Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Chromatography A, 1063 (2005) 201–210
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Determination of 266 pesticide residues in apple juice by matrix solid-phase dispersion and gas chromatography–mass selective detection

Xiao-Gang Chu[a], Xiao-Zhong Hu[b,c,d,*], Hui-Yuan Yao[a]

[a] School of Food Science & Technology, Southern Yangtze University, Wuxi, Jiangsu 214036, PR China
[b] State Key Laboratory of Freshwater Ecology and Biotechnology, Wuhan, Hubei 430072, PR China
[c] Institute of Hydrobiology, Chinese Academy of Sciences, Wuhan, Hubei 430072, PR China
[d] Hubei Entry-Exit Inspection and Quarantine Bureau, Technology Center, No. 3 Wansongyuan Road, Wuhan, Hubei 430022, PR China

Received 25 September 2004; received in revised form 27 November 2004; accepted 1 December 2004

Abstract

A macro matrix solid-phase dispersion (MSPD) method was developed to extract 266 pesticides from apple juice samples prior to gas chromatography–mass selective detection (GC–MSD) determination. A 10 g samples was mixed with 20 g diatomaceous earth. The mixture was transferred into a glass column. Pesticide residues were leached with a 160 mL hexane–dichloromethane (1:1) at 5 mL/min. Two hundred and sixty-six pesticides were divided into three groups and detected by GC–MSD under selective ion monitoring. The proposed method takes advantage of both liquid–liquid extraction and conventional MSPD methods. Application was illustrated by the analysis of 236 apple juice samples produced in Shaanxi province China mainland this year.

Keywords: Apple juice; Food analysis; Matrix solid-phase dispersion; Pesticides

1. Introduction

Pesticide is a term used for a broad range of chemicals, synthetic or natural, that serve to control insects, fungi, bacteria, weeds, nematodes, rodents and other pests. Since the era of synthetic organic pesticides began around 1940, pesticides have been providing enormous benefits for increasing agricultural production and quality due to the fact that pests and diseases damage up to one-third of crops whether in growing or in harvesting or in storage. However, most pesticides fail in natural degradation. The rapidly growing use of pesticides, often accompanied insufficient technical research or advice, and has unfortunately generated many environmental problems. As a result, human beings are exposed indirectly under pesticides, which are usually in small amount of certain foodstuff.

In this connection, monitoring pesticide residues is one of the most important aspects in minimizing potential hazards to human health. In 2002, a research program named Pivotal Technology of Food Safety was launched by the Ministry of Science and Technology in China, with two basic objectives, namely, to establish a technological regulation system on food safety, and to research on the multi-residual analysis approach for pesticides and veterinary medicines, antibiotics and synthetic hormones in foodstuff.

The goal of our research team is to develop a multi-residual analytical method for pesticides in apple juice, because China mainland is one of the largest producers of fruit juices, and several pesticides, such as acepmate, were once found in U.S. in apple juice exported by China. The benefit of multi-residual method is evident, for it allows more pesticides to be analyzed at one time with less resource and time consumption.

Numerous analytical methods for determining pesticides residues in various fruits and fruit juices have been published [1–8]. The ones most frequently used are gas chromatography

* Corresponding author. Tel.: +86 27 8579 3771; fax: +86 27 8579 3771.
E-mail address: huxz2002@sohu.com (X.-Z. Hu).

0021-9673/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2004.12.003

with electron-capture (ECD), nitrogen–phosphorus (NPD), flame photometric detection (FPD), mass spectrometric detection (MSD) and high performance liquid chromatography (HPLC) with diode-array detection (DAD) and fluorescence detection. Before the residues were determined, samples required extraction and purification, and in this respect liquid–liquid extraction (LLE) [9], solid-phase extraction (SPE) [10], accelerated solvent extraction (ASE) [11], gel permeation chromatography (GPC) [12] and matrix solid-phase dispersion (MSPD) [13] served as common methods.

MSPD is a sample pretreatment technique based on SPE, thus, with much easier application than that of SPE, MSPD also helps prevent emulsion from happening in liquid distribution, reduce the volume of organic solvents and accelerate the analysis, as SPE does. MSPD was first applied to extract and purify drug residues in animal tissue samples [14], and in recent years its application became popular in pesticide detection and has been introduced to multi-residual analysis [13–21] on pesticides in vegetal samples such as fruits, vegetables, fruit juices, etc.

In previous paper [22] we established a rapid and reliable multi-residual method based on MSPD for determining in apple juice the residues of 106 pesticides widely used in agricultural production. Some experimental parameters were optimized, for example, the pesticide-to-matrix ratio, composition of organic solvent, elution volume, elution rate, etc. By taking these measures we have reached an optimum experimental condition, which determines the ratio at 2:1, the hexane–dichloromethane solution volume (1:1) at 160 mL and the flow rate at 5 mL/min.

In this paper we will elaborate on the development of the multi-residual method. Two hundred and sixty-six pesticides were divided into three groups, prepared by the same MSPD procedure, and detected by gas chromatography–mass selected detection under selective ion monitoring (SIM). The analysis required three separate injections to cover all of the pesticides. The accuracy, precision, limits of detection, and linearity of the method were verified according to Residues Analysis Quality Control Guide (RAQCG) [23] as constituted by the General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China.

2. Experimental

2.1. Chemicals and reagents

Pesticide analytical standards were purchased from Riedel-de Haën (Seelze, Germany) and Dr. Ehrenstorfer (Augsburg, Germany). Acetone, dichloromethane and hexane, all residue analysis grades, were purchased from Dikma (Ontario, Canada). Individual stock standards were prepared in acetone for all compounds and stored at 4 °C with concentrations ranged from 100 mg/L to 500 mg/L, according to individual solubility. Three sets of standard mixtures in acetone have also been prepared for fortifying samples. Diatomaceous earth, Extrelut, was purchased from Merck (Darmstadt, Germany).

