DETERMINATION OF 24 PESTICIDES RESIDUES IN LEATHER PRODUCTS BY SOLID-PHASE MICROEXTRACTION COUPLED WITH GAS CHROMATOGRAPHY–MASS SPECTROMETRY

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DETERMINATION OF 24 PESTICIDES RESIDUES IN LEATHER PRODUCTS BY SOLID-PHASE MICROEXTRACTION COUPLED WITH GAS CHROMATOGRAPHY–MASS SPECTROMETRY

ABSTRACT. Considering the high content of oil and complex residual additives in leather samples, a new analytical method based on the solid-phase extraction technique and gas chromatography-selected ion monitoring mass spectrometry (GC-SIM-MS) was developed to determine 24 organic compounds involving the organochlorine pesticides (OCPs), organophosphorous pesticides (OPPs) and pyrethroids pesticides residues in leather. The extraction conditions (such as the extraction solution, purification procedure and solid-phase extraction column) were optimized using the positive leather samples based on the recovery rates of the pesticides. The best extraction solution, solid-phase extraction column and chromatography column were n-hexane and ethyl acetate (1+1, volume) mixed solution, Carb-PSA (1.0 g, 6mL) and DB-1701 (length: 30 m, inside diameter: 0.25 mm, film thickness: 0.25 μm). The optimized extraction time and temperature were 20 min and 25°C, respectively. The detection limits of 24 pesticide residues range from 0.05 to 0.10 mg/kg, and the recoveries range from 74% to 116%. The relative standard deviations (RSD, n=6) range from 5.42% to 12.00%. The developed method presented a simple, rapid, sensitive, and inexpensive method to detect 24 pesticides in skin and leather and was successfully applied to the detect them in leather products (cowhide, sheep leather and pig leather).

KEY WORDS: leather, organochlorine pesticides, organophosphorous pesticides, pyrethroids pesticides, GC-MS

DETERMINAREA A 24 DE REZIDUURI DE PESTICIDE ÎN PRODUSELE DIN PIELE PRIN MICROEXTRACȚIE ÎN FAZĂ SOLIDĂ CUPLATĂ CU CROMATOGRAFIE DE GAZE - SPECTROMETRIE DE MASĂ

REZUMAT. Având în vedere conținutul ridicat de ulei și aditivi reziduali complecși din probele de piele, s-a dezvoltat o nouă metodă analitică bazată pe tehnica de extracție în fază solidă și cromatografie de gaze cuplată cu spectrometria de masă, prin monitorizarea ionilor selecționați (GC-SIM-MS) pentru a determina reziduurile a 24 de compuși organici printre care pesticide organoclorurate (OCP), pesticide organofosforice (OPP) și piretroizi. Condițiile de extracție (cum ar fi soluția de extracție, procedura de purificare și coloana de extracție în fază solidă) au fost optimizate folosind probe de piele pozitive pe baza ratelor de recuperare a pesticidelor. Cea mai bună soluție de extracție, coloană de extracție în fază solidă și coloană de cromatografie au fost soluția mixtă de n-hexan și acetat de etil (1+1, volum), Carb-PSA (1,0 g, 6 ml) și DB-1701 (lungime: 30 m, diametru interior: 0,25 mm, grosime film: 0,25 μm). Timpul și temperatura de extracție optimizate au fost de 20 min și respectiv 25°C. Limitele de detecție a celor 24 de reziduuri de pesticide variază de la 0,05 la 0,10 mg/kg, iar recuperările variază de la 74% la 116%. Abaterile standard relative (RSD, n=6) variază de la 5,42% la 12,00%. Metoda dezvoltată pentru a detecta 24 de pesticide în piele este simplă, rapidă, sensibilă și ieftină, și a fost aplicată cu succes pentru a detecta aceste reziduuri în produse din piele (de vacă, de oaie și de porc).

CUVINTE CHEIE: piele, pesticide organoclorurate, pesticide organofosforice, pesticide piretroide, GC-MS

DÉTERMINATION DE 24 RÉSIDUS DE PESTICIDES DANS LES PRODUITS EN CUIR PAR MICROEXTRACTION EN PHASE SOLIDE COUPLÉE AVEC LA CHROMATOGRAPHIE GAZEUSE - SPECTROMÉTRIE DE MASSE

RÉSUMÉ. Compte tenu de la teneur élevée en huile et en additifs résiduels complexes dans les échantillons de cuir, une nouvelle méthode analytique basée sur la technique d'extraction en phase solide et la chromatographie en phase gazeuse couplée avec la spectrométrie de masse à contrôle d'ions sélectionnés (GC-SIM-MS) a été développée pour déterminer 24 composés organiques impliquant les pesticides organochlorés (OCP), les pesticides organophosphorés (OPP) et les pesticides pyréthrinoïdes dans le cuir. Les conditions d'extraction (telles que la solution d'extraction, la procédure de purification et la colonne d'extraction en phase solide) ont été optimisées en utilisant les échantillons de cuir positifs basés sur les taux de récupération des pesticides. La meilleure solution d'extraction, la colonne d'extraction en phase solide et la colonne de chromatographie étaient une solution mixte de n-hexane et d'acétate d'éthyle (1+1, volume), Carb-PSA (1,0 g, 6 ml) et DB-1701 (longueur : 30 m, diamètre à l'intérieur : 0,25 mm, épaisseur du film : 0,25 μm). Le temps et la température d'extraction optimisés étaient respectivement de 20 min et 25°C. Les limites de détection de 24 résidus de pesticides vont de 0,05 à 0,10 mg/kg et les taux de récupération vont de 74% à 116%. Les écarts types relatifs (RSD, n=6) vont de 5,42% à 12,00%. La méthode développée pour détecter 24 pesticides dans la peau est une méthode simple, rapide, sensible et peu coûteuse et a été appliquée avec succès pour les détecter les résidus dans les produits en cuir (vache, mouton et porc).

MOTS CLÉS : cuir, pesticides organochlorés, pesticides organophosphorés, pesticides pyréthrinoïdes, GC-MS

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INTRODUCTION

Skins and leather were widely used in clothing, shoes, automobile, packaging, and decoration industry [1-3]. To obtain good quality of leather, a variety of pesticides were often used in the different stage of leather storage and production [4, 5]. In 1950s, when the raw skin was preserved by air drying in Africa, DDT and lindane were used widely to protect raw skin from putrefaction. Organochlorine and dieldrin were applied to protect against ectoparasites. Lindane was widely used to protect hides and skins from insects in 1990s [6, 7].

Pesticide is a substance or mix-up substances which were used to prevent, destroy, repel, or lessen the damage of any injurious insects. According to the source of raw materials, there are many kinds of pesticide, such as chemical substance, biological agent (such as virus or bacteria), antimicrobial or disinfectant. Some of the used pesticides are persistent organic pollutants (POPs). Compared to conventional pollutants, POPs can cause more hazards on human health and the natural environment due to their persistence, bioaccumulation and high toxicity [8, 9]. The persistence of these compounds in the environment is due to their low degradation by biotic and abiotic process, leading to a long half-live time [8]. Because most of the pesticides in leather, especially OCPs are lipophilic, can be absorbed by living organisms through alimentation, breathing and the skin. After absorption, these compounds usually distributed in various tissue including blood [10-12]. The toxicity of these contaminants is very complex and is specific to each compound. Therefore, multiple toxic responses can occur according to the species, gender and organ affected [13-15]. Previous reports showed that high levels of DDT and pentachlorophenol were detected in the children and adolescents of Germany, because of a leather jacket impregnated with some pesticides, pyrethroid, organophosphorus insecticides, pentachlorophenol (PCP), lindane (γ-HCH), and dichloro(diphenyl)ethylene (DDE) [16, 17].

The trace pesticides in leather may come from livestock breeding process, delivery in the animal food chain, used as preservatives in storage, transportation or processing [18]. These additives may remain in the final products as volatile and semi-volatile organic compounds [8].

The critical substances potentially presented in footwear and footwear components are listed in ISO/TR 16178:2012 [19]. But there are very few sensitive analytical methodologies published and only few related standards and methods for testing pesticides residue in textiles [20-23]. Until now, there has been no responding fast detection method and standard for many kinds of pesticides involved in shoe materials, especially in leather. To protect environment and human health [24-27], it is urgent and necessary to develop methods and international detection standard to monitor and detect these substances.

This paper described a method for the quantitative analysis of 24 pesticide residues in leather. Using small sample volumes, solid phase extraction combined with GC–MS was used to identify 24 pesticide residues at trace concentrations.

MATERIALS AND METHODS

Chemicals and Reagents

Certified standards of the 24 kinds of pesticide (purity of 97 % or more) were obtained from Dr.E of Germany. Their retention time, quantitative and qualitative ions and ion abundance ratios were shown in Table 1. The standard stock solution of pesticides was 1 μg/ml in n-hexane. The standard stock solution was stored at 4°C, and the shelf life is one month. The standard calibration solutions of pesticides are in the range of 10 ng/ml to 1000 ng/ml, and were prepared before using. Chromatographic pure grade of N-hexane, ethyl acetate, acetonitrile, toluene were purchased from TEDIA USA. Solid phase extraction (SPE) column is graphitized carbon black - ethylenediamine - N - propyl methyl silane (Carb – PSA, 1.0 g, 6mL), Carb-NH2, Carb-PSA, PSA, Carb-NH2, Florisil and Alumina N. All the analytical solvents were supplied by Sigma–Aldrich.

