Original Article

Development of the Solid Phase Micro Extraction Gas Chromatography Mass Spectrometry (SPME-GC-MS) for Determination of 35 Pesticides in Plasma

Tummarintra P, MSc[1], Duongkaew M, BSc[1], Mitsungnern T, MD[2], Jiranantakan T, MD, MPH[1,3,4,5]

[1] Siriraj Poison Control Center, Siriraj Hospital, Faculty of Medicine, Mahidol University, Bangkok, Thailand
[2] Department of Emergency Medicine, Faculty of Medicine, Khon Kaen University, Khon Kaen, Thailand
[3] Department of Preventive and Social Medicine, Siriraj Hospital, Faculty of Medicine, Mahidol University, Bangkok, Thailand
[4] New South Wales Poisons Information Centre, Sydney Children's Hospitals Network, Sydney, Australia
[5] Drug Health Clinical Service, Royal Prince Alfred Hospital, Sydney, Australia

Background: Contamination of pesticide to human is difficult to detect, especially in low concentration setting. So we need to develop a technique that accurately detect the types and amount of common pesticides in Thailand.

Objective: To investigate 35 pesticides in five major classes consist of organophosphorus, organonitrogen, pyrethroid organochlorine and fungicide by using solid phase micro extraction (SPME) vial headspace followed by gas chromatography mass spectrometry (GC-MS).

Materials and Methods: An experimental study based on solid phase micro extraction (SPME) vial headspace followed by gas chromatography mass spectrometry (GC-MS) was developed for the determination of 35 pesticides in plasma.

Results: Types of fibre coating were tested, 50/30 µm Polydimethylsiloxane/Divinylbenzene/Carboxen (PDMS/DVB/CAR) showing higher recoveries of the compound. The main factors affecting the SPME process, such as adsorption and desorption times (40 and 5 min, respectively), incubation temperature (70°C), NaCl addition were optimized. The procedure was validated in terms of linearity r^2>0.995 for concentrations ranging from 0.05 to1.0 µg/mL, intra and interday precision % CV <15, sensitivity was 0.02 µg/mL for LLOQ and % recovery >85% to <120%.

Conclusion: HS-SPME in combination with GC-MS is an effective method for the determination of 34 of 35 pesticides (except abamectin) in human plasma and shows a great potential for using in rapid on-site analytical work, which may be needed in clinical toxicology.

Keywords: Pesticide, Solid phase micro extraction, SPME, Gas chromatography mass spectrometry, GC-MS

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The problem of contamination of pesticides in environmental affects ecological systems and human health(1). Although the dangers of exposure to pesticides have been well known, pesticide use has increased in recent years because it protects agricultural products; it's important for humanity. The exposure to pesticides caused by accidental or by suicidal attempt affect the body systemically and may be fatal.

Currently, sample preparations of pesticide analysis are of a variety and depend on the type of pesticides(2-5), such as liquid-liquid extraction of pesticides followed by GC-MS (LLE-GC-MS), solid phase extraction (SPE) of pesticide followed by GC-MS, high performance liquid chromatography (HPLC), and ultra-performance liquid chromatography (UPLC). However, those methods have several steps and may lose the substance in the extraction prevent detecting low concentrations. Solid phase micro-extraction (SPME) is an extraction method and an alternative to sample preparation before sample analysis. The principle of SPME techniques, the small particles coated with fiber, which is specific to the substance and the fiber adsorbs the required substances for analysis. After absorption, the fiber will emancipate the desired substance into the instrument for analysis. SPME techniques reduce to the process of LLE and SPE techniques. Using SPME techniques, the condition of the samples for analysis must be properly prepared before the extraction and depends on the types of substance.

Currently, SPME techniques were applied to extraction of blood, urine, food, air, etc. Moreover, this techniques used for drugs, smell of food, volatile and pesticide analysis also SPME is used to extract pesticides in the blood

Correspondence to:
Jiranantakan T.
Department of Preventive and Social Medicine, Siriraj Hospital, Faculty of Medicine, Mahidol University, Bangkok 10700, Thailand.
Phone: +66-2-4197284, **Fax:** +66-2-4115034
E-mail: Thanjira.Jiranantakan@gmail.com

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sample, there were many studies about the SPME technique for various classes of pesticides in some types of human specimen such as blood, urine, and breast milk[5-23]. We chose 35 pesticides from 5 major classes (organophosphorus, organonitrogen, pyrethroid, orgonochlorine, and fungicide) that commonly used and led to mortality in Thailand. So we want to explore what kinds of pesticides can use this extraction technique[5-22].