2.2. Instruments and apparatus

Agilent Technologies (Delaware, USA) 6890N network GC system equipped with an automatic split-splitless injector, Agilent Technologies 7683 series autosampler and mass-selective detector (MSD) Model Agilent Technologies 5973 network. A DB-5 ms fused-silica column (30 m × 0.25 mm i.d.) was used, with 5% phenyl-95% methylsilicone (film thickness 0.25 μm). Carrier gas was helium (99.999% purity, Wugang, Hubei, China) at a flow-rate of 1 mL/min. The injection port temperature and detector temperature were set at 250 and 280 °C, respectively. The oven temperature was programmed at 80 °C for 1 min, then raised to 160 °C at the rate of 10 °C/min and held for 5 min, afterwards raised to 240 °C at 3 °C/min, and then raised to 280 °C at 25 °C/min and eventually held for 10 min. The sample (1 μL) was injected in splitless mode (1 min). The MS system was routinely set in selective ion monitoring (SIM) mode and each compound was quantitated based on peak area using one target and one or two qualifier ions. Mass spectrometric parameters were set as follows: electron impact ionization with 70 eV energy; ion source temperature, 230 °C; MS quad temperature, 150 °C; EM voltage, 1450; and solvent delay 3.5 min.

A commercial glass column with a polytetrafluoroethylene stopper (30 cm × 20 mm i.d., Tianbo, Tientsin, China), a Mettler-Toledo (Greifensee, Switzerland) AG 245 analytical balance, a Supleco (Bellefonte, PA) VISIPREP 24 DL nitrogen evaporator and a Model Büchi (Flawil, Switzerland) R-134 rotary evaporator equipped with Model Eyela (Tokyo, Japan) CA-1200 cooler were employed.

2.3. MSPD procedure

A 10 g representative portion of the sample was transferred into a 500 mL beaker. A portion of 20 g diatomaceous earth was mixed with the juice until the sample was completely adsorbed under solid phase. Then the mixture was transferred with a funnel into a glass column. Pesticide residues were eluted with a 160 mL hexane–dichloromethane (1:1) at 5 mL/min. Eighty milliliter solvent was used to backwash the beaker. The effluent was also collected in a pear-shape flask and evaporated to dryness using a rotary vacuum evaporator in a water bath at 40 °C. The glycol should be added into circulating water as antifreeze, of which the temperature should be set to −20 °C for higher cooling efficiency. During rotary evaporation the degree of vacuum should be gradually lowered to avoid boiling liquid expanding vapor explosion. The residues were transferred to a graduated conical tube and adjusted to 1 mL with a gentle stream of nitrogen before GC–MSD analysis.

Spiking samples were prepared for recovery study by fortifying 100 g apple juice with three sets of known volume of solution at working standard. For each kind of pesticide, concentrations stood at 0.01 mg/kg, 0.02 mg/kg, 0.04 mg/kg and 0.08 mg/kg. The samples were kept for 3 h in dark place while being cooled at 4 °C before MSPD procedure. Unspiked samples were used for blanks.

2.4. Determination

Matrix induced enhancement is a phenomenon commonly encountered in gas chromatographic analysis of pesticides in foods [24,25]. Some factors, such as the nature of pesticide, the nature of matrix, the pesticide-to-matrix ratio, may affect sample matrix enhancement. Using of standards in blank matrix (matrix-matched standards) is the commonest approach followed in many papers due to its convenient application and high efficiency.

For identification to be confirmed in SIM mode, GC–MSD must be conducted by monitoring at least three ions [26]. We carried out full scan detection with a scan range from 50 to 550*m*/*z* on all the pesticides standard samples respectively in El mode, in which two or three characteristic ions were chosen in each kind of pesticides and one served as the target ion, while other ions served as characteristic ones, of which the natures were determined in accordance with chromatographic retention time and ionic ratio [27].

However, some indefinite positive results should be identified through dual-column confirmation and by resorting to different modes of ionization (e.g. CI mode) or high resolution GC–MS. In previous paper [22], a dual-column confirmation was used by our team. A DB-1701 fused-silica column (30 m × 0.32 mm i.d.) was also used with 14% cyanopropvlphenyl methylpolysiloxane (film thickness 0.25 μm). The oven temperature was programmed at 60 °C for 1 min, and then raised to 160 °C at the rate of 25 °C/min, afterwards raised to 250 °C at 5 °C/min, and eventually raised to 300 °C at 10 °C/min and held for 10 min (flow-rate at 1.5 mL/min). In this way, pesticides were identified by ion ratios and retention times obtained on two different columns.

2.5. Quality control

Our laboratory has established a quality assurance system as per ISO/IEC 17025:1999 for strict controls over personnel, conditions of instruments, experimental situation, etc. At the same time, it has also implemented the standard operating procedures (SOPs) based on the MSPD method, about which once daily sample inspection is carried out, detections must also be carried out on two known blank samples, two blank spiked samples and two known positive samples for verifying the reliability of operators, instruments and other materials.

3. Results and discussion

3.1. Feature of the proposed MSPD procedure

Typically, MSPD applies low sample size, i.e. 0.5 g sample of biological tissue. This research program has taken apple juice as the sample, which contained a slight amount of pigments, organic acids and aromatic substances, with water as its major constituent, thus this was a relatively simple matrix. Considering the strict requirements on MRLs by other countries, a sample size as high as 10 g has been taken in this program to ensure the requirements were met. Table 1 has made comparisons between the method discussed here and the MSPD procedures reported by related references, and reference 13, 28 and 29 covered typical operating methods of MSPD, while reference 30 refers to a micro method on MSPD.

Meanwhile, the method [22] formulated by our research team may be regarded a new macro MSPD approach with the unique characteristics. Compared with the method of LLE, this method can be also operated easily; meanwhile, it has the advantage of not causing emulsification appearance like the conventional MSPD method. However, compared with conventional MSPD, this method applies larger size of sample and solvent, because the sample size per microliter of final solution, which is treated by conventional MSPD, generally stands at 1–2 mg, and the sample size of this kind treated by the method described in this article reaches 10 mg. The significant figure means a more favorable limit of detection is obtained on the sample, given identical sensitivity of analyzing instruments.