Table 1: Retention time, quantitative and qualitative ions and ion abundance ratios of the 24 pesticides

Series Number	Pesticides	Retention time /min	Characteristic fragment ions /amu		
			Quantitative ion	Qualitative ion	Abundance ratio
1	Pentachloroanisole	10.52	280	265,237,263	100:100:82:63
2	α-BHC	11.26	181	183,217,254	100:97:69:4
3	Lindane	12.41	181	183,217,254	100:98:64:11
4	Aldrin	13.78	263	265,261,293	100:67:65:38
5	Chlorothalonil	14.64	266	264,268	100:78:48
6	β- BHC	14.87	181	183,217,254	100:98:74:9
7	δ- BHC	15.65	181	183,217,254	100:97:70:8
8	Malathion	15.84	173	158.256.285	100:48:8:5
9	Dichlofluanide	16.05	123	224,226,332	100:37:26:5
10	Ethylparathion	16.10	275	220,247,232	100:82:77:68
11	Heptachloroepoxide	16.36	353	355,351,317	100:81:52:68
12	o,p'-DDE	16.74	246	318,176,248	100:34:29:65
13	α-Endosulfan	17.16	241	265,277,339	100:63:57:40
14	Tolyfluanide	17.85	238	240,181	100:69:63
15	p,p'-DDE	17.97	318	316,246,248	100:78:130:84
16	Dieldrin	18.55	263	277,345,380	100:79:27:24
17	o,p'-DDD	19.21	235	237,165,199	100:65:44:17
18	o,p'-DDT	19.72	235	237,165,199	100:65:40:15
19	p,p'-DDD	21.10	235	237,165,199	100:64:42:12
20	β-Endosulfan	21.30	241	265,237,339	100:49:84:35
21	p,p'-DDT	21.68	235	237,165,199	100:65:39:12
22	Mirex	22.85	272	274,237,332	100:80:53:11
23	Methoxychlor	23.41	227	228,212,274	100:20:17:15
24	Permethrin	25.70	183	163,165,184	100:20:17:15
		26.13	183	163,165,184	100:27:22:15

Instrument

SPE was performed using a Bond Elut Carbon column (Agilent technologies, USA). GC-MS analysis was achieved using GC with mass-selective detector (MSD) and electron impact source (EIS). Separation was performed on Agilent DB-1701 capillary column (30 m × 0.25 mm, 0.25 µm film thickness). The optimized GC–MS conditions were as follows: injection mode: without split; injector port temperature: 280°C; injection volume: 1.0 µL; carrier gas: helium with flow rate 1.2 mL min^{-1}. Oven program: 50°C for 2 min, increased to 185°C at 30.0°C min^{-1}, held for 1 min and raised to 240°C at a rate of 4.0°C min^{-1} and raised to 270°C at a rate of 20.0°C min^{-1} then held for 5 min. Finally, selected 280°C and held for 2 min to remove impurities. All data were analyzed using Agilent Chem Station software.

Methods

Preparation of Positive Samples

The positive leather samples were prepared and just added the 24 pesticides to the samples in Jinjiang Chenxin Tannery according to usual process, meanwhile blank leather samples were prepared with the same process without pesticides.

Sample Extraction and Purification

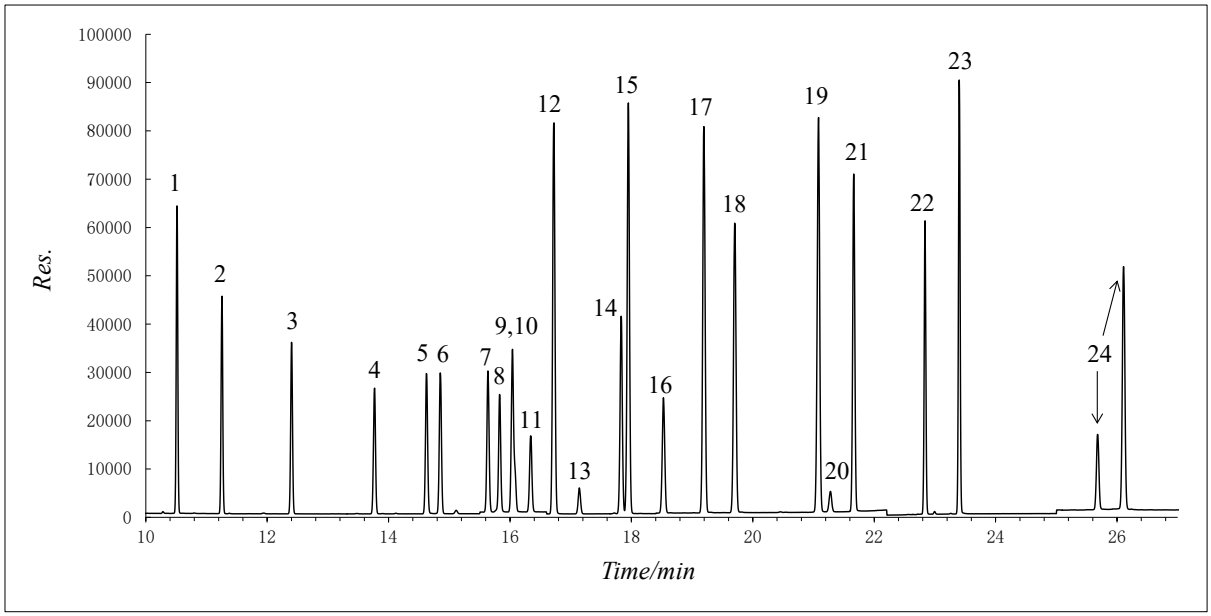
Blank and leather samples 2.0 g was extracted with 20 mL hexane-ethyl acetate (v/v 1:1), vortex oscillated for 10 min and then

extracted for 20 min by ultrasonic extraction under 25°C±2°C. The extraction was centrifuged for 5 min at 5000rpm, and the supernatant was transferred into a brown conical flask. The above procedure was repeated twice. Then combined supernatant was concentrated by a vacuum rotary evaporator at 35°C ± 5°C to approximately 2 ml to 5 ml for further purification.

Before injection into the GC-MS system, the sample solution needs to be concentrated and purified. Firstly, SPE Carb column was pre-rinsed with acetonitrile- toluene (3:1, v/v), and the conical flask was rinsed twice with 3 mL acetonitrile and toluene (3:1, v/v) mixed solution and transfer the washing solutions to the Carb column.

Secondly, the extraction solution flew through the pre-prepared SPE Carb column, 15 mL acetonitrile-toluene (3:1, v/v) as the eluent. Combined and concentrated the solution, then added 5 mL hexane to exchange the solvent and evaporated to be dry at 35°C± 5°C (Solvent displacement was used to change the polarity of the solvent to protect chromatographic column). Repeat this operation. Finally, 2.0 mL hexane was used to dissolve the analytes and the sample was filtered with 0.22 μm membrane for further GC-MS analysis. The 100% ion abundance of fragment ion in the mass spectrum of each underivatized drug was chosen as the quantitative ion. The selective representative ions of 24 kinds of pesticides for quantification were shown in Table 2.

Under the optimized instrument conditions, the chromatograms of 24 pesticides in the standard solutions were shown in Figure 1.



1-Pentachloroanisole,10.52min	2-α-BHC, 11.26min	3-Lindane, 12.40min	4-Aldrin, 13.77min
5-Chlorthalonil, 14.63min	6-β-BHC, 14.85min	7-δ-BHC, 15.64min	8-Malathion, 15.83min
9-Dichlofluanide, 16.04min	10-Ethylparathion, 6.09min	11-Heptachloroepoxide, 16.35min	12-o,p'-DDE, 16.73min
13-α-Endosulfan, 17.14min	14-Tolyfluanide, 17.84min	15-p,p`-DDE, 17.95min	16-Dieldrin, 18.53min
17-o,p`-DDD, 19.20min	18-o,p`-DDT, 19.70min	19-p,p`-DDD, 21.08min	20-β-Endosulfan, 21.28min
21-p,p`-DDT, 21.67min	22-Mirex, 22.84min	23-Methoxychlor, 23.40min	24-Permethrin, 25.68 and 26.11min

Figure 1. The chromatograms of 24 pesticides

RESULTS AND DISCUSSION

Method Development

Through preliminary test, it was found out that hexane-ethyl acetate system was the suitable extraction solvent. So then the effect of extraction solvent on the efficiency was studied by different ratio of hexane and ethyl acetate (5:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:5, v/v). The results showed that the recoveries of p, p'-DDD, p, p'-DDT, methoxychlor were lower than 60% when the ratio was 5:1,3:1, or 2:1. Besides, when the ratio was 1:2, 1:3, or 1:5, the recoveries of p, p'-DDD, p, p'-DDT, methoxychlor were 85-107%, which satisfied the requirement, but those of chlorothalonil, dichlofluanide, tolyfluanide were very low. Generally considering the total analytes, the ratio 1:1 was chosen as the optimum ratio of hexane and ethyl acetate solvent system. The experimental results were shown in supplemental materials (Table S2).

