$ | 0.9924 | 0.0015 | 0.005 | 80.80 | 4.61 |
| 30 | Acephate | 10.676 | 0.0040-0.8 | $Y = 0.5482X-0.1073$ | 0.9946 | 0.0012 | 0.004 | 99.70 | 4.32 |
| 31 | 3-Hydroxycarbofuran | 11.115 | 0.0050-1.0 | $Y = 1.0725X + 0.7429 \times 10^{-2}$ | 0.9927 | 0.0015 | 0.005 | 80.42 | 5.11 |
| 32 | Phorate | 14.617 | 0.0050-1.0 | $Y = 0.4127X-4.2746 \times 10^{-2}$ | 0.9948 | 0.0015 | 0.005 | 107.79 | 3.29 |
| 33 | Carbofuran | 15.211 | 0.0010-0.2 | $Y = 0.2847X + 1.2376 \times 10^{-2}$ | 0.9964 | 0.0003 | 0.001 | 112.26 | 6.43 |
| 34 | Quintozene | 15.541 | 0.0020-0.4 | $Y = 0.1832X + 0.3729 \times 10^{-2}$ | 0.9916 | 0.0006 | 0.002 | 101.17 | 6.70 |
| 35 | Chlorothalonil | 16.088 | 0.0020-0.4 | $Y = 0.9217X-0.9261 \times 10^{-2}$ | 0.9982 | 0.0006 | 0.002 | 101.28 | 5.19 |
| 36 | Vinclozolin | 17.296 | 0.0050-1.0 | $Y = 0.8937X + 1.2643 \times 10^{-2}$ | 0.9917 | 0.0015 | 0.005 | 91.11 | 4.24 |
| 37 | Metalaxyl | 17.580 | 0.0020-0.4 | $Y = 0.2643X + 3.1927 \times 10^{-2}$ | 0.9926 | 0.0006 | 0.002 | 83.50 | 6.79 |
| 38 | Malathion | 18.239 | 0.0020-0.4 | $Y = 0.6372X + 2.1347 \times 10^{-2}$ | 0.9952 | 0.0006 | 0.002 | 95.65 | 6.12 |
| 39 | Fenthion | 18.558 | 0.0050-1.0 | $Y = 3.4017X + 7.9287 \times 10^{-2}$ | 0.9966 | 0.0015 | 0.005 | 102.13 | 3.76 |
| 40 | Triadimefon | 18.727 | 0.0100-2.0 | $Y = 1.3729X + 5.2014 \times 10^{-2}$ | 0.9952 | 0.003 | 0.01 | 93.24 | 3.38 |
| 41 | Procymidone | 19.809 | 0.0020-0.4 | $Y = 0.5429X + 9.2834 \times 10^{-2}$ | 0.9904 | 0.0006 | 0.002 | 85.21 | 8.57 |
| 42 | p,p′-DDE | 21.064 | 0.0010-0.2 | $Y = 0.7842X + 0. 2134 \times 10^{-2}$ | 0.9986 | 0.0003 | 0.001 | 108.06 | 7.31 |
| 43 | Iprodione | 21.948 | 0.0100-2.0 | $Y = 0.2827X-0.8246 \times 10^{-2}$ | 0.9964 | 0.003 | 0.01 | 108.04 | 5.56 |