What is more, based on the conventional method, the low sample size, such as 1 g of sample and 2 g of diatomaceous earth which are leached with 16 mL of solvent and given that the volume is finally set as 0.1 mL, would also reach 10 mg per microliter of final solution, identical in terms of effect, theoretically. Nevertheless, the excessively small final volume of concentrated solution during multi-residual analysis

Table 1
Comparison of several different MSPD approaches

	Ref. [13]	Ref. [22]	Ref. [28]	Ref. [29]	Ref. [30]
Sample type	Fruit juice	Apple juice	Semi-solid solid	Fruits and vegetables	Fruits
Sorbent	Diatomaceous earth	Diatomaceous earth	C8 or C18	C8	C8
Sample size	1 g	10 g	0.5 g	0.5 g	25 mg
Sorbent size	1 g	20 g	2 g	0.5 g	25 mg
Elution volume	8 mL	160 mL	8 mL	10 mL	100 μL
Final volume	0.5 mL	1 mL	–	0.5 mL	100 μL
Sample size/final extract	2 mg/μL	10 mg/μL	–	1 mg/μL	0.25 mg/μL

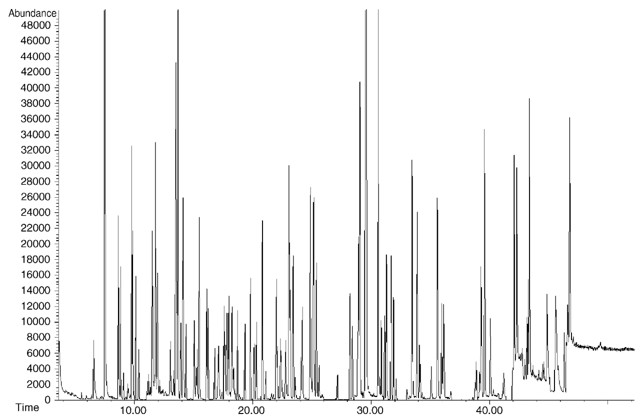

Fig. 1. The total ion chromatography of 97 pesticides in G0 group (matrix-matched standards), the concentration and retention time of each pesticide see Table 2.

may increase the difficulty of operation or even reduce recovery of certain pesticides.

It is no doubt that large size of sample may also bring about a problem, which requires longer analyzing time than the conventional MSPD does. To be specific, the new method lower the efficiency of the conventional MSPD method, to certain extent. However, this multi-residual analysis for 266 pesticides simultaneously is still acceptable, in view of the sample pre-treatment in no more than an hour.

3.2. Peak resolution

The 266 pesticide samples were divided into three groups, namely, 97 pesticides in G0 group, 86 in G1 group and 83 in G2 group. Several temperature programs have been used for chromatographic fractionation of the three groups, and the final temperature study has worked out favorably on the pesticides. Ninety-two chromatographic peaks were extracted from the 97 pesticides in G0 group (Fig. 1), 84 chromatographic peaks from G1 group (Fig. 2) and 80 from G2 group (Fig. 3). The chromatographic peaks, such as parathion-methyl and chlorpyrifos-methyl in G0 group, dimefuron and isopropalin in G1 group, and captan and phosfolan in G2 group, which cannot be separated on the TIC diagram can be separated by the way of extraction ion chromatography (EIC).

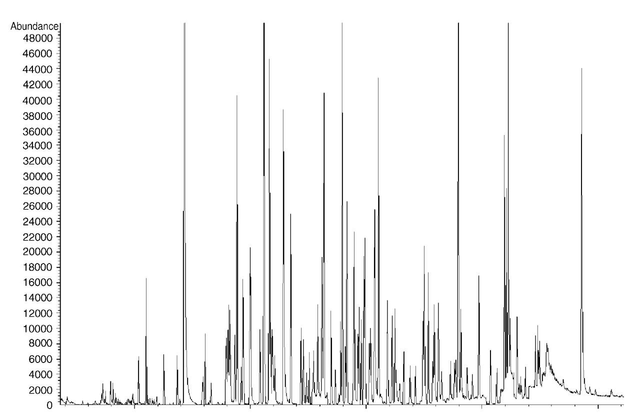

Fig. 2. The total ion chromatography of 86 pesticides in G1 group (matrix-matched standards), the concentration and retention time of each pesticide see Table 3.

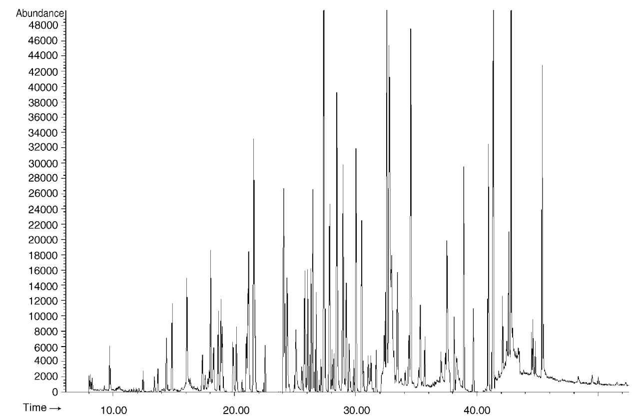

Fig. 3. The total ion chromatography of 83 pesticides in G2 group (matrix-matched standards), the concentration and retention time of each pesticide see Table 4.

3.3. Linearity and limit of detection (LOD)

Standard solutions in terms of micro-liters, at variable concentrations and containing all pesticides, were divided into individual amounts of 10 g for each sample, with the interval 0.05–4.00 mg/kg for injected solutions. Tests were repeated for three times at each concentration, proving favorable linear relationship of the pesticides. Correlation coefficients ranged from 0.98 to 1.00.

The LOD is defined as three times the standard deviation of a minimum of six replicate analyses of samples fortified as 2–3 times the estimated LOD. Tables 2–4 summarized the LODs for the pesticides in extracts of fruit juice.