A list of the analyst and classes to which they belong is shown in Table 1.

Materials and Methods

An experimental study on the applicability of the HS-SPME method was combined with GC-MS. Development and optimization of SPME procedures were carried out separately for several pesticides by using GC-MS. Quantization has been performed using calibration curves prepared by spike blank blood samples and using labeled surrogate standards. The development will be applied to serum samples from patients. The study protocol was approved from the Siriraj Hospital Ethics Committee in Human Research (633/2556).

Reagents

All pesticide standards of 96.5 to 99.7% purity were purchased from Dr. Erhenstorfer (Promochem, Wesel Germany). Stock standards solution mixtures were prepared in methanol (Merck, Germany) and stored at -20°C. Working standards were prepared by dilution with methanol and stored at 4°C. Samples were prepared by doling the appropriate volume of the methanol standard solution, maintaining a final concentration lower than 1% methanol in the samples; sodium chloride (NaCl) and HCI of analytical grade (Scharlan) were used.

Samples

Plasma sample used for optimization were obtained from healthy supposed non-exposed subjects (Siriraj hospital, Blood Bank). Plasma samples were then stored at -20°C until analysis. Then we spiked pesticide standards into plasma samples as EURACHEM protocol and followed by HS-SPME procedure.

Headspace solid phase micro extraction procedure

The SPME fibers (Supleco, Bellefonte) were conditioned in the GC-MS injection at 270°C for 30 min Polydimethylsiloxane (PDMS), Polydimethylsiloxane (PDMS)/Divinylbenzene (DVB), Polydimethylsiloxane (PDMS)/Divinylbenzene (DVB)/Carboxen (CAR), and polyacrylate (PA), Prior to their first use as recommended by the manufacturer. Optimization of parameters and analysis were performed in a 10 ml glass vial containing 0.5 ml of sample containing 30% of NaCI used for method development. The vials containing the sample were shaken for 10 min, then agitated and incubated for 40 min at 70°C in the auto sampler agitator, followed by the exposure of the fiber to the headspace of the sample in the vial scaled with polytetrafluoroethylene (PTFE)/silicone septum.

GC-MS analysis

The extraction and analysis of pesticides were carried out with CTC Combi AAL auto sampler equipped with agitator and needle heater (for fiber conditioning and inter-extraction clean up coupled to a GC-MS (Agilent Technologies 7890A system)) and operated in the split/splitless mode at an injection temperature of 270°C. The separation of target analytes was achieved on a DB-5MS fused capillary column containing 5% dipheny and 95% dimethylpolysiloxane (30 m x 0.25 mm i.d. x 0.25 µm film thickness). Helium (carrier gas) was set to a constant flow rate of 1 ml/min with linear velocity of 40 cm/s. The GC column oven temperature program was set as follows: initially set at 60°C for 2 min, ramped at 30°C/min to 180°C, then ramped to 210°C at 5°C/min, and finally to 270°C held for 5 min, for a total runtime of 24.50 min. The MS operation condition includes transferline of 300°C, ion source of 230°C electron ionization (EI) of 70 eV. The optimization of methods was done in scan mode while quantitation was done by selected ion monitoring (SIM) mode. A target ion and other reference ions were monitored for the target analytes. The investigated pesticides were identified by comparing the mass spectrum obtained for each analyte to that of the reference compound in GC-MS library using the US national Institute of Standards and Technology (NIST) and PT35 libraries search. In case of conclusion, easy spectral identification and integration was achieved by using the disconsolation feature of the GC-MS system. The developed method was fully validated according to the USFDA guideline and EURACHEM guide 1998 were applied[23].

Results

Studies on optimal conditions for extraction and absorption of SPME technique should be considered and to understand the behavior of the substance to be analyzed.

GC-MS, the retention times and chromatography resolution were using a 10 µg/ml mixture standard for scan to quantify the pesticides in the sample.