To optimize the extraction efficiency, three extraction methods (votex oscillation, sonication, mixed votex and sonication) were evaluated. The experiments results showed that the extraction efficiency of the analytes was the highest when hexane-ethyl acetate (1:1, v/v) was used as the solvent and sonicated for 20 min after votex oscillation for 10 min at 25°C.

The extraction efficiency at different extraction time was studied. The test samples were extracted for 10 min, 20 min, 30 min, 40 min, 50 min and 60 min at the temperature of 25°C ± 2°C. Each sample was tested twice, and the results are shown in Figure 2. From the results, it was found that with the extraction time increasing, the pesticide content increased in the beginning, and then decreased. For most of the 24 kinds of pesticide (except tolyfluanide and chlorothalonil), the concentration reached the highest when the extraction time was 20 min. So 20 min was chosen as the optimum extraction time.

To study the effect of the temperature on the extraction efficiency, the test samples were extracted at the temperatures of 25°C, 30°C, 35°C, and 40°C for 20 min, respectively. It was found that the highest extraction content was obtained at the temperature of 25°C. So the temperature of 25°C was chosen as the optimized extraction temperature. The result for each test piece was the average content of the two-test piece, and the test results are shown in Figure 3.

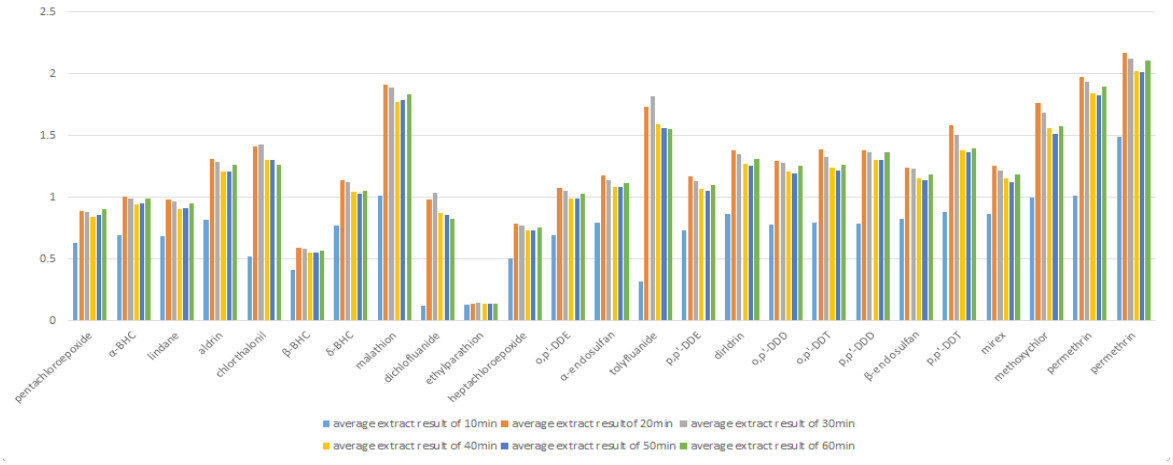


Figure 2. Extraction results at different extraction time

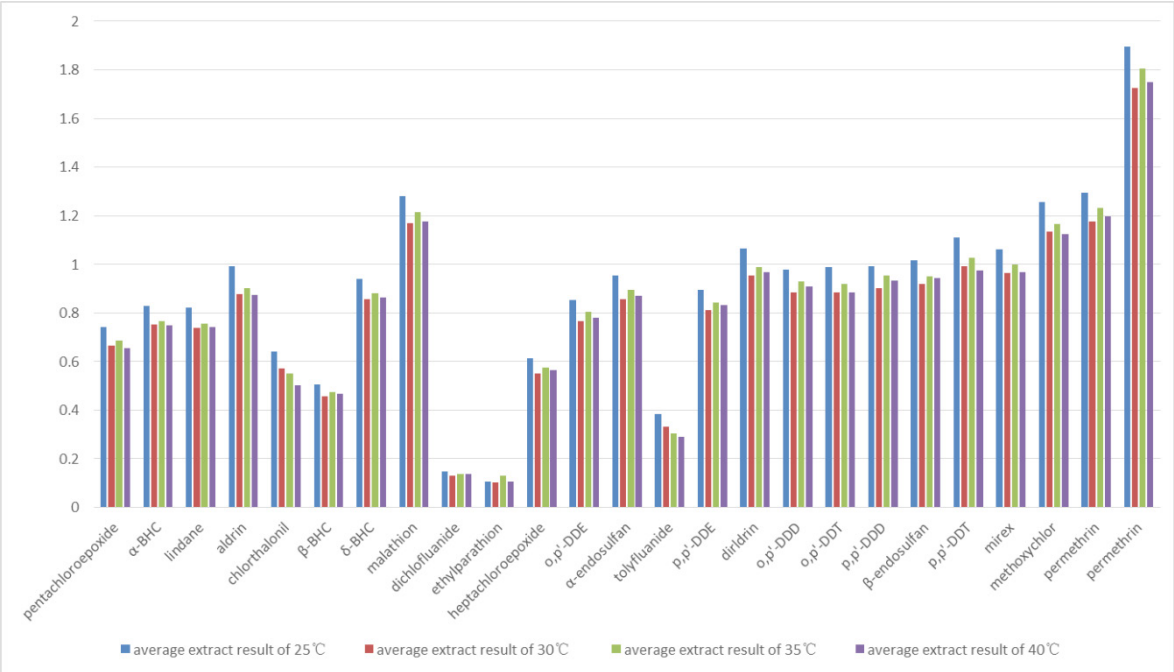


Figure 3. Extraction results at different extraction temperature

Linearity and limit of detection (LOD)

A series of mixed standard working solutions (10, 20, 50, 100, 200, 500, 1000 ng mL^{-1}) were prepared and all determined under the optimal pretreatment and instrument conditions. Then the standard curves were plotted between the peak areas and corresponding concentrations and it showed linear regression relationship in the certain range. Limit of detection (LOD) and limit of quantitation (LOQ) were performed using spiked standard samples method and LOQ of the method for the analytes were calculated at signal-to-noise (S/N) ratio of 3 and 10. All the above experimental results, retention time, quantitative and qualitative ions and ion abundance ratios of 24 pesticide residues were listed in Table 3.

From the results in Table 3, it was revealed that 24 analytes presented good linearity, with coefficient of determination (R^2) between 0.9983 and 0.9998. The LODs were in the range of 0.3–15.0 ng/mL (0.01-0.15 mg/kg), and the LOQ ranged from 2.0 to 50.0 ng/mL.

Matrix Effects

For GC–MS analysis, it is necessary to evaluate method matrix effects for each analyte, because they may result from various physical and chemical processes which are difficult to eliminate in analysis. To estimate matrix effects, the slopes of the matrix-matched calibration curves are compared with those obtained in solvent without matrices, and matrix effect (ME%) is evaluated as the following equation:

$$ME\ (\%) = B/A \times 100 \quad (1)$$

where A and B are the slopes of calibration curve without matrix and with different matrix [15-17]. ME% values suggest that the ionization signals of target compounds were enhanced and suppressed by the matrix, respectively. Generally, ME% ranging from 85% to 115% indicate that the signal enhancement or suppression is acceptable, while ME values < 85% or >115% refer to strong matrix effects.

From Table 3, it was known that ME% of most of pesticides were between 85% and 115% in solvent, blank, cow leather, sheep leather, pig leather, PU and PVC and the matrix effects were very small and could be ignored according to the requirements. The ME% of malathion, ethylparathion, o,p'-DDD, p,p'-DDD was more than 115%, and it meant that they had strong matrix enhancement effect. Meanwhile, the ME% of α-endosulfan, β-endosulfan, o,p'-DDT, p,p'-DDT, and methoxychlor was less than 85%, and it showed that these analytes had strong signal suppression effect by matrix. To obtain the results more accurately, it was necessary to use the blank negative sample to calibrate the working curve.

Table 3: Overview of the methodological characteristics including linear range, linear equation, coefficient of determination (R^2), matrix effect (ME), LOD, and LOQ for each analyte in different samples