3.4. Recovery

Recoveries of Amitraz, bromocyclen, chlormephos, chlorthiamid, endothal, hexachlorobenzene and methamidophos were all below 60%, and the recovery of dichlone only stood at 63.8%, indicating that these pesticides may only be partly recovered. With regard to rest pesticides, average recoveries from the 10 tests stood between 70.8 and 116.8% with coefficient of variation lower than 24%, as shown in Tables 2–4. According to RAQCG, a typical recovery range is recommended to be 70–110% and a typical coefficient of variation is recommended to be less than 21 at 0.01 mg/kg peak level. Results have proved that the recoveries and precisions of most of the pesticides meet the requirement in the Guide.

3.5. Application for apple juice

The established analytical procedure applies to the analysis on apple juices produced in Shaanxi province, which bears

Table 2
Retention time, target ions, qualifier ions, recoveries, RSDs and LODs of G0 pesticides ($n = 10$)

Pesticide	Retention time (min)	Target (*m/z*)	Q1 (*m/z*)	Q2 (*m/z*)	Spike level (mg/kg)	Recovery (%)	RSD (%)	LOD (μg/kg)
Ametryn	22.65	227	170	212	0.02	99.5	3.0	6
Atrazine	17.54	200	173	215	0.02	99.5	2.9	7
Azinphos-ethyl	42.17	132	77	160	0.04	97.5	4.5	4
Azinphos-methyl	40.52	160	104	132	0.04	96.6	4.7	4
Bendiocarb	15.23	151	126	166	0.08	93.7	3.7	9
Benfluralin	15.58	292	264	276	0.04	88.3	6.2	6
Bifenox	39.71	341	173	310	0.08	92.7	12.9	11
Bifenthrin	39.16	181	165	166	0.02	88.4	6.3	4
Bromophos-ethyl	28.85	359	97	125	0.02	92.5	6.5	4
Bromopropylate	38.57	341	157	183	0.04	96.7	5.2	12
Buprofezin	31.54	105	172	305	0.02	97.9	4.4	3
Butylate	9.73	146	156	174	0.02	79.0	9.6	4
Carbaryl	22.23	144	115	116	0.02	89.9	6.8	11
Carbofuran	17.37	164	131	149	0.02	95.7	4.1	3
Chinomethionate	28.04	234	116	206	0.02	92.6	6.4	8
Chlorfenson	29.80	111	175	302	0.02	95.5	6.9	4
Chlorobenzilate	32.82	251	139	253	0.02	97.8	4.2	5
Chlorpropham	14.49	127	171	213	0.02	98.0	3.8	5
Chlorpyrifos-methyl	22.00	286	109	125	0.02	95.1	4.6	8
Coumaphos	43.26	362	109	226	0.04	94.1	3.6	3
lambda-Cyhalothrin	42.02	181	197	208	0.04	88.2	6.8	5
p,p′-DDD	33.26	235	165	237	0.02	88.8	7.1	3
p,p′-DDE	30.76	246	176	318	0.02	85.4	7.2	3
o,p′-DDT	33.40	235	165	237	0.02	88.7	10.5	3
p,p′-DDT	35.46	235	165	237	0.02	91.6	9.7	3
Deltamethrin	47.87	181	152	253	0.04	81.4	5.5	8
Demeton-*S*-methyl	13.62	88	109	142	0.08	97.2	8.0	15
Demeton-*S*-methyl sulphone	23.20	169	125	109	0.08	92.4	8.1	12
Diazinon	19.37	179	199	304	0.08	96.8	3.8	9
Dichlobenil	8.60	171	100	173	0.02	78.0	9.9	8
Dicloran	16.62	206	124	176	0.02	97.7	4.7	8
trans-Dicrotophos	15.15	127	109	193	0.02	97.8	12.8	7
Dimethoate	16.81	87	125	229	0.02	101.0	5.9	4
Dioxathion	18.09	97	125	270	0.08	93.4	6.2	12
Diphenylamine	13.62	169	167	168	0.02	88.5	4.9	5
Disulfoton	19.41	88	142	186	0.02	91.4	6.2	4
Edifenphos	35.03	109	173	310	0.02	97.0	2.9	6
EPN	38.60	157	141	185	0.04	93.5	12.3	5
EPTC	8.72	128	86	132	0.02	78.4	10.2	4
Esfenvalerate	46.62	167	125	225	0.04	84.6	5.1	9
Ethion	33.81	231	125	153	0.04	93.9	5.2	7
Ethoprophos	14.01	158	139	200	0.02	97.8	3.1	5
Etrimfos	20.25	292	153	181	0.02	96.4	4.5	5
Fenamiphos sulphone	38.34	320	292	321	0.08	100.6	5.2	8
Fenchlorphos	22.90	285	109	125	0.02	87.7	9.4	6
Fenitrothion	23.76	277	109	125	0.08	97.4	3.1	9
Fenobucarb	13.32	121	91	150	0.02	97.7	4.7	6
Fenpropathion	39.42	181	208	265	0.04	90.9	6.0	11
Fenthion	25.00	278	109	125	0.02	94.8	5.9	6
Fenvalerate	46.18	167	125	225	0.04	89.0	6.3	7
Folpet	27.76	260	104	130	0.08	86.3	12.3	12
Formothion	20.67	93	125	172	0.04	92.8	5.2	4
alpha-HCH	15.94	183	181	219	0.02	84.2	5.9	3
beta-HCH	17.55	219	181	109	0.02	94.5	7.9	3
delta-HCH	19.37	219	181	109	0.02	90.1	9.5	3
Iprodione	38.21	314	187	245	0.08	95.5	6.9	8
Isoprocarb	11.67	121	91	136	0.02	97.3	3.2	7
Lenacil	35.25	153	110	154	0.02	99.1	7.6	6
Lindane	17.87	181	217	219	0.02	88.5	11.5	3
Malathion	24.67	173	125	158	0.04	98.3	7.2	8
Mecarbam	27.94	131	159	329	0.04	98.6	5.3	9
Metalaxyl	22.94	206	132	160	0.02	94.5	5.9	9