We found what was the most appropriate way for the determining the validity of the analytical method. The SPME method was PDMS/DVB/CAR and was used to extract pesticides, in this study: NaCI 30% weight by volume (w/v) was used to increase performance with the extraction, the temperature was 80°C and the headspace technique was used. Analyzing samples of 35 pesticides were added to the plasma. The results of the analysis should not interfere with the sample, as shown in Figure 1. The chromatogram standard was extracted directly from the matrix and the analysis was GC-MS in SIM mode.

We considered using four different types of SPME, including non-polar phase (PDMS), two-polar phase (PDMS/DVB), and tri-polar phase (Divinylbenzene/Carboxen/Polydimethy lsiloxane/-DVB/CAR/PDMS). Comparative studies have shown that DVB/CAR/PDMS-SPME has better ability to extract pesticides in samples,

Table 1. The precision, accuracy (inter-day and intra-day) %recovery and r^2 of 35 pesticides in plasma samples

Pesticides	Precision (% CV)								Accuracy (% RV)	r^2	% recovery 0.02 to 1.00 ppm
	Within-run (n = 6)				Between-run (n = 18)						
	LLOQ	LQD	MQD	HQD	LLOQ	LQD	MQD	HQD			
Aldicarb	10.62	2.38	3.08	7.79	13.61	3.34	2.52	6.7	94.61 to 110.48	0.998	92.91 to 115.86
Methomyl	10.72	1.83	1.44	6.84	11.4	1.93	1.9	5.38	88.07 to 101.17	0.998	83.57 to 102.71
Diazinon	7.82	1.73	2.07	2.86	12.32	7.79	2.01	8.11	92.77 to 107.00	0.997	81.52 to 106.54
Dichlorvos	10.28	3.23	1.48	5.6	9.03	3.9	2.15	7.27	95.33 to 106.66	0.995	84.49 to 115.02
Methiocarb	3.48	5.35	0.82	2.69	5.83	4.86	2.19	2.66	97.00 to 102.45	0.995	94.94 to 121.34
Propoxur	4.1	3.06	0.86	6.11	9.57	3.04	1.9	7.77	96.33 to 107.05	0.995	87.79 to 105.6
Bendiocarb	4.13	3.36	1.19	5.93	8.71	4.37	1.83	5.23	97.00 to 103.05	0.995	86.62 to 91.39
Dimethoate	4.13	3.01	0.61	6.54	3.54	3.24	0.89	6.88	96.00 to 111.17	0.996	92.68 to 106.33
Carbafuran	5.89	5.8	0.67	6.22	10.75	4.61	1.91	7.43	94.66 to 100.53	0.997	91.91 to 111.72
Atrazine	5.81	5.99	0.89	3.91	5.44	4.66	1.31	3.68	99.00 to 105.90	0.995	88.04 to 118.88
gamma-BHC	4.82	3.63	3.76	5.18	7.84	2.76	2.6	4.68	97.46 to 103.33	0.996	85.65 to 103.23