The analyte	Quantitative ion m/z	matrix	Linear range (ng/mL)	Linear equation	Coefficient R^2	ME (%)	LOD ng/mL	LOQ ng/mL
Pentachloroanisole (1)	280	solvent	10~1000	Y=31.58X+2.004	0.9998	100.00	1	3
		blank	10~1000	Y=30.48X+229.1	0.9996	96.52	3	10
		cowhide	20~1000	Y=33.74X+127.8	0.9978	106.84	5	15
		Sheep leather	20~1000	Y=27.87X+345.9	0.9934	88.25	6	20
		Pig leather	50~1000	Y=27.94X+722.1	0.9956	88.47	10	30
		PU	20~1000	Y=29.03X-738.1	0.9965	91.93	5	15
		PVC	20~1000	Y=27.98X+913.3	0.9949	88.60	5	15
α-Benzenehexachloride (α-BHC, 2)	181	solvent	10~1000	Y=32.17X-34.99	0.9997	100.00	2	6
		blank	20~1000	Y=30.68X+38.54	0.9974	95.37	8	25
		cowhide	50~1000	Y=35.08X+39.66	0.9997	109.05	10	30
		Sheep leather	50~1000	Y=27.85X+57.12	0.9965	86.57	15	50
		Pig leather	50~1000	Y=27.49X+331.1	0.9971	85.45	15	50
		PU	50~1000	Y=35.64X-1004	0.9971	110.79	10	30
		PVC	50~1000	Y=30.52X+382.7	0.9983	94.87	10	30
Lindane (3)	181	solvent	10~1000	Y=27.36X-37.28	0.9998	100.00	2	6
		blank	20~1000	Y=25.36X+163.3	0.9972	92.69	8	25
		cowhide	50~1000	Y=28.67X-626	0.9989	104.79	10	30
		Sheep leather	50~1000	Y=27.89X-424	0.9962	101.94	15	50
		Pig leather	50~1000	Y=26.92X-81.29	0.9969	98.39	15	50
		PU	50~1000	Y=30.88X-672	0.9964	112.87	10	30
		PVC	50~1000	Y=24.27X+570.7	0.9981	88.71	10	30
Aldrin (4)	263	solvent	10~1000	Y=18.12X-23.22	0.9998	100.00	2	6
		blank	10~1000	Y=18.26X+76.58	0.9981	100.77	8	25
		cowhide	50~1000	Y=20.67X-60.11	0.9994	114.07	15	50
		Sheep leather	100~1000	Y=19.87X+234	0.9924	109.66	30	100
		Pig leather	100~1000	Y=18.31X+73.76	0.9978	101.05	30	100
		PU	50~1000	Y=20.46X-478.3	0.9972	112.91	10	30
		PVC	50~1000	Y=18.53X+371	0.9968	102.26	10	30
Chlorothalonil (5)	266	solvent	50~1000	Y=23.75X-1291	0.9978	100.00	15	50
		blank	100~1000	Y=26.09X-147	0.9989	109.85	23	75
		cowhide	100~1000	Y=27.39X+5290	0.9903	115.33	30	100
		Sheep leather	100~1000	Y=19.13X-1323	0.9931	80.55	30	100
		Pig leather	100~1000	Y=20.38X+3425	0.9921	85.81	30	100
		PU	100~1000	Y=17.16X-1467	0.9951	72.25	23	75
		PVC	50~1000	Y=26.38X-2422	0.9954	111.07	15	50
β-BHC (6)	181	solvent	10~1000	Y=25.83X-61.41	0.9999	100.00	2	6
		blank	50~1000	Y=24.88X+82.35	0.9981	96.32	10	30
		cowhide	50~1000	Y=28.35X-11.34	0.9996	109.76	15	50
		Sheep leather	50~1000	Y=22.64X-2441	0.9932	87.65	15	50
		Pig leather	50~1000	Y=23.03X+691	0.9954	89.16	15	50
		PU	50~1000	Y=29.54X-704.8	0.9967	114.36	10	30
		PVC	50~1000	Y=22.24X+684.9	0.9943	86.10	10	30
δ-BHC (7)	181	solvent	10~1000	Y=23.09X-106.5	0.9997	100.00	2	6
		blank	50~1000	Y=21.11X+258.9	0.9951	91.42	10	30
		cowhide	50~1000	Y=25.72X+443.3	0.9984	111.39	15	50
		Sheep leather	50~1000	Y=24.71X+148.4	0.9927	107.02	15	50
		Pig leather	50~1000	Y=21.23X+868.2	0.9931	91.94	15	50
		PU	50~1000	Y=26.46X+167.1	0.9964	114.60	10	30
		PVC	50~1000	Y=26.51X-220	0.9983	114.81	10	30

The analyte	Quantitative ion m/z	matrix	Linear range (ng/mL)	Linear equation	Coefficient R^2	ME (%)	LOD ng/mL	LOQ ng/mL
Malathion (8)	173	solvent	10~1000	Y=36.24X-515.1	0.9987	100.00	2	6
		blank	20~1000	Y=41.95X+309.1	0.9965	115.76	6	20
		cowhide	50~1000	Y=57.42X-912.5	0.9987	158.44	15	50
		Sheep leather	100~1000	Y=45.78X-893	0.9952	126.32	20	60
		Pig leather	100~1000	Y=46.51X-1840	0.9957	128.34	30	100
		PU	50~1000	Y=55.75X-747.1	0.9976	153.84	10	30
		PVC	20~1000	Y=50.51X+1106	0.9986	139.38	6	20
Dichlofluanide (9)	123	solvent	10~1000	Y=51.09X-126.4	0.9976	100.00	3	10
		blank	50~1000	Y=43.79X-1112	0.9961	85.71	30	100
		cowhide	100~1000	Y=60.91X-1854	0.9988	119.22	30	100
		Sheep leather	100~1000	Y=45.87X-1242	0.9967	89.78	30	100
		Pig leather	100~1000	Y=41.87X+2126	0.9975	81.95	30	100
		PU	100~1000	Y=62.87X-4773	0.9994	123.06	30	100
		PVC	100~1000	Y=59.14X-1769	0.9989	115.76	20	60
Ethylparathion (10)	275	solvent	20~1000	Y=3.879X-14.57	0.9976	100.00	6	20
		blank	20~1000	Y=4.639X+30.11	0.9943	119.59	20	60
		cowhide	50~1000	Y=8.189X-42.11	0.9989	211.11	23	75
		Sheep leather	100~1000	Y=7.231X-452	0.9936	186.41	30	100
		Pig leather	100~1000	Y=7.041X+218.6	0.9934	181.52	30	100
		PU	100~1000	Y=7.907X-267.9	0.9953	203.84	20	60
		PVC	50~1000	Y=7.642X-33.66	0.9971	197.01	10	30
Hepta-chloroepoxide (11)	353	solvent	20~1000	Y=3.445X+1.98	0.9997	100.00	6	20
		blank	20~1000	Y=3.734X+3.592	0.9989	108.39	15	50
		cowhide	50~1000	Y=3.926X-4.895	0.9992	113.96	15	50
		Sheep leather	50~1000	Y=3.532X+32.56	0.9974	102.53	15	50
		Pig leather	50~1000	Y=3.405X+42.79	0.9962	98.84	15	50
		PU	50~1000	Y=3.489X-90.61	0.9959	101.28	10	30
		PVC	50~1000	Y=3.567X+77.34	0.9981	103.54	10	30
o,p'dichloro (diphenyl) ethylene (o,p'-DDE, 12)	246	solvent	10~1000	Y=84.93X-81.78	0.9998	100.00	0.3	1
		blank	10~1000	Y=86.34X+304.3	0.9981	101.66	3	10
		cowhide	10~1000	Y=95.54X-156.8	0.9996	112.49	3	10
		Sheep leather	20~1000	Y=84.67X-245	0.9972	99.69	3	10
		Pig leather	20~1000	Y=88.01X+789.3	0.9966	103.63	3	10
		PU	10~1000	Y=79.06X+570.1	0.9923	93.09	3	10
		PVC	10~1000	Y=87.77X+3034	0.9985	103.34	3	10
α-Endosulfan (13)	241	solvent	50~1000	Y=3.992X+17.7	0.9998	100.00	8	25
		blank	50~1000	Y=4.263X+182.2	0.9986	106.79	30	100
		cowhide	100~1000	Y=3.156X-243.9	0.9966	79.06	30	100
		Sheep leather	100~1000	Y=3.032X+563	0.9951	75.95	30	100
		Pig leather	100~1000	Y=2.681X+244.7	0.9943	67.16	30	100
		PU	100~1000	Y=3.606X+207	0.9944	90.33	30	100
		PVC	100~1000	Y=4.235X+152.1	0.9962	106.09	30	100
Tolyfluanide (14)	238	solvent	10~1000	Y=21.51X-465.9	0.9978	100.00	3	10
		blank	50~1000	Y=20.53X-445	0.9988	95.44	15	50
		cowhide	100~1000	Y=22.39X-181.1	0.9987	104.09	30	100
		Sheep leather	100~1000	Y=21.63X-242.1	0.9963	100.56	30	100
		Pig leather	100~1000	Y=20.89X+170.8	0.9939	97.12	30	100
		PU	50~1000	Y=21.89X-6996	0.9972	101.77	15	50
		PVC	50~1000	Y=24.55X-159.4	0.9973	114.13	10	30