Table 2 (*Continued*)

Pesticide	Retention time (min)	Target (*m*/*z*)	Q1 (*m*/*z*)	Q2 (*m*/*z*)	Spike level (mg/kg)	Recovery (%)	RSD (%)	LOD (μg/kg)
Methidathion	28.55	145	85	93	0.02	98.8	7.3	6
Methiocarb	23.74	168	109	153	0.02	92.6	5.7	6
Metolachlor	24.77	162	146	238	0.02	98.3	2.9	6
Metribuzin	21.57	198	103	199	0.08	98.7	3.5	15
cis-Mevinphos	9.75	127	109	192	0.02	96.6	5.7	7
Molinate	11.62	126	83	187	0.02	92.1	5.4	5
Omethoate	12.86	156	110	126	0.08	94.4	8.5	8
Oxadiazon	31.37	175	258	302	0.02	95.6	5.0	5
Oxyfluorfen	31.79	252	300	361	0.08	95.2	7.7	5
Parathion	25.17	291	155	235	0.08	96.6	6.1	4
Parathion-methyl	22.00	109	125	263	0.04	97.8	3.9	3
Pendimethalin	27.12	252	162	281	0.04	91.9	7.0	5
Permethrin[a]	43.01, 43.21	183	163	184	0.04	88.1	6.3	5
o-Phenylphenol	11.21	170	115	169	0.08	95.6	3.4	6
Phorate	15.82	75	121	260	0.02	88.5	6.8	3
Phosalone	40.65	182	121	154	0.04	97.6	8.7	5
Pirimicarb	20.91	166	72	238	0.02	99.2	6.7	3
Profenofos	30.61	337	208	374	0.08	95.9	7.7	12
Prometryn	22.94	241	184	226	0.02	99.0	3.0	4
Propachlor	13.41	120	169	176	0.02	97.6	3.5	9
Propoxur	13.41	110	81	152	0.02	97.5	3.5	8
Prothiofos	30.41	267	162	309	0.08	90.5	5.9	12
Quinalphos	27.84	146	129	298	0.02	98.3	4.1	6
Quizalofop-*P*-ethyl	44.69	299	272	372	0.04	95.3	4.4	8
Simazine	17.17	201	173	186	0.02	99.8	6.6	7
Taufluvalinate[a]	46.66, 46.82	250	181	209	0.04	84.6	6.5	5
Terbufos	18.40	231	153	186	0.02	91.6	6.5	5
cis-Tetrachlorvinphos	29.37	331	109	329	0.02	97.3	5.4	5
Thiobencarb	24.39	100	72	125	0.02	96.7	5.2	3
Thiometon	16.36	88	93	125	0.02	91.8	5.1	3
Triazophos	34.58	161	134	172	0.08	99.5	6.2	5
Trifluralin	15.45	306	264	290	0.02	87.1	6.8	3
Vamidothion	29.06	87	109	145	0.08	100.6	7.2	6
Vernolate	9.98	128	146	161	0.02	82.9	7.8	4
Vinclozlin	22.05	212	198	285	0.04	96.7	4.3	6

[a] Calculation of the general amount of the isomers.

Table 3
Retention time, target ions, qualifier ions, recoveries, RSDs and LODs of G1 pesticides ($n = 10$)

Pesticide	Retention time (min)	Target (*m*/*z*)	Q1 (*m*/*z*)	Q2 (*m*/*z*)	Spike level (mg/kg)	Recovery (%)	RSD (%)	LOD (μg/kg)
2-Benzyl-4-chlorophenol	22.15	218	140	183	0.01	103.0	4.4	4
Aldrin	24.25	263	261	293	0.01	79.8	5.0	4
Azoxystrobin	48.62	344	388		0.04	105.2	4.3	8
Benalaxyl	35.02	148	206	325	0.01	103.5	2.5	4
Benfuracarb	42.41	190	163	353	0.01	90.1	5.8	5
Benfuresate	21.23	163	121	256	0.01	102.4	1.7	3
Benoxacor	20.53	120	176	259	0.01	103.0	4.9	4
Benthiazole	29.55	180	136	238	0.04	104.3	1.9	6
Bioresmethrin	37.43	123	143	171	0.01	100.5	8.7	4
Bitertanol[a]	42.82, 42.96	170	112		0.01	104.8	6.4	4
Butachlor	29.69	176	160	237	0.01	103.4	6.0	5
Butocarboxim	9.59	108	86		0.04	94.6	4.9	4
Cadusafos	15.61	159	127	213	0.01	102.8	5.9	3
Carboxin	31.15	143	87	235	0.01	96.3	6.1	4
Carpropamid	32.47	139	180	250	0.01	104.1	5.3	6
Chlorbufam	17.45	53	127	223	0.02	104.4	4.5	4
Chlorfenvinphos[a]	27.11, 27.57, 27.76	267	295	323	0.01	102.8	5.3	6
Chlorpyrifos	25.14	314	197	258	0.01	102.7	7.2	7
Chlorthiophos	33.99	269	325	360	0.01	101.8	8.3	4
Crotoxyphos	28.49	127	105	193	0.01	103.4	10.4	8
Cycluron	18.18	72	127	198	0.01	102.5	8.8	6

Table 3 (*Continued*)