BETA-BHC	3.37	3.83	1.41	3.56	6.66	2.57	2.31	3.79	98.45 to 107.95	0.997	99.17 to 108.22
DELTA-BHC	9.63	4.33	1.26	8.37	9.31	3.26	2.02	8.3	74.40 to 104.39	0.995	83.33 to 91.51
Chlopyrifos-methyl	3.41	5.81	3.95	5.43	5.49	3.86	2.39	5.46	98.07 to 105.17	0.996	81.09 to 112.54
Parathion methyl	12.12	3.22	2.96	7.21	10.55	3.68	2.41	7.18	93.63 to 101.09	0.995	85.41 to 113.14
Carbaryl	8.4	3.65	3.72	5.04	6.95	4.25	3.4	7.01	92.44 to 103.83	0.995	95.90 to 106.96
Ametryn	2.77	3.06	2.33	7.01	6.59	2.52	2.05	6.29	98.00 to 106.67	0.995	85.42 to 115.64
Primiphos-methyl	15.75	2	5.99	5.96	10.71	3.68	5.49	3.57	97.17 to 106.99	0.996	83.99 to 102.20
Malathion	3.41	3.06	5.95	5.16	2.84	2.92	5.49	3.92	97.66 to 104.40	0.995	97.72 to 102.11
Chlorpyrifos	11.88	3.86	6.7	2.8	8.57	2.39	5.71	2.17	96.00 to 105.65	0.995	82.39 to 108.88
Aldrin	10.21	2	6.47	6.21	10.48	1.89	6.2	4.09	96.66 to 106.93	0.996	88.71 to 95.83
Parathion ethyl	6.99	1.29	6.68	5.34	4.23	2.71	5.34	4.42	98.00 to 102.17	0.996	80.67 to 100.17
Dieldrin	11.96	1.93	6.53	5.05	7.57	4.98	5.31	3.74	95.30 to 103.18	0.995	81.16 to 98.67
Endrin	11.2	1.54	7.6	6.89	8.05	2.76	5.84	5.44	98.00 to 103.27	0.996	88.91 to 104.64
Endrosunfan-sulfate	6.72	3.63	4.73	4.61	8.58	2.76	4.9	4.82	91.76 to 105.83	0.995	99.46 to 104.31
DDT	11.45	1.56	4.55	6.92	10.71	2.54	4.29	5.77	94.27 to 108.50	0.995	94.97 to 115.42
Carbosulfan	9.09	2	6.81	4.56	13.73	1.97	5.75	4.43	88.05 to 104.50	0.996	94.22 to 102.23
Endrin-aldehyde	3.63	4.04	6.63	7.65	4.07	3.02	5.66	6.49	97.33 to 107.07	0.995	93.18 to 103.80
Bifenthrin	7.88	2.7	6.58	5.24	6.64	1.9	5.89	6.91	96.33 to 107.17	0.997	93.15 to 103.14
Lambda-cyhalothrin	4.27	2.77	5.84	5.6	7.12	1.73	5.46	5.02	98.06 to 103.08	0.996	89.68 to 99.76
Permethrin	4.44	3.78	6.34	5.86	6.95	2.77	5.27	4.99	93.76 to 106.47	0.995	84.99 to 101.68
Baythroid	3.9	2.39	4.79	5.35	8.84	1.9	4.83	4.51	96.66 to 107.05	0.995	91.07 to 100.50
Cypermethrin	4.39	2.99	5.7	5.8	5.04	2.25	4.68	5.58	99.23 to 107.00	0.996	85.53 to 110.19
Fenvalerate	4.39	2.39	4.87	7.67	7.4	1.84	4.82	5.25	94.50 to 107.67	0.996	92.00 to 103.17
Abamectin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND = not detected, n = number of replicate