The analyte	Quantitative ion m/z	matrix	Linear range (ng/mL)	Linear equation	Coefficient R^2	ME (%)	LOD ng/mL	LOQ ng/mL
p,p'-DDE (15)	318	solvent	10~1000	Y=51.26X-53.69	0.9997	100.00	0.6	2
		blank	10~1000	Y=54.29X+105.1	0.9991	105.91	1	3
		cowhide	10~1000	Y=56.69X+2.21	0.9996	110.59	3	10
		Sheep leather	10~1000	Y=42.89X+345	0.9962	83.67	3	10
		Pig leather	10~1000	Y=43.47X+1612	0.9938	84.80	3	10
		PU	10~1000	Y=48.58X+272.8	0.9932	94.77	2	6
		PVC	10~1000	Y=45.47X+1791	0.9934	88.70	2	6
Dieldrin (16)	263	solvent	10~1000	Y=8.776X+51.73	0.9995	100.00	4	10
		blank	10~1000	Y=9.157X+50.29	0.9953	104.34	15	50
		cowhide	50~1000	Y=7.971X-495.6	0.9924	90.83	15	50
		Sheep leather	50~1000	Y=7.672X+241	0.9935	87.42	15	50
		Pig leather	50~1000	Y=8.471X+1.368	0.9976	96.52	15	50
		PU	50~1000	Y=8.522X-32.01	0.9931	97.11	15	50
		PVC	50~1000	Y=10.11X+1.474	0.9981	115.20	15	50
o,p'-dichloro bis(4-chlorophenyl) ethane (o,p'-DDD, 17)	235	solvent	10~1000	Y=97.91X-150	0.9997	100.00	0.6	2
		blank	10~1000	Y=113.4X+243.5	0.9989	115.82	2	6
		cowhide	20~1000	Y=122.5X-410.7	0.9997	125.11	6	20
		Sheep leather	50~1000	Y=117.3X-652	0.9954	119.80	10	30
		Pig leather	50~1000	Y=121.8X+513.2	0.9964	124.40	10	30
		PU	10~1000	Y=121.3X+496.6	0.9933	123.89	2	6
		PVC	10~1000	Y=120.7X+3018	0.9974	123.28	2	6
o,p'-dichloro (diphenyl) trichloroethane (o,p'-DDT, 18)	235	solvent	10~1000	Y=76.68X-1140	0.9989	100.00	1	3
		blank	10~1000	Y=71.71X+306.4	0.9981	93.52	3	10
		cowhide	20~1000	Y=77.69X+138.3	0.9998	101.32	5	15
		Sheep leather	50~1000	Y=54.82X+2834	0.9931	71.49	10	30
		Pig leather	50~1000	Y=51.02X+2938	0.9929	66.54	10	30
		PU	20~1000	Y=68.87X+606.4	0.9934	89.81	5	15
		PVC	10~1000	Y=54.46X+1291	0.9926	71.02	3	10
p,p'-DDD (19)	235	solvent	10~1000	Y=106.1X-335	0.9997	100.00	0.6	2
		blank	10~1000	Y=127.3X+225.9	0.9984	119.98	2	6
		cowhide	10~1000	Y=133.5X-87.84	0.9998	125.82	3	10
		Sheep leather	50~1000	Y=132.4X+4522	0.9935	124.79	10	30
		Pig leather	50~1000	Y=126.1X+2374	0.9925	118.85	10	30
		PU	10~1000	Y=116.7X+334	0.9937	109.99	2	6
		PVC	10~1000	Y=120.3X+5296	0.9944	113.38	2	6
β-Endosulfan (20)	241	solvent	50~1000	Y=2.642X+120.1	0.9991	100.00	15	50
		blank	50~1000	Y=2.151X+616.6	0.9955	81.42	15	50
		cowhide	100~1000	Y=2.127X-73.08	0.9905	80.51	30	100
		Sheep leather	100~1000	Y=2.034X+1312	0.9902	76.99	30	100
		Pig leather	100~1000	Y=1.903X+1049	0.9918	72.03	30	100
		PU	100~1000	Y=1.797X+1765	0.9913	68.02	20	60
		PVC	100~1000	Y=2.253X+390	0.9979	85.28	20	60
p,p'-DDT (21)	235	solvent	10~1000	Y=77.75X-1764	0.9976	100.00	1	3
		blank	10~1000	Y=67.17X+223.9	0.9964	86.39	3	10
		cowhide	10~1000	Y=67.99X+1329	0.9997	87.45	3	10
		Sheep leather	50~1000	Y=53.45X+5631	0.9937	68.75	10	30
		Pig leather	50~1000	Y=44.01X+6144	0.9957	56.60	10	30
		PU	10~1000	Y=66.03X+289.5	0.9925	84.93	3	10
		PVC	10~1000	Y=47.62X+1058	0.9929	61.25	3	10

The analyte	Quantitative ion m/z	matrix	Linear range (ng/mL)	Linear equation	Coefficient R^2	ME (%)	LOD ng/mL	LOQ ng/mL
Mirex (22)	272	solvent	10~1000	Y=48.08X+22.72	0.9996	100.00	3	10
		blank	10~1000	Y=47.28X+62.23	0.9985	98.34	3	10
		cowhide	10~1000	Y=41.22X-164.1	0.9998	85.73	3	10
		Sheep leather	20~1000	Y=43.67X+452	0.9978	90.83	6	20
		Pig leather	20~1000	Y=42.76X+649.2	0.9961	88.94	6	20
		PU	10~1000	Y=41.98X+268.6	0.9934	87.31	3	10
		PVC	10~1000	Y=44.73X+961.3	0.9972	93.03	3	10
Methoxychlor (23)	227	solvent	10~1000	Y=140.4X-2725	0.9983	100.00	0.6	2
		blank	10~1000	Y=126.4X+98.56	0.9985	90.03	2	6
		cowhide	10~1000	Y=129.1X+1090	0.9998	91.95	3	10
		Sheep leather	20~1000	Y=132.4X+1343	0.9976	94.30	6	20
		Pig leather	20~1000	Y=102.8X+6422	0.9935	73.22	6	20
		PU	10~1000	Y=117.1X+1178	0.9942	83.40	3	10
		PVC	10~1000	Y=110.4X+265.1	0.9983	78.63	2	6
Permethrin (24)	183	solvent	10~1000	Y=116.6X+26.87	0.9998	100.00	3	10
		blank	10~1000	Y=128.1X+622.8	0.9952	109.86	3	10
		cowhide	20~1000	Y=125.2X+1069	0.9999	107.38	5	15
		Sheep leather	20~1000	Y=127.7X+2234	0.9987	109.52	6	20
		Pig leather	20~1000	Y=119.5X+7337	0.9977	102.49	6	20
		PU	20~1000	Y=111.9X+1962	0.9937	95.97	6	20
		PVC	10~1000	Y=124.4X+3987	0.9992	106.69	3	10

Recovery and Precision Test

Blank negative leather samples (including cow leather, sheep leather, and pig leather) at 100, 300, 600 μg/kg levels of mixed standard solutions were selected to perform the recovery experiment. Precisions were evaluated by using the relative standard deviation (RSD) of six measurements. The average recoveries for 24 analytes were in the range of 75.49%-131%. The precision was 1.14%-14.37%. The experimental results were shown in supplemental materials (Tables S2A, S2B and S2C). These results can satisfy the requirement of testing the pesticide residues in leather product.

Determination of 24 Pesticide Residues in Leather Samples

The developed and validated method was applied to detect the presence and quantify 24 pesticide residues in three positive samples. Results were shown in Table 4. The experimental results showed that the concentrations of most pesticide residues in these samples were about 200, 500, 1000μg/kg. And the RSD was the range of 2%~13%. However, chlorothalonil, dichlofluanide, and tolyfluanide were not detected because of degradation.

Table 4: The average content of 24 pesticide residues in three positive leather samples

Analyte	Sample number	Content (μg/kg) 1	2	3	4	5	6	Average (μg/kg)	RSD (%)
1	4#	205.7	216.7	194.2	198.7	204.3	197.3	202.8	3.97
	5#	508.6	482.6	486.4	493.1	477.6	493.1	490.2	2.21
	6#	949.3	953.7	1015.3	986.1	948.7	986.1	973.2	2.78
2	4#	186.1	176	176.1	182.7	177.4	194.2	182.1	3.95
	5#	417.3	443.9	417.7	487.5	480.7	404.8	442.0	7.94
	6#	932.2	932.9	1079	986.5	938	977.2	974.3	5.79
3	4#	197.4	173.7	166.4	172.5	209.3	163.4	180.5	10.27
	5#	463.2	438	450.6	416.6	450.8	418.6	439.6	4.29
	6#	818.5	1006.9	1044	1025.4	1001.9	1025.4	987.0	8.50

Analyte	Sample number	Content (μg/kg)						Average (μg/kg)	RSD (%)
		1	2	3	4	5	6		
	4#	219.4	213.2	225.2	213	211.7	213.4	216.0	2.43
4	5#	557.8	543.4	542	542.8	538.4	542.8	544.5	1.24
	6#	1072.3	1069.3	1167.9	1142.2	1064.3	1142.2	1109.7	4.15
	4#	--	--	--	--	--	--	--	--
5	5#	--	--	--	--	--	--	--	--
	6#	--	--	--	--	--	--	--	--
	4#	213.7	191.3	201.2	188.2	211.6	162.4	194.7	9.71
6	5#	451.1	424.8	408.8	445.4	367	445.4	423.8	7.56
	6#	1142.5	925.2	903	1151.5	892.6	863.1	979.7	13.39
	4#	145.8	165.4	143.8	140.2	120.6	136.2	142.0	10.25
7	5#	298.6	229.8	220.3	254.1	224.8	254.1	247.0	11.83
	6#	563.6	606.7	665.2	683.7	601.7	683.7	634.1	7.93
	4#	82	86.3	72.8	75.5	58.7	81.4	76.1	12.89
8	5#	171.4	192.7	194	191.6	187.7	191.6	188.2	4.51
	6#	540.5	537.6	521.6	569.9	532.6	569.9	545.4	3.68
	4#	--	--	--	--	--	--	--	--
9	5#	--	--	--	--	--	--	--	--
	6#	--	--	--	--	--	--	--	--
	4#	54.65	56.46	50.5	44.85	58.61	65.6	55.1	12.85
10	5#	90.2	79.5	84.4	78.9	74.5	78.9	81.1	6.75
	6#	229.3	230.4	248.4	242.4	225.4	242.4	236.4	3.89
	4#	178	170.6	143.2	150.7	155.7	150.9	158.2	8.42
11	5#	390.5	402.2	437.4	407.9	397.2	407.9	407.2	3.99
	6#	872.3	854	928.5	930.7	849	930.7	894.2	4.47
	4#	178.6	174.9	175.5	166.2	169.5	168.2	172.2	2.83
12	5#	447.3	441.7	480.6	464.3	436.7	464.3	455.8	3.67
	6#	945.7	947	1025.3	997.1	942	997.1	975.7	3.62
	4#	336.2	271.2	351.8	307	325	291.1	313.7	9.51
13	5#	582.5	659	715.2	587.7	654	587.7	631.0	8.54
	6#	1211.2	1222.2	1347.2	1249.4	1217.2	1249.4	1249.4	4.05
	4#	--	--	--	--	--	--	--	--
14	5#	--	--	--	--	--	--	--	--
	6#	--	--	--	--	--	--	--	--
	4#	151.1	145.2	141	126.4	134.3	126.6	137.4	7.34
15	5#	364.5	359.4	398.2	389	354.4	389	375.8	4.91
	6#	943.4	945.1	1006.5	972	940.1	972	963.2	2.66
	4#	234.4	227.9	170.7	184.6	221.7	218.3	209.6	12.28
16	5#	524	526.2	566.4	574.5	521.2	570.7	547.2	4.71
	6#	1054.2	1036.3	1098.5	1095	1047.7	1103.5	1072.5	2.77
	4#	169.6	168.1	162.4	155.8	159.4	157.9	162.2	3.45
17	5#	443.1	436.7	463.4	443.7	423	454.3	444.0	3.15
	6#	864.5	863.4	909.1	881.2	858.4	881.2	876.3	2.13