Pesticide	Retention time (min)	Target (*m*/*z*)	Q1 (*m*/*z*)	Q2 (*m*/*z*)	Spike level (mg/kg)	Recovery (%)	RSD (%)	LOD (μg/kg)
Cypermethrin[a]	44.48, 44.64, 44.78, 44.85	163	209		0.04	103.9	12.9	10
Cyproconazol	31.96	222	139	224	0.01	103.4	13.1	4
p,*p*′-DDM	20.88	201	165	236	0.01	71.0	5.1	4
Desmetryn	21.27	213	171	198	0.01	103.8	12.0	4
Diallate[a]	15.79, 16.27	86	128	234	0.01	92.6	10.8	4
Dichlofluanid	24.14	123	167	224	0.01	102.5	4.2	4
Dichlone	19.00	191	163	226	0.04	63.8	16.4	9
Diethatyl-ethyl	30.18	188	238	262	0.01	103.7	8.2	4
Difenoxuron	24.72	241	198	226	0.01	94.3	7.5	5
Dimefuron	26.80	131	166	293	0.04	107.9	4.8	12
Dimepiperate	27.66	119	103	145	0.01	103.8	3.2	6
Dinitramine	19.81	305	261		0.01	103.7	8.3	4
alpha-Endosulfan	28.92	241	195	265	0.01	98.4	2.9	5
beta-Endosulfan	32.37	195	237	267	0.01	102.1	3.2	5
Endrin	31.76	263	243	281	0.01	101.2	5.8	4
Ethiofencarb	20.77	107	168		0.02	95.1	6.7	5
Fenarimol	41.85	139	219	251	0.01	105.4	8.2	4
Fenfuram	19.50	109	201		0.01	102.7	7.6	4
Fenothiocarb	29.07	72	160		0.01	103.6	5.4	4
Fenson	25.59	141	77	268	0.01	102.9	8.9	4
Fenuron	14.04	72	119	164	0.04	90.6	3.3	6
Flubenzimine	31.24	135	186	212	0.01	86.7	12.2	5
Fluorodifen	30.36	190	126	328	0.04	112.9	7.8	3
Fluoroglycofen	42.41	344	207	447	0.04	116.8	5.1	7
Fluridone	45.61	328	329	330	0.01	91.4	10.0	6
Fluroxypyr methyl ester	36.85	209	181	366	0.01	102.3	5.7	4
Fonfos	18.49	109	137	246	0.01	99.6	8.8	3
Heptenophos	12.56	124	109	215	0.01	102.7	3.2	6
Hexazinone	36.17	171	128	252	0.01	101.6	5.0	7
Isazofos	20.08	161	119	257	0.01	103.3	9.9	6
Isopropalin	26.81	280	238	264	0.02	101.2	5.7	11
Isoprothiolane	30.58	162	118	189	0.01	103.7	8.1	5
Kresoxim-methyl	32.05	116	131	206	0.01	103.6	5.2	5
Mephacrifos	11.00	125	180	208	0.01	97.5	5.6	4
Mepronil	34.27	119	91	269	0.01	104.4	8.0	4
Methamidophos	6.94	94	141		0.04	42.7	11.6	5
Methoprene	28.57	73	111	191	0.02	101.7	7.3	8
Naptalam	41.65	273	228		0.01	104.0	8.5	4
Nitralin	37.78	316	274	300	0.01	111.1	4.3	6
Nitrothal-isopropyl	25.86	236	194	212	0.01	108.1	9.0	3
Norflurazon	35.42	303	102	145	0.01	101.8	10.6	3
Octachlorodipropyl ether	22.89	130	79	181	0.01	95.3	11.8	3
Ofurace	34.67	132	160	232	0.01	101.9	6.0	3
Oxadixyl	33.57	163	105	132	0.01	101.7	5.3	3
Pebulate	10.21	128	161	203	0.01	84.2	8.0	4
Pentachlorophenol	17.67	266	264	268	0.04	105.0	5.0	3
Pentanochlor	23.96	141	197	239	0.01	105.0	4.3	4
Phenthoate	27.91	274	125	246	0.01	104.0	3.7	3
Phosphamidon[a]	19.30, 21.58	127	264		0.04	102.9	10.5	7
Piperonyl butoxide	32.19	176	149	193	0.04	116.2	19.4	18
Pretilachlor	30.91	162	176	238	0.01	103.4	10.1	5
Procymidone	28.15	283	96	285	0.01	103.7	8.0	3
Propanil	21.43	161	163	217	0.02	102.2	7.5	8
Propazine	17.85	214	172	229	0.01	103.7	9.8	4
Propetamphos	18.61	138	194	236	0.01	103.2	6.8	5
Propiconazole[a]	35.37, 35.74	173	191	259	0.01	101.1	10.6	4
Prothoate	21.85	115	97		0.01	103.4	8.4	4
Pyrazophos	42.29	221	373		0.01	103.7	9.7	4
Pyridaphenthion	38.38	340	188	204	0.01	105.4	7.8	4
Pyrifenox[a]	27.36, 28.92	262	171	187	0.01	103.8	9.4	4
Siduron	29.83	93	119		0.04	100.3	5.6	11
Teramethrin[a]	38.60, 39.06	164	123		0.01	94.1	11.4	3
Tetradifon	40.00	159	229	356	0.01	103.5	7.1	3
Thiabendazole	27.11	201	174		0.04	88.9	8.2	4
Triadimfon	25.33	208	57	181	0.01	103.9	7.2	3

[a] Calculation of the general amount of the isomers.

Table 4
Retention time, target ions, qualifier ions, recoveries, RSDs and LODs of G2 pesticides ($n = 10$)