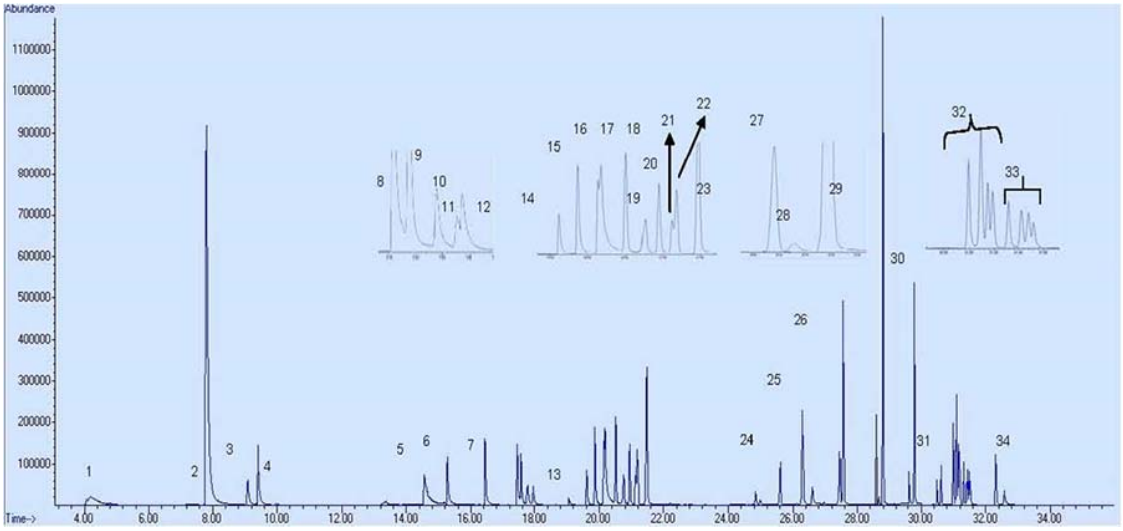


Figure 1. Chromatogram (SIM mode) of a 10 µg/ml pesticide standard extracted by HS-SPME from the matrix extract. Peak identification: 1, Aldicarb; 2, Methomyl; 3, Diazinon; 4, Dichlorvos; 5, Methiocarb; 6, Propoxur; 7, Bendiocarb; 8, Dimethoate; 9, Carbofuram; 10, Atrazine; 11, gamma-BHC; 12, BETA-BHC; 13, DELTA-BHC; 14, Chlopyrifos-methyl; 15, Parathion methyl; 16, Carbaryl; 17, Ametryn; 18, Primiphos-methyl; 19, Malathion; 20, Chlorpyrifos; 21, Aldrin; 22, Parathion ethyl; 23, Dieldrin; 24, Endrin; 25, Endrosunfan-sulfate; 26, DDT; 27, Carbosulfan; 28, Endrin-aldehyde; 29, Bifenthrin; 30, Lambda-cyhalothrin; 31, Permethrin; 32, Baythroid; 33, Cypermethrin; 34, Fenvalerate; 35, Abamectin (not detected).

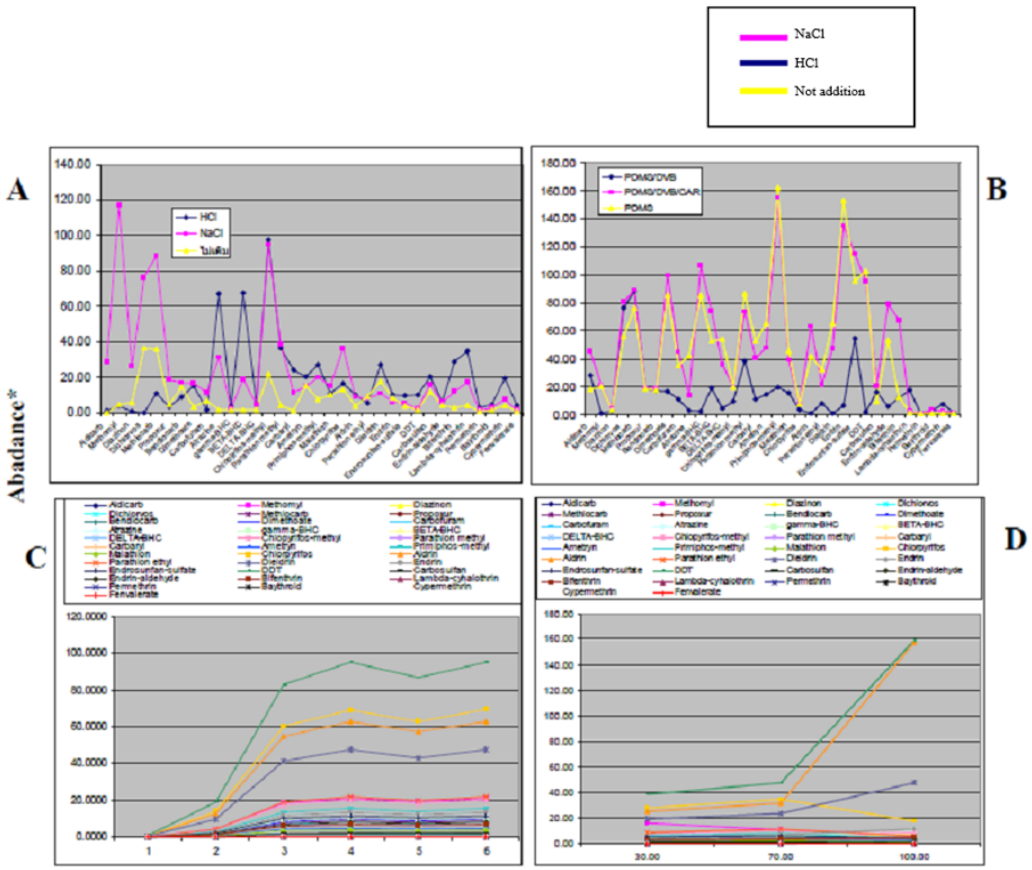
compared to the four types. Figure 2 shows the performance of each SPME is used to extract pesticides. Therefore, this study selected PDMS/DVB/CAR-SPME for the validity of the analytical method. SPME adsorption, Direct immerse (DI) into aqueous samples has more sensitivity than Headspace (HS) but the sample must be clear. For dirty samples such as blood, soil, biological samples etc., HS-SPME is infrequently chosen.