Analyte	Sample number	Content (μg/kg)						Average (μg/kg)	RSD (%)
		1	2	3	4	5	6		
	4#	178.3	184.3	180.2	179	179.9	179.7	180.2	1.17
18	5#	453.4	444	504.3	500.3	439	500.3	473.6	6.58
	6#	1126.5	1117.1	1196.3	1155.5	1112.1	1155.5	1143.8	2.78
	4#	177.6	171.3	160	157.8	167.4	157.1	165.2	5.02
19	5#	439.8	427.9	455	443.6	422.9	443.6	438.8	2.66
	6#	708.1	690.8	768.6	687.1	685.8	687.1	704.6	4.61
	4#	548	440.2	399.1	519.8	497.4	491	482.6	11.24
20	5#	1213.1	1135	1085.6	1206.9	1091.4	1162.8	1149.1	4.80
	6#	2080.3	2022.6	2200.3	1979.2	2064.1	2025.3	2062.0	3.71
	4#	215.4	226.9	181.5	209.6	202.4	210	207.6	7.31
21	5#	571.2	580.9	649.8	638.6	575.9	638.6	609.2	6.02
	6#	1537	1511.5	1582.1	1515.5	1506.5	1515.5	1528.0	1.86
	4#	186.5	181	174.4	163.9	177.6	164	174.6	5.24
22	5#	431.1	425.1	481.9	475.5	420.1	475.5	451.5	6.40
	6#	1010.9	1005.5	1059.4	1019.8	1000.5	1019.8	1019.3	2.07
	4#	180.3	188.4	181	171	181.4	176	179.7	3.25
23	5#	449.1	446.4	481.8	478.3	441.4	478.3	462.6	4.05
	6#	979	963.7	1009.6	983.4	958.7	983.4	979.6	1.84
	4#	223.97	213.12	204.5	208.5	220.44	205.91	212.7	3.75
24	5#	514.36	502.69	568.55	562.16	497.69	562.16	534.6	6.18
	6#	1175	1178.6	1198.2	1153.3	1173.6	1153.3	1172.0	1.45

CONCLUSIONS

This study contributed to a validated method detection standard for quantitative detecting common pesticide residues in leather. Small sample volumes, solid phase extraction and GC–MS was used to identify these 24 pesticide residues at trace concentrations. The method established has been successfully applied in detecting the pesticide residues in cowhide, sheep leather and pig leather. In the future, the supervisor can use this method to monitor the content of the harmful chemicals. It will gain more practical applications in shoe materials and provide the reference and advises for the detection of these pesticides residues in other industry products.

Author Contributions

Method development, Jinlan Dai and Honglei Yin; Experiment, Jinlan Dai and Hang Wei; Application, Jinlan Dai, and Lei Zhou, Director, Minghua Liu.

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REFERENCES

1. Kim, W., Lee, Y., Lee, J.H., Shin, G.W., Yun, M.H., A comparative study on designer and customer preference models of leather for vehicle, *Int J Ind Ergonom*, **2018**, 65, 110-121, https://doi.org/10.1016/j.ergon.2017.07.009.
2. Adigüzel Zengin, A.C., *Örk*, N., Yiğit, Ü., Bitlisli, B.O., Leather as a potential liner for the prosthetic leg users, *Leather and Footwear Journal*, **2018**, 18, 4, 321-326, https://doi.org/10.24264/lfj.18.4.7.

3. Indian Leather Group, Furniture and Automotive Leathers, **2015**, 49, 5-8.
4. Kvitko, K., Bandinelli, E., Henriques, J.A.P., Heuser, V.D., Rohr, P., da Silva, F.R., Schneider, N.B., Fernandes, S., Ancines, C., da Silva, J., Susceptibility to DNA damage in workers occupationally exposed to pesticides, to tannery chemicals and to coal dust during mining, *Genet Mol Biol*, **2012**, 35, 4 Suppl, 1060–1068, https://doi.org/10.1590%2Fs1415-47572012000600022.
5. Lin, F., Chen, X.C., Li, X.Y., Wu, Z.Y., Chen, H.L., Application status of biocides and fungicide in shoe material and its determination methods, *China Leather*, **2010**, 10, 110-115.
6. Corning, D.R., Cory, N.J., Sykes, R.L., Studies on pesticides used for the protection of skins during storage and transportation. Part 2: Analytical studies and environmental impact, *J Soc Leath Tech Ch*, **1993**, 77, 3-13.
7. Golob, P., Robinson, F.V., Gutu, S., Studies on pesticides used for the protection of skins during storage and transportation. Part 1: Protection of goat skins against beetle damage using insecticides in Zimbabwe, *J Soc Leath Tech Ch*, **1992**, 76, 83-88.
8. Jin, J., Yu, L.Y., Dong, W., Wu, M.R., Liu, S.R., Study on determination of carbendazim, chlorothalonil and thiophanate-methyl in Leather, *Leath Ch*, **2014**, 31, 16-20.
9. Li, Z.J., Yang, W.H., Qiu, M.J., Guangdong chemical industry, **2002**, 2, 17-19.
10. Nunes, R.R., Bontempi, R.M., Mendonça, G., Galetti, G., Rezende, M.O.O., Vermicomposting as an advanced biological treatment for industrial waste from the leather industry, *J Environ Sci Health B*, **2016**, 51, 5, 271-277.
11. De La Cruz, A.R.H., Ferreira, L.D.S.C., Andrade, V.P., Gioda, A., Biomonitoring of Toxic Elements in Plants Collected Near Leather Tanning Industry, *J Braz Chem Soc*, **2019**, 30, 2, 256-264, https://doi.org/10.21577/0103-5053.20180174.
12. Shi, J.J., Chen, H.L., Arocena, J.M., Whitcombe, T., Thrig, R.W., Memiaghe, J.N., Elemental sulfur amendment decreases bio-available Cr-VI in soils impacted by leather tanneries, *Environ Pollut*, **2016**, 212, 57-64, https://doi.org/10.1016/j.envpol.2016.01.045.
13. Balaji, A.P.B., Sastry, T.P., Manigandan, S., Mukherjee, A., Chandrasekara, N., Environmental benignity of a pesticide in soft colloidal hydrodispersive nanometric form with improved toxic precision towards the target organisms than non-target organisms, *Sci Total Environ*, **2017**, 579, 190-201, https://doi.org/10.1016/j.scitotenv.2016.10.240.
14. Sundaramoorthy, R., Velusamy, Y., Balaji, A.P.B., Mukherjee, A., Chandrasekaran, N., Comparative cytotoxic and genotoxic effects of permethrin and its nanometric form on human erythrocytes and lymphocytes in vitro, *Chem Biol Interact*, **2016**, 257, 119-124, https://doi.org/10.1016/j.cbi.2016.08.001.
15. Fritschi, L., Benke, G., Risch, H.A., Schulte, A., Webb, P.M., Whiteman, D.C., Fawcett, J., Neale, R.E., Occupational exposure to *N*-nitrosamines and pesticides and risk of pancreatic cancer, *Occup Environ Med*, **2015**, 72, 9, 678-683, https://doi.org/10.1136/oemed-2014-102522.
16. Mikoczy, Z., Hagmar, L., Cancer incidence in the Swedish leather tanning industry: updated findings 1958–99, *Occup Environ Med*, **2005**, 62, 7, 461-464, https://doi.org/10.1136/oem.2004.017038.
17. Heudorf, U., Angerer, J., Drexler, H., Current internal exposure to pesticides in children and adolescents in Germany: Blood plasma levels of pentachlorophenol (PCP), lindane (γ-HCH), and dichloro(diphenyl)ethylene (DDE), a biostable metabolite of dichloro(diphenyl) trichloroethane (DDT), *Int J Hyg Environ Health*, **2003**, 206, 6, 485-491.
18. Heudorf, U., Angerer, J., Drexler, H., Current internal exposure to pesticides in children and adolescents in Germany: urinary levels of metabolites of pyrethroid and organophosphorus insecticides, *Int Arch Occup Environ Health*, **2004**, 77, 67-72,