Pesticide	Retention time (min)	Target (m/z)	Q1 (m/z)	Q2 (m/z)	Spike level (mg/kg)	Recovery (%)	RSD (%)	LOD (μg/kg)
Alachlor	22.53	160	188	237	0.01	96.4	3.2	8
Amitraz	41.64	162	132	147	0.04	45.2	6.2	10
Ancymidol	32.25	228	107	121	0.01	96.3	2.2	4
Anilazine	27.06	239	143	178	0.04	110.6	2.8	12
Azamethiphos	34.59	215	109	183	0.04	110.6	23.3	15
Benodanil	33.69	231	203	323	0.01	97.6	6.1	4
Benzoximate	12.37	213	170		0.01	93.4	3.3	4
Binapacryl	32.50	83	55		0.04	91.1	12.2	8
Bromacil	24.05	205	190	233	0.04	97.4	7.9	6
Bromocyclen	20.17	357	237	272	0.01	57.4	4.7	4
Bromophos-methyl	26.06	331	125	329	0.01	91.2	2.4	4
Captan	27.35	79	107	149	0.04	93.2	4.8	16
Carbosulfan	38.75	160	118	323	0.01	92.6	4.5	4
Carfentrazone-ethyl	35.42	312	290	340	0.01	96.5	4.1	4
Chlorfluazuron	24.87	347	349		0.04	99.2	20.4	7
Chloribensid	28.00	268	125	127	0.01	88.9	7.6	4
Chlormephos	9.90	121	97	234	0.01	59.0	10.0	3
Chlorthiamid	21.33	170	100	205	0.04	43.7	13.9	6
Clomazone	17.62	125	127	204	0.01	95.1	7.5	9
Cyanazine	25.33	225	198	240	0.01	95.6	11.4	10
Cycloate	14.00	83	154	215	0.01	89.5	10.8	4
Cyfluthrin[a]	43.98, 44.14, 44.27, 44.33	163	206	226	0.02	99.6	9.5	11
Cyprofuram	33.16	211	69	279	0.01	97.4	4.1	4
o,p′-DDE	28.78	246	176	318	0.01	87.5	3.4	4
Dialifos	42.39	173	208	357	0.01	96.8	4.6	4
Dibrom	14.71	109	145	185	0.04	92.2	15.0	10
Dichlofenthion	21.48	279	162	251	0.01	89.4	12.1	4
Dieldrin	30.50	79	263	345	0.01	92.8	11.1	4
Difenzoquat	31.10	234	233	235	0.01	83.3	6.5	4
Dinobuton	28.19	211	163	240	0.04	90.8	3.1	6
Dioxacarb	21.23	166	121	122	0.04	92.6	5.8	9
Diphenamid	26.22	167	72	239	0.01	96.7	4.2	3
N,N′-Diphenyluren	31.96	93	119	212	0.04	86.9	7.4	4
Ditalimfos	29.62	130	209	299	0.01	93.9	3.4	4
Endothal	10.78	68	100	140	0.04	45.4	6.3	10
Etofenprox	45.00	163	107	135	0.01	97.1	4.6	6
Famphur	34.86	218	93	125	0.01	97.9	7.3	4
Fenamiphos	30.18	303	154	288	0.01	95.7	10.6	4
Fenazaflor	34.21	281	77	374	0.04	77.3	17.2	9
Fenpiclonil	37.92	236	174	238	0.04	97.0	4.3	10
Fludioxonil	30.89	248	127	154	0.01	97.0	6.9	4
Flumetralin	29.82	143	159	360	0.01	90.5	4.9	3
Furathiocarb	40.67	163	194	325	0.04	96.0	7.6	5
Furmecyclox	20.82	123	221	251	0.01	90.9	3.5	4
Halosulfuron-methyl	35.61	327	139	260	0.02	103.7	6.3	5
Haloxyfop-2-ethoxy ether ester	37.72	302	288	316	0.01	96.2	3.6	5
Hexachlorobenzene	16.33	284	214	249	0.01	52.4	7.3	8
Imazalil	30.38	215	159	173	0.01	93.6	5.2	4
Iodfenphos	30.12	377	125	250	0.01	92.2	7.3	4
Isocarbamid	18.09	142	113	130	0.01	96.5	9.5	3
Isofenphos	27.80	213	121	255	0.01	95.8	6.8	5
Kinoprene	16.86	135	84	285	0.04	90.9	8.6	9
Methfuroxam	25.38	137	229		0.01	70.8	4.9	3
Methoprotryne	31.74	256	226	240	0.01	95.9	8.9	5
Methoxychlor	39.06	227	228	274	0.01	93.2	3.8	4
Monalide	20.57	85	127	197	0.01	94.9	11.4	3
Monocrotophos	15.54	127	97	192	0.04	92.0	13.1	7
Nitrofen	31.96	202	253	283	0.04	93.2	6.9	5
Octhilinone	20.33	101	180	213	0.01	96.6	8.0	3
Orbencarb	23.47	100	72	222	0.01	95.6	7.0	4
Oxycarboxin	37.05	175	147	267	0.04	98.3	20.1	3
Paclobutrazol	28.83	236	125	167	0.01	96.4	5.6	4

Table 4 (*Continued*)

Pesticide	Retention time (min)	Target (*m/z*)	Q1 (*m/z*)	Q2 (*m/z*)	Spike level (mg/kg)	Recovery (%)	RSD (%)	LOD (μg/kg)
Pencycuron	15.34	125	180	209	0.01	101.0	3.5	4
Phenothrin[a]	40.26, 40.60	183	123	350	0.01	91.6	5.4	3
Phosfolan	27.35	140	196	255	0.01	96.4	9.0	3
Pirimiphos-ethyl	26.78	333	304	318	0.01	94.5	5.7	3
Pirimiphos-methyl	24.08	290	276	305	0.01	96.7	7.8	3
Promecarb	15.80	135	91	150	0.01	95.8	6.4	4
Propamocarb	9.18	58	129	188	0.01	92.2	8.8	4
Propargite[a]	36.82, 36.89	135	150	173	0.01	97.0	5.4	4
Propyzamide	18.62	173	145	255	0.01	96.6	3.6	4
Prowl	27.11	252	281		0.01	90.6	4.8	4
Pyraclofos	42.44	360	138	194	0.04	99.6	10.8	9
Pyroquilon	18.34	173	130	144	0.01	96.5	8.0	4
Secbumeton	19.69	196	169	210	0.01	96.5	3.3	4
Tebuconazol	36.26	250	125	252	0.01	97.9	3.7	5
Terbacil	19.58	161	117	160	0.01	95.5	9.2	4
Terbutryn	23.67	226	185	241	0.01	96.2	3.2	3
Thionazin	13.28	97	107	143	0.01	95.4	3.7	3
Triadimenol[a]	27.86, 28.29	168	112	128	0.04	96.3	3.1	5
S,S,S-Tributyl phosphorotrithioate	30.89	169	202	258	0.01	94.7	4.9	4
Trichloronate	25.80	297	109	269	0.01	89.4	6.7	3
Trietazine	18.50	200	186	229	0.01	96.6	8.1	3