The HS-SPME extractions were more efficient in extracting the more volatile compounds such as organophosphorus pesticides (OPs), organochlorine pesticide (OCs), and pyrethrin. However, they were not successful in extracting the less volatile pesticides such us organonitrogen pesticides (ONs). After following our protocol, the HS-SPME mode extracted 34 of 35 pesticides succesfully, but they were less sensitivity than the DI-SPME method. However, most of samples were dirty, so, the HS-SPME method were better choice for these pesticide analyses.

GC conditions, the conditions of desorption were there for 270°C and 10 min. The extraction temperatures were performed at 70°C. The extraction time, the time required to reach equilibrium in the fiber stationary phase was 40 min. This time was therefore selected, since on average it represents the best condition for the set under study.

The strength of the ion increases the strength of the weak interaction between the ions and the sample Matrix, thus contributing to the extraction with fiber. Influence of ion strength is evaluated by adding the quantity of aqueous HCl and NaCl with extraction of evaluation through 10, 20, and 30% (weight by weight: w/w) of sodium chloride and 30% (w/w) of hydrogen chloride; the concentration of sodium chloride are the best results of this study. However, this concentration and stability of slurry sedimentation of salt due to sodium chloride. While the number of the accommodation. On the other hand, 10% of HCl found the best results for the insecticides, and does not affect the stability of the solution, and was therefore selected.

Method validation, no interference of matrix compound was observed in selectivity testing as shown in Figure 1. The limit of quantification (LOQ) was demonstrated at 0.02 µg/ml for all which used 500 µL of plasma sample. This method had good accuracy, the percent relative value (% RV) was found to be in the range of 92.77 to 111.17% for all pesticides. High precision was shown in both inter-day and intra-day testing variation, and the range of precision (%CV) was found to be in the range of 0.64 to 15.75%. The accuracy and precision were acceptable as summarized in Table 1. This method had a good linearity with the coefficient of determination (r^2) more than 0.995 as summarized in Table 1. All were within the acceptable range (r^2>0.995). The extraction efficiency (% RE) was found to be in the range of 81.52 to 115.64% and this study show that the plasma samples containing 34 pesticides were stable in various tested condition as demonstrated the percentage of variation in each condition was within the acceptable range (not show). This method can not detect abamectin in plasma sample.



* The abadance be adjusted to suit. The comparison clearly

Figure 2. A) Effect of addition of salt 30% w/w and acid 10% w/w to the serum sample (10 µg/ml), B) Comparison between the SPME extraction efficiencies in the headspace mode, C) Influence of the extraction time on the extraction efficiency (1 = 10, 2 = 20, 3 = 30, 4 = 40, 5 = 50, 6 = 60 min), D) Influence of temperature on the extraction efficiency.

Discussion

After review the literature, there are no study about single analysis technique for accurately determine types and amount of various pesticides in human plasma HS-SPME followed by GC-MS can be used to determine quantitative and qualitative pesticide residues in samples of plasma; also other types of biological methods are important and allow selection and determination of pesticides in 34 samples with great accuracy; the rate was established as outlined.

SPME procedure in this document allows for the reduction of the importance of keeping samples in comparison with other techniques such as liquid-liquid extraction and solid phase even if headspace SPME is often used in the extraction mode, we perform complex matrix of HS-mode plasma sample; therefore, using the calibration graph with blank blood pierced the correct results for the quantitation of isotopically label surrogate internal standard and is also required to correct the result matrix. In addition, GC-MS applications show satisfactory sensitivity and how to avoid interferences from the matrix of this type of complex biological.

GC-MS-SPME integration steps, we can examine the organochlorine, organophosphorus pesticides, pyrethroids, and many organonitrogen, fungicide simultaneously in plasma leading to lower detection limit for most of the pesticides studied (0.02 to 1.0 µg/ml). The method can be suitable for monitoring pesticides in various population.