https://doi.org/10.1007/s00420-003-0470-5.
19. ISO/TR 16178:2012 Footwear Critical substances potentially present in footwear and footwear components.
20. GB/T 18412.1-2006 The detection of pesticide residues in textiles Part one: 77 kinds of pesticides.
21. GB/T 18412.2-2006 The detection of pesticide residues in textiles Part two: organochlorine pesticides.
22. GB/T 23204-2008 The detection of 519 kinds of pesticide residues and related chemicals in Chinese tea by GC-MS.
23. Gong, T.S., Dong, S.M., Lin, F., Lian, X.B., Determination of Salicylanilide in Leather Fungicides by HPLC, *Leather Science and Industry*, **2011**, 21, 43-47.
24. Frenich, A.G., Romero-González, R., *Gómez-Pérez, M.L.*, Martinez Vidal, J.L., Multi-mycotoxin analysis in eggs using a QuEChERS-based extraction procedure and ultra-high-pressure liquid chromatography coupled to triple quadrupole mass spectrometry, *J Chromatogr A*, **2011**, 1218, 28, 4349–4356, https://doi.org/10.1016/j.chroma.2011.05.005.
25. Xian, Y., Dong, H., Wu, Y., Guo, X., Hou, X., Wang, B., QuEChERS-based purification method coupled to ultrahigh performance liquid chromatography–tandem mass spectrometry (UPLC–MS/MS) to determine six quaternary ammonium compounds (QACs) in dairy products, *Food Chem*, **2016**, 212, 96–103, https://doi.org/10.1016/j.foodchem.2016.05.151.
26. Xian, Y., Guo, X., Hou, X., Wang, L., Wu, Y., Chen, L., Dong, H., Wang, B., A modified quick, easy, cheap, effective, rugged, and safe cleanup method followed by liquid chromatography-tandem mass spectrometry for the rapid analysis of perchlorate, bromate and hypophosphite in flour, *J Chromatogr A*, **2017**, 1526(Supplement C), 31–38, https://doi.org/10.1016/j.chroma.2017.10.047.
27. Xian Y., Wu, Y., Dong, H., Guo, X., Wang, B., Wang, L., Dispersive micro solid phase extraction (DMSPE) using polymer anion exchange (PAX) as the sorbent followed by UPLC–MS/MS for the rapid determination of four bisphenols in commercial edible oils, *J Chromatogr A*, **2017**, 1517(Supplement C), 35–43, https://doi.org/10.1016/j.chroma.2017.08.067.

SUPPLEMENTAL MATERIALS

Table S1: Detailed information of 24 pesticides

Series Number	Pesticide	CAS number	Chemical formula
18	o,p'-DDT	789–02–6	$C_{14}H_9Cl_5$
21	p,p'-DDT	50–29–3	$C_{14}H_9Cl_5$
17	o,p'-DDD	53–19–0	$C_{14}H_{10}Cl_4$
19	p,p'-DDD	72–54–8	$C_{14}H_8Cl_4$
12	o,p'-DDE	3424–82–6	$C_{14}H_8Cl_4$
15	p,p'-DDE	72–55–9	$C_{14}H_8Cl_4$
2	α-BHC	319–84–6	$C_6H_6Cl_6$
6	β-BHC	319–85–7	$C_6H_6Cl_6$
7	δ-BHC	319–86–8	$C_6H_6Cl_6$
3	Lindane	58–89–9	$C_6H_6Cl_6$
8	Malathion	121–75–5	$C_{10}H_{19}O_6PS_2$
23	Methoxychlor	72–43–5	$C_{16}H_{15}Cl_3O_2$
4	Aldrin	309–00–2	$C_{12}H_8Cl_6$
16	Dieldrin	60–57–1	$C_{12}H_8Cl_6O$
10	Ethylparathion	56–38–2	$C_{10}H_{14}NO_5PS$
13	α-Endosulfan	115–29–7	$C_9H_6Cl_6O_3S$
20	β-Endosulfan	33213–65–9	$C_9H_6Cl_6O_3S$
22	Mirex	2385–85–5	$C_{10}Cl_{12}$
9	Dichlofluanide	1085–98–9	$C_9H_{11}Cl_2FN_2O_2S_2$
11	Heptachloroepoxide	1024–57–3	$C_{10}H_5Cl_7O$
1	Pentachloroanisole	1825–21–4	$C_7H_3Cl_5O$
24	Permethrin	52645–53–1	$C_{21}H_{20}Cl_2O_3$
14	Tolyfluanide	731–27–1	$C_{10}H_{13}Cl_2FN_2O_2S_2$
5	Chlorothalonil	1897–45–6	$C_8Cl_4N_2$

Table S2: The extraction effect of different ratio of n-hexane-ethyl acetate on 24 pesticide residues in leather sample

Analyte	Concentration (added) ng mL^{-1}	Recovery (%) Ratio (n-hexane-ethyl acetate)						
		5:1	3:1	2:1	1:1	1:2	1:3	1:5
1	200	104.99	98.51	88.60	93.24	81.09	82.34	78.46
2	200	100.78	97.57	84.05	101.75	85.72	87.86	84.93
3	200	96.56	87.19	76.52	110.41	92.88	92.70	92.99
4	200	94.36	88.54	85.45	105.98	87.90	93.11	91.09
5	200	107.82	42.40	55.44	57.66	45.33	53.45	39.20
6	200	94.44	89.55	92.92	99.81	83.66	86.03	85.45
7	200	129.78	119.05	111.83	117.92	104.36	109.34	104.68
8	200	132.41	121.99	114.86	127.30	115.29	118.32	116.72
9	200	53.49	53.14	55.72	53.94	36.75	23.64	27.11
10	200	142.86	131.11	124.11	126.81	112.13	114.13	118.79
11	200	92.14	85.07	79.99	96.68	86.44	92.69	88.78
12	200	91.31	85.71	86.32	103.70	84.83	94.50	89.10
13	200	138.75	162.17	130.85	112.79	149.26	147.74	126.97

14	200	95.41	57.25	46.34	57.29	44.17	29.61	31.04
15	200	97.04	87.37	83.97	99.91	85.19	91.74	89.24
16	200	98.00	84.55	81.43	109.29	86.50	85.50	83.50
17	200	113.23	106.95	100.65	104.25	93.18	97.53	93.69
18	200	55.05	42.23	37.00	120.70	91.48	98.33	105.27
19	200	124.64	113.29	105.25	111.34	101.00	104.92	97.56
20	200	142.04	141.02	129.22	109.96	105.81	89.64	100.15
21	200	37.85	23.78	20.62	114.72	83.86	92.14	106.92
22	200	77.31	67.89	55.64	93.00	77.19	83.76	83.86
23	200	44.29	29.60	27.31	110.22	84.68	94.79	101.00
24	200	101.22	136.02	117.00	107.80	94.05	119.83	129.82

Table S2A: Recovery and precision test in Cowhide sample

Analyte	Added (μg/kg)	Found Average (n=6, μg/kg)	Average recovery (%)	SD (μg/kg)	RSD (%)
	100	107.1	107.1	2.41	2.25
1	300	322.6	107.5	8.61	2.66
	600	666.6	111.1	22.3	3.35
	100	109.9	109.9	5.98	5.44
2	300	331.8	110.6	8.62	2.61
	600	676.3	112.7	20.4	3.01
	100	80.0	80.0	4.20	5.25
3	300	303.1	101.0	16.9	5.58
	600	636.4	106.1	21.6	3.40
	100	113.3	113.3	7.21	6.37
4	300	337.7	112.6	9.61	2.84
	600	700.9	116.8	19.1	2.73
	100	78.4	78.4	5.68	7.24
5	300	312.3	104.1	34.8	11.16
	600	733.0	122.2	62.3	8.50
	100	83.6	83.6	3.87	4.63
6	300	306.7	102.2	9.00	2.93
	600	660.2	110.0	24.9	3.77
	100	91.8	91.8	6.05	6.60
7	300	336.1	112.0	10.2	3.02
	600	681.6	113.6	20.8	3.05
	100	114.9	114.9	10.8	9.40
8	300	394.8	131.6	35.2	8.90
	600	675.8	112.6	24.2	3.59
	100	114.3	114.3	6.09	5.33
9	300	330.7	110.2	28.4	8.60
	600	732.4	122.1	14.9	2.03
	100	114.4	114.4	9.36	8.18
10	300	335.0	111.7	6.2	1.84
	600	702.3	117.0	13.4	1.91
	100	117.1	117.1	4.26	3.64
11	300	343.1	114.4	7.41	2.16
	600	709.2	118.2	20.9	2.95
	100	109.0	109.0	4.76	4.37
12	300	337.4	112.5	11.0	3.27
	600	693.7	115.6	21.8	3.14
	100	115.2	115.2	3.85	3.34
13	300	394.0	131.3	22.3	5.67
	600	762.2	127.0	33.8	4.43