[a] Calculation of the general amount of the isomers.

the largest apple juice output in China. Pesticide residues have been found from 9 out of 236 apple juice samples produced in 2004. Positive samples were identified through dual-column confirmation as described in Section 2.4. Among these samples, five have been proved fenvalerale, of which the content was 0.015–0.047 mg/kg (MRL of China is 2 mg/kg); two have been proved deltamethrin, of which the content was 0.024 and 0.017 mg/kg, respectively (MRL of China is 0.05 mg/kg); and two have been proved benfuracarb and imazalil, separately, of which the content was 0.012 mg/kg (MRL of China is 0.05 mg/kg) and 0.023 mg/kg (MRL of China is 0.05 mg/kg), respectively. Facts have proved the fenpropathrin was most frequently used in apple production in Shaanxi Province, its residue meet the requirement of MRL published in China, and the application of apple pesticides meet related state standards [31].

4. Conclusion

This method has proved favorable sensitivity and recoveries and realized rapid sample analysis. It applies to a wide range of pesticides, applicable for apple juice detection and much suitable for use regulatory laboratories. Moreover, with respect to the sample pretreatment technology, the MSPD approached applied here takes advantage of both LLE and conventional MSPD methods. It is not only its uniqueness, but a progress of conventional methods.

Acknowledgement

We greatly appreciate the financial support from the Ministry of Science and Technology on research project No. 2001BA804A11, and we also wish to express our sincere gratitude to Prof. Daning Wang and Prof. Yingzhang Tang of the Chinese Academy of Inspection and Quarantine for their joint preparation of this report.

References

[1] X.G. Chu, W. Yong, Chin. J. Chromatogr. 19 (2001) 19.
[2] X.Z. Hu, X.G. Chu, J.X. Yu, Y.B. Zhang, Z.G. Yan, L.S. Ni, Y.F. Lin, P. Wang, X. Huang, Chin. J. Instrum. Anal. 22 (2003) 26.
[3] C.M. Torres, Y. Picó, J. Mañes, J. Chromatogr. A 754 (1996) 301.
[4] A.I. Valenzuela, D.S. Popa, M.J. Redondo, J. Manes, J. Chromatogr. A 918 (2001) 59.
[5] A.L. Simplicio, L.V. Boas, J. Chromatogr. A 833 (1999) 35.
[6] A. Sannino, M. Bandini, L. Bolzoni, J. AOAC Int. 86 (2003) 101.
[7] D.A. Lambropoulou, T.A. Albanis, J. Agric. Food. Chem. 50 (2002) 3359.
[8] M. Oishi, K. Onischi, I. Kano, H. Nakazawa, S. Tanabe, J. AOAC Int. 77 (1994) 1293.
[9] J. Fillion, R. Hindle, M. Lacroix, J. Selwyn, J. AOAC Int. 78 (1995) 1252.
[10] J. Fillion, F. Sauvě, J. Selwyn, J. AOAC Int. 83 (2000) 698.
[11] K. Adou, W.R. Bontoyan, R.J. Sweeney, J. Agric. Food Chem. 49 (2001) 4153.
[12] A. Sannino, M. Bandini, L. Bolzoni, J. AOAC Int. 82 (1999) 1229.
[13] D. Perret, A. Gentili, S. Marchese, M. Sergi, G. D'Ascenzo, J. AOAC Int. 85 (2002) 724.
[14] S.A. Barker, A.R. Long, C.R. Short, J. Chromatogr. 475 (1989) 353.
[15] L. Kandenczki, Z. Arpad, I. Gardi, J. AOAC Int. 75 (1992) 53.
[16] Y.C. Ling, I.P. Huang, J. Chromatogr. A 695 (1995) 75.
[17] S.C. Stafford, W. Lin, J. Agric. Food Chem. 40 (1992) 1026.
[18] C.M. Torres, Y. Picó, J. Mañes, J. Chromatogr. A 719 (1996) 95.
[19] M. Bozena, Chem. Anal. 47 (2002) 571.
[20] M. Anastassiades, S.J. Lehotay, D. Stajnbaher, F.J. Schenck, J. AOAC Int. 86 (2003) 412.
[21] B. Albero, C.S. Brunete, J.L. Tadeo, J. Agric. Food. Chem. 51 (2003) 6915.

[22] X.Z. Hu, X.G. Chu, J.X. Yu, Y.B. Zhang, Z.G. Yan, L.S. Ni, Y.F. Lin, P. Wang, J. Li, X. Huang, J. AOAC Int. 87 (2004) 972.
[23] Residues Analysis Quality Control Guide, General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China, Beijing, China, 2002.
[24] D.R. Erney, A.M. Gillespie, D.M. Gylvidis, C.F. Poole, J. Chromatogr. 638 (1993) 57.
[25] F.J. Schenck, S.J. Lehotay, J. Chromatogr. A 868 (2000) 51.
[26] Pesticide Analytical Manual, Food and Drug Administration, Washington, DC, 1994.
[27] A. Sannino, P. Mamrriani, M. Bandini, L. Bolzoni, J. AOAC Int. 78 (1995) 1502.
[28] S.A. Barker, J. Chromatogr. A 880 (2000) 63.
[29] M. Fernandez, Y. Picó, J. Mañes, J. Chromatogr. A 871 (2000) 43.
[30] E.M. Kristenson, E.G.J. Haverkate, C.J. Slooten, L. Ramos, R.J.J. Vreuls, U.A.T. Brinkman, J. Chromatogr. A 917 (2001) 277.
[31] GB/T 8321-2000 Guideline for safety application of pesticides, State Administration of Quality and Technology, Beijing, China, 2002.