Abamectin was not detected by GC-MS, because of their large molecular size and low volatility; both avermectin and hydramethylnon were analyzed via SPME/HPLC/MS. the SPME is not suitable for desorption in GC[23]. The substance has a derivative form before injection to GC-MS. In the stability of the samples analyzed, the authors found examples of poor stability. Samples should be analyzed immediately or stored for up to two weeks.

Conclusion

The HS-SPME-GC-MS analysis is a promising method for detecting wide range of pesticides totally 34 pesticides. However, it cannot detect abamectin.

What is already known on this topic?

The SPME-GC-MS analysis is suitable for detecting many xenobiotic agents especially pesticides even in low concentration and in human specimen.

What this study adds?

So HS-SPME in combination with GC-MS is an effective method for the determination of 34 pesticides in human plasma and shows a great potential for use in rapid on-site analytical work, which may be needed in clinical toxicology.

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Potential conflicts of interest

The authors declare no conflicts of interest.

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พัฒนาการตรวจสารกำจัดศัตรูพืช 35 ชนิดในพลาสม่าด้วยเทคนิคโซลิดเฟสไมโครเอ็กแทรคชั่นแก๊สโครมาโตกราฟี่

ไพบูลย์ ทุมรินทร์, มาริสา ดวงแก้ว, ฐปนวงศ์ มิตรสูงเนิน, ธัญจิรา จิรนันทกาญจน์

ภูมิหลัง: การปนเปื้อนของสารกำจัดศัตรูพืชในมนุษย์ยากที่จะตรวจพบ โดยเฉพาะอย่างยิ่งในกรณีที่มีความเข้มข้นต่ำ ผู้นิพนธ์จึงต้องการหาวิธีในการตรวจสอบชนิดและปริมาณของสารกำจัดศัตรูพืชที่พบบ่อยในประเทศไทยได้อย่างถูกต้องแม่นยำ

วัตถุประสงค์: เพื่อตรวจสอบสารกำจัดศัตรูพืช 35 ชนิดประกอบด้วย organophosphorus, organonitrogen, pyrethroid, organochloride และ fungicide ด้วยเทคนิคโซลิดเฟสไมโครเอ็กแทรคชั่นแก๊สโครมาโตกราฟี่

วัสดุและวิธีการ: นำสารกำจัดศัตรูพืช 35 ชนิดในพลาสม่า มาวิเคราะห์ด้วยเทคนิคโซลิดเฟสไมโครเอ็กแทรคชั่นแก๊สโครมาโตกราฟี่ ซึ่งเป็นวิธีที่สะดวก รวดเร็ว

ผลการศึกษา: ชนิดของการเคลือบไฟเบอร์ PDMS/DVB/CAR ขนาด 50/30 ไมโครเมตร แสดงให้เห็นการคืนตัวที่ดีกว่าปัจจัยหลักที่ส่งผลต่อขั้นตอน SMPE คือเวลาการดูดซับและการคายสารออก (40 และ 5 นาที) อุณหภูมิของเครื่องอยู่ที่ 70 องศาเซลเซียส เติมโซเดียมคลอไรด์เพื่อปรับให้เหมาะสมกระบวนการเหล่านี้ ได้ผ่านการตรวจสอบความสอดคล้องเป็นเส้นตรง r^2>0.995 สำหรับช่วงความเข้มข้นที่ 0.05 จนถึง 1.0 μg/mL ค่าความแม่นยำในวันเดียวกันและข้ามวัน (%CV) <15 โดยมีความไวของการตรวจพบที่ความเข้มข้นของสารน้อยที่สุดในเลือด (LLOQ) คือ 0.02 มก. ต่อ มล. และเปอร์เซ็นการคืนตัวของสาร >85% ถึง <120%

สรุป: วิธี HS-SPME ร่วมกับ GC-MS เป็นวิธีที่มีประสิทธิภาพในการระบุสารกำจัดศัตรูพืช 34 จาก 35 ชนิด (ยกเว้น Abamectin) และมีศักยภาพในการวิเคราะห์ซึ่งมีความต้องการสูงในพิษวิทยาคลินิก