

APPLICATION OF AN AUTOMATED IDENTIFICATION AND QUANTIFICATION SYSTEM WITH A GC/MS DATABASE (AIQS-DB) FOR SIMULTANEOUS ANALYSIS OF PHTHALATE ESTERS AND STEROLS IN AIR PARTICLES

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Abstract. The aim of this study is to apply an automated identification and quantification system with a GC-MS database (AIQS-DB) for simultaneous analysis of phthalate esters (PAEs) and sterols in air particles. Air particles samples were collected on the roof of a building near congested traffic road (Pham Van Dong street, Ha Noi) (AP1) and in a highly populated residential area (Phu Do town) (AP2). At each sampling location, samples were collected separately for 10 hours each at day and night, during continuously 6 days by Kimoto high-volume air sampler. Air particle samples were then extracted by dichloromethane and quantified by GC/MS instrument with the AIQS-DB. Analytical results of 12 PAEs and 13 sterols in air particles samples showed that five out of 12 PAEs and seven out of 13 sterols were detected. Di(2-ethylhexyl)phthalate (DEHP), di-n-butyl phthalate (DBP) and di-iso-butyl phthalate (DiBP) concentrations were highest, contributed 94 % of the total detected phthalates concentration. Cholesterol and beta-sitosterol were detected in all the samples and their total concentration contributed over 70 % of the total detected sterols concentration at Phu Do town. This is the first study on the application of AIQS-GC for simultaneous determination of PAE and sterols in the air particle. This finding provides new important information about the level and occurrence of sterol in air in Viet Nam.

Keywords: air particles, GCMS, AIQS-DB, phthalate esters, sterol.

Classification numbers: 2.3

1. INTRODUCTION

Air pollution in Viet Nam, especially in the big cities such as Ha Noi and Ho Chi Minh are getting more serious due to the rapid urbanization, industrial development and population. According to the results of air pollution survey in Ha Noi in 2016, the concentration of air particles in Ha Noi in April 2016 was over two times higher than the limitation value of the national standard for ambient air quality (QCVN 05:2013/ BTNMT) and five times higher than those recommended by the World Health Organization [1]. The concentrations of PM10 and

PM_{2.5} in 400 locations in Ha Noi in 2006 and 2008 ranged from 60-157 $\mu\text{g}/\text{m}^3$ and 42-134 $\mu\text{g}/\text{m}^3$, respectively. PM_{2.5} concentrations were higher than those as the recommended by United States Environmental Protection Agency (at 35 $\mu\text{g}/\text{m}^3$) and the World Health Organization (at 25 $\mu\text{g}/\text{m}^3$) [2].

Fine air particles (PM_{2.5} or smaller) caused serious impacts on the human's respiratory system. Recently, many researchers [3, 4, 5] have demonstrated that the air particles can absorb and carry many of organic pollutants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, dioxins, etc. Especially, PAHs is one of the main air pollution sources in the big cities with high traffic density such as Hanoi and Ho Chi Minh city, where there is a huge number of low-quality vehicles with no efficient exhaust gas treatment system. This is considered to be the main PAHs source in ambient air in cities and caused a serious threat to human health.

Phthalate esters are a class of chemical compounds widely used in different industrial activities. Their main applications are as plasticizers for polyvinyl chloride (PVC) resins, adhesives, and cellulose film coating (about 85 % of the whole production). Minor applications are in cosmetics, repellent, insecticide carriers and propellents. The most common PEAs used are dimethyl phthalate (DMP), diethyl phthalate (DEP), di-iso-propyl phthalate (DiPP), dipropyl phthalate (DPP), DiBP, DBP, n-butyl benzyl phthalate (BBP), DEHP and di-n-octyl phthalate (DOP) [6]. Previous studies showed that PAEs poses a serious risk to human health such as damages on DNA, reproductive hormones. The International Agency for Research on Cancer (IARC, 1982) has classified phthalate as possible human carcinogens (group 2B). Human exposure to phthalate mainly from indoor dust, air, water and soil, mostly through inhalation, digestion and skinabsorption.