| 44 | p′p′-DDD | 22.118 | 0.0010-0.2 | $Y = 8.9362X + 6.3827 \times 10^{-2}$ | 0.9932 | 0.0003 | 0.001 | 103.30 | 6.04 |
| 45 | o′p′-DDT | 22.198 | 0.0010-0.2 | $Y = 1.1827X + 2.3418 \times 10^{-2}$ | 0.9987 | 0.0003 | 0.001 | 106.74 | 5.65 |
| 46 | p′p′-DDT | 23.069 | 0.0020-0.4 | $Y = 4.1329X- 3.2718 \times 10^{-2}$ | 0.9965 | 0.0006 | 0.002 | 102.67 | 3.39 |
| 47 | Bifenthrin | 24.168 | 0.0100-2.0 | $Y = 0.5212X- 1.7835 \times 10^{-2}$ | 0.9926 | 0.003 | 0.01 | 104.60 | 4.50 |
| 48 | Phosalone | 25.115 | 0.0050-1.0 | $Y = 0.5317X + 2.1273 \times 10^{-2}$ | 0.9973 | 0.0015 | 0.005 | 81.34 | 4.47 |
| 49 | Cyfluthrin-1 | 27.971 | 0.0025-0.5 | $Y = 1.3257X- 1.2374 \times 10^{-2}$ | 0.9928 | 0.00075 | 0.0025 | 100.54 | 4.44 |
| 50 | Cyfluthrin-2 | 28.175 | 0.0025-0.5 | $Y = 1.2812X - 3.2793 \times 10^{-2}$ | 0.9916 | 0.00075 | 0.0025 | 98.17 | 3.34 |
| 51 | Cyfluthrin-3 | 28.308 | 0.0025-0.5 | $Y = 1.0237X -1.2836 \times 10^{-2}$ | 0.9972 | 0.00075 | 0.0025 | 105.14 | 4.57 |
| 52 | Cyfluthrin-4 | 28.410 | 0.0025-0.5 | $Y = 0.1827X-1.2364 \times 10^{-2}$ | 0.9961 | 0.00075 | 0.0025 | 107.81 | 4.09 |
| 53 | Flucythrinate-1 | 29.105 | 0.0050-1.0 | $Y = 0.1234X-7.3349 \times 10^{-2}$ | 0.9918 | 0.0015 | 0.005 | 103.73 | 3.41 |
| 54 | Flucythrinate-2 | 29.599 | 0.0050-1.0 | $Y = 0.0742X-4.2317 \times 10^{-2}$ | 0.9943 | 0.0015 | 0.005 | 107.97 | 4.51 |
| 55 | Fluvalinate-1 | 31.464 | 0.0050-1.0 | $Y = 1.3255X + 1.2195 \times 10^{-2}$ | 0.9926 | 0.0003 | 0.001 | 90.28 | 4.65 |
| 56 | Fluvalinate-1 | 31.671 | 0.0050-1.0 | $Y = 1.0283X + 0.9374 \times 10^{-2}$ | 0.9917 | 0.0003 | 0.001 | 90.25 | 3.21 |
| 57 | Deltamethrin | 33.632 | 0.0200-4.0 | $Y = 0.2342X-9.3571 \times 10^{-2}$ | 0.9919 | 0.006 | 0.02 | 96.56 | 2.84 |