Analyte	Added (µg/kg)	Found Average (n=6, µg/kg)	Average recovery (%)	SD (µg/kg)	RSD (%)
	100	110.2	110.2	10.1	9.14
14	300	341.9	114.0	39.2	11.46
	600	574.5	95.8	19.6	3.41
	100	118.2	118.2	3.91	3.31
15	300	340.2	113.4	9.72	2.85
	600	695.5	115.9	23.0	3.31
	100	90.6	90.6	7.80	8.60
16	300	217.1	72.4	24.3	11.18
	600	482.1	80.3	37.9	7.85
	100	127.5	127.5	6.49	5.09
17	300	392.8	130.9	21.7	5.52
	600	737.0	122.8	45.3	6.15
	100	108.7	108.7	3.95	3.63
18	300	323.9	108.0	15.3	4.72
	600	653.1	108.8	24.9	3.81
	100	113.5	113.5	8.84	7.79
19	300	368.7	122.9	25.73	6.98
	600	680.2	113.4	49.4	7.26
	100	95.2	95.2	6.72	7.05
20	300	290.2	96.7	32.3	11.14
	600	552.6	92.1	51.3	9.29
	100	106.0	106.0	9.11	8.59
21	300	314.8	104.9	27.5	8.75
	600	616.3	102.7	52.3	8.48
	100	104.6	104.6	2.37	2.27
22	300	318.4	106.1	7.1	2.23
	600	655.9	109.3	17.2	2.63
	100	102.5	102.5	9.59	9.36
23	300	325.1	108.4	12.9	3.98
	600	645.0	107.5	26.1	4.04
	100	124.8	124.8	8.35	6.69
24	300	373.9	124.6	12.8	3.41
	600	763.7	127.3	25.7	3.37

Table S2B: Recovery and precision test in sheep leather sample (n=6)

Analyte	Added (µg/kg)	Found Average (n=6, µg/kg)	Average recovery (%)	SD (µg/kg)	RSD (%)
	100	107.97	107.97	1.42	1.32
1	300	325.42	108.47	4.77	1.46
	600	667.72	111.29	10.76	1.61
	100	100.90	100.90	3.06	3.03
2	300	326.18	108.73	4.58	1.40
	600	676.63	112.77	13.22	1.95
	100	105.94	105.94	3.58	3.38
3	300	323.86	107.95	5.70	1.76
	600	667.29	111.22	12.32	1.85
	100	114.16	114.16	2.63	2.30
4	300	342.56	114.19	5.11	1.49
	600	700.92	116.82	11.80	1.68
	100	78.36	78.36	1.97	2.52
5	300	231.27	77.09	11.65	5.04
	600	492.19	82.03	44.17	8.97

Analyte	Added (μg/kg)	Found Average (n=6, μg/kg)	Average recovery (%)	SD (μg/kg)	RSD (%)
	100	107.61	107.61	2.43	2.26
6	300	333.12	111.04	6.36	1.91
	600	687.42	114.57	16.79	2.44
	100	106.23	106.23	5.94	5.59
7	300	311.20	103.73	6.50	2.09
	600	640.76	106.79	16.96	2.65
	100	111.49	111.49	3.77	3.39
8	300	387.82	129.27	5.97	1.54
	600	746.45	124.41	16.27	2.18
	100	72.78	72.78	5.70	7.84
9	300	240.82	80.27	13.07	5.43
	600	480.29	80.05	14.65	3.05
	100	87.98	87.98	3.90	4.43
10	300	363.85	121.28	8.10	2.23
	600	649.37	108.23	14.74	2.27
	100	118.06	118.06	4.40	3.72
11	300	348.46	116.15	7.72	2.21
	600	653.41	108.90	14.48	2.22
	100	118.33	118.33	3.38	2.86
12	300	351.02	117.01	5.77	1.64
	600	653.99	109.00	13.68	2.09
	100	103.37	103.37	6.18	5.98
13	300	377.60	125.87	20.07	5.32
	600	679.32	113.22	12.90	1.90
	100	81.10	81.10	7.51	9.26
14	300	262.55	87.52	25.76	9.81
	600	528.26	88.04	16.33	3.09
	100	118.80	118.80	2.42	2.03
15	300	358.31	119.44	6.69	1.87
	600	664.75	110.79	15.21	2.29
	100	103.82	103.82	3.16	3.04
16	300	329.67	109.89	13.56	4.11
	600	659.88	109.98	16.17	2.45
	100	104.65	104.65	7.96	7.60
17	300	380.88	126.96	22.95	6.03
	600	737.28	122.88	45.95	6.23
	100	100.54	100.54	8.60	8.56
18	300	304.30	101.43	24.92	8.19
	600	560.08	93.35	41.59	7.43
	100	98.32	98.32	10.58	10.76
19	300	395.68	131.89	30.27	7.65
	600	724.84	120.81	55.60	7.67
	100	79.73	79.73	6.22	7.80
20	300	304.06	101.35	15.80	5.20
	600	617.20	102.87	15.47	2.51
	100	81.23	81.23	2.57	3.16
21	300	318.60	106.20	6.92	2.17
	600	561.11	93.52	26.22	4.67
	100	109.71	109.71	4.83	4.40
22	300	327.41	109.14	4.18	1.28
	600	604.07	100.68	7.49	1.24

Analyte	Added (µg/kg)	Found Average (n=6, µg/kg)	Average recovery (%)	SD (µg/kg)	RSD (%)
	100	93.40	93.40	9.56	10.23
23	300	280.94	93.65	27.78	9.89
	600	511.95	85.33	46.06	9.00
	100	107.68	107.68	4.05	3.76
24	300	364.06	121.35	8.80	2.42
	600	657.94	109.66	17.62	2.68

Table S2C: Recovery and precision test in pig leather sample (n=6)

Analyte	Added (µg/kg)	Average content (n=6, µg/kg)	Average recovery (%)	SD (µg/kg)	RSD (%)
	100	80.53	80.5	5.96	7.40
1	300	228.53	76.18	2.93	1.28
	600	509.46	84.91	9.88	1.94
	100	111.32	111.3	9.66	8.68
2	300	239.73	79.91	9.69	4.04
	600	535.16	89.19	9.28	1.73
	100	104.72	104.7	7.33	7.00
3	300	291.07	97.02	26.79	9.21
	600	585.58	97.60	12.26	2.09
	100	110.65	110.65	9.92	8.97
4	300	282.99	94.33	5.86	2.07
	600	602.71	100.45	9.53	1.58
	100	82.92	82.92	8.57	10.33
5	300	347.82	115.94	19.41	5.58
	600	578.61	96.44	15.99	2.76
	100	100.20	100.2	9.12	9.10
6	300	335.92	111.97	12.80	3.81
	600	542.62	90.44	49.73	9.17
	100	116.45	116.5	11.98	10.29
7	300	331.24	110.41	8.46	2.55
	600	573.56	95.59	15.60	2.72
	100	110.17	110.2	11.47	10.41
8	300	330.24	110.08	20.94	6.34
	600	682.62	113.77	56.30	8.25
	100	90.58	90.58	9.65	10.66
9	300	270.29	90.10	36.70	13.58
	600	545.94	90.99	14.30	2.62
	100	123.00	123.00	12.09	9.83
10	300	298.87	99.62	7.88	2.64
	600	607.05	101.17	11.69	1.93
	100	119.42	119.42	6.61	5.54
11	300	289.43	96.48	6.44	2.23
	600	604.65	100.77	9.24	1.53
	100	99.87	99.87	4.34	4.34
12	300	280.76	93.59	10.43	3.72
	600	608.38	101.40	8.64	1.42
	100	82.89	82.89	11.91	14.37
13	300	381.80	127.27	12.92	3.38
	600	618.21	103.04	24.07	3.89
	100	92.92	92.92	12.09	13.01
14	300	280.07	93.36	18.58	6.63
	600	565.14	94.19	16.42	2.91

Analyte	Added (μg/kg)	Average content (n=6, μg/kg)	Average recovery (%)	SD (μg/kg)	RSD (%)
	100	118.77	118.77	4.59	3.87
15	300	257.68	85.89	6.89	2.67
	600	533.98	89.00	7.56	1.42
	100	84.36	84.36	11.88	14.08
16	300	274.41	91.47	15.69	5.72
	600	603.08	100.51	29.49	4.89
	100	123.49	123.49	12.61	10.21
17	300	335.66	111.89	4.34	1.29
	600	727.10	121.18	7.91	1.09
	100	104.94	104.94	7.65	7.29
18	300	235.10	78.37	2.80	1.19
	600	452.92	75.49	5.37	1.18
	100	129.02	129.02	9.60	7.44
19	300	324.75	108.25	3.71	1.14
	600	713.24	118.87	8.22	1.15
	100	116.48	116.48	13.40	11.50
20	300	312.64	104.21	32.49	10.39
	600	645.48	107.58	39.55	6.13
	100	89.25	89.25	7.00	7.84
21	300	258.12	86.04	7.66	2.97
	600	443.00	73.83	7.23	1.63
	100	105.16	105.16	2.66	2.53
22	300	258.73	86.24	6.25	2.42
	600	541.44	90.24	8.75	1.62
	100	103.27	103.27	4.37	4.23
23	300	222.43	74.14	3.22	1.45
	600	462.89	77.15	6.64	1.43
	100	125.62	125.62	4.16	3.31
24	300	304.41	101.47	4.31	1.42
	600	662.45	110.41	8.21	1.24