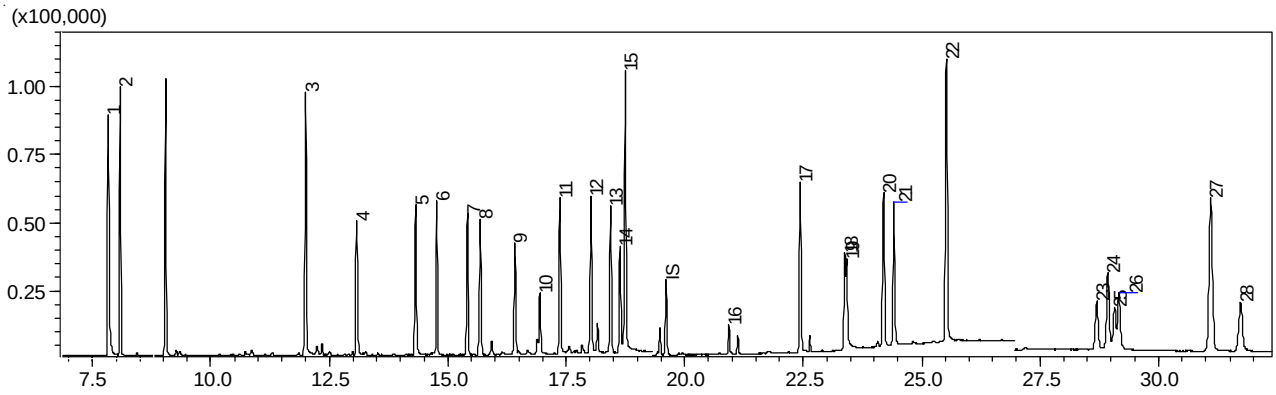


Fig. 2. Chromatogram of a pesticide standard mixture in group A using SIM mode

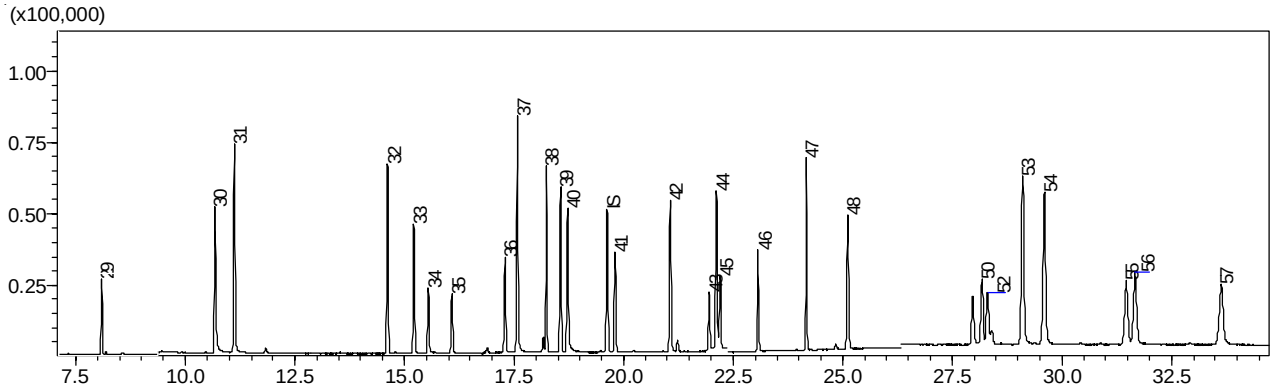


Fig. 3. Chromatogram of a pesticide standard mixture in group B using SIM mode

corresponding concentration from the mixed standard stock solution. The standard curves of peak area (Y) on the concentration (X) were achieved. The concentration of each pesticide of which the signal to noise ratio ≥ 3 was identified as the limits of detection (LOD) and the concentration of which the signal to noise ratio ≥ 10 was identified as the limits of quantification (LOQ). Retention time, selected ion parameters, the linear range, correlation coefficients, LOD and LOQ of the tested pesticides are listed in Table-1. It can be seen that a good linear relationship between the response values and concentration of each pesticide was achieved in the corresponding range of concentration. The correlation coefficients were higher than 0.99, the LOD of the method were between 0.0003 and 0.006 mg/kg, the LOQ were between the range of 0.001- 0.02 mg/kg.

**Recoveries and relative standard deviations:** The recoveries of eight kinds of Chinese herbal medicine such as *Aucklandiae lappa*, *Paris polyphylla smith* var. (*French*), *Polygonum multiflorum*, *Poria*, *Pistacia chinensis*, *Forsythia suspensa*, *Flos lonicerae*, *Panax notoginseng* were studied in this paper. The experimental results are listed in Table-1. It can be seen that the recoveries of 57 kinds of pesticide are ranged between 80.86 and 112.26 %, the relative standard deviations are ranged between 2.84 and 8.57 %.

## Conclusion

The analytical methods of 57 kinds of pesticide residues using online gel permeation chromatography (GPC) purification and gas chromatography-mass spectrometry (GC-MS) were established. Eight kinds of traditional Chinese herbal medicine such as *Aucklandiae lappa*, *Paris polyphylla smith* var. (*French*), *Polygonum multiflorum*, *Poria*, *Pistacia chinensis*, *forsythia suspensa*, *Flos lonicerae*, *Panax notoginseng* were studied. Satisfactory separation and detection sensitivity, recovery and precision were obtained. The correlation coefficients were higher than 0.99, the LOD of the method were between 0.0003 and 0.006 mg/kg, the LOQ were between the range of 0.001-0.02 mg/kg. The recoveries of 57 kinds of pesticides are ranged between 80.86 and 112.26 %, the relative standard deviations are ranged between 2.84 and 8.57 %.

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