There have been many studies on PAEs in air and air particles in the world. Ma et al. [7] studied on the phthalate diesters in airborne PM_{2.5} and PM₁₀ in a suburban area of Shanghai: Seasonal distribution and risk assessment. The results showed that DMP, DEP, DBP, DiBP, benzyl butyl phthalate (BzBP), and DEHP were frequently detected in airborne particulate matter with their sum concentrations ranging from 13.3 to 186 ng/m^3 (average 59.8 ng/m^3) in PM_{2.5}, and from 10.1 to 445 ng/m^3 (average 132 ng/m^3) in PM₁₀. DEHP, DBP, and DiBP were the major phthalate diesters detected in particulate matter samples. DEHP was found predominantly in coarse (size fraction of between PM_{2.5} and PM₁₀) particles, whereas DMP, DEP, DBP, DiBP, and BzBP were found predominantly in fine (PM_{2.5}) particles. The concentrations of PAEs in PM during warm season (207 ng/m^3 for PM₁₀ and 71.9 ng/m^3 for PM_{2.5}, on average) were significantly higher than those during cold season (76.9 ng/m^3 for PM₁₀ and 50.4 ng/m^3 for PM_{2.5}).

Tran et al. [8] have studied the occurrence of phthalate diesters in indoor air from several northern cities in Viet Nam. The results showed that the mean concentrations of total phthalates (sum of ten phthalates) in particulate and gas phases ranged from 95.2 to 13,100 $\mu\text{g g}^{-1}$ and from 57.0 to 14,900 ng m^{-3} , respectively. In bulk indoor air samples (gas plus particulate phase), the concentration of total phthalates ranged from 106 to 16,000 ng m^{-3} (mean of 1040 ng m^{-3}). Diethyl phthalate was found at the highest concentration 12,400 ng m^{-3} (mean 376 ng m^{-3}) in indoor air. The highest concentrations of PAEs were found in indoor air samples from Ha Noi among 4 northern Vietnamese cities studied.

Sterols are the indicator compounds of water pollution. Sterols are naturally derived in plants, animals and fungi [9], and can also be produced by some bacterias. Sterols concentrations are usually high in untreated domestic wastewater and their bioaccumulative capability in sediment is quite high [10]. He et al. [11] measured the emission of the fine particulate organic

matter from Chinese cooking. There were over 90 species of organic compounds were identified and quantified, fatty acids, diacids and steroids were the major organic compounds emitted from cooking duration.

There are some studies which analyzed organic compounds (including sterols) in air particles. Omar et al. [12] have studied the levels and distributions of organic source tracers in air and roadside air particles of Kuala Lumpur, Malaysia. The results showed that n-alkane, PAHs, petroleum (pristane, phytane, hopanes, steranes), sterols (cholesterol, campesterol, stigmasterol, sitosterol) were detected in PM10 and roadsidedust particles. Especially, the concentrations of sterols in urban atmospheric particles were 10 times higher than those in roadsidedust particles.

So far, there is no study that have been carried out on the sterol pollution in air and air particle, and also there is no report on the effects of sterol on human health in Vietnam. From this reason, the study on the occurrence of phthalate esters and sterols in air especially in air particles in Viet Nam is needed. Therefore, the objective of this study is to apply the automated identification and quantification system with a GC-MS database (AIQS-DB) for simultaneous analysis of phthalate esters and sterols in air particles. This method is successfully applied to monitor the occurrence of organic micro-pollutants (including sterols and PAEs) in water and sediment in Viet Nam, China, Japan [13-17]. This would be a promising analytical method, which may overcome the difficulties and problems of analytical condition in Viet Nam.

2. MATERIALS AND METHODS

2.1. Reagents and materials

Table 1. Phthalate esters, sterol and internal standard compounds.

No.	PAEs	Sterols	Internal standard
1	Dimethyl phthalate	Cholestanol	1,4- Dichlorobenzene-d4
2	Dimethylterephthalate	Coprostanol	Naphthalene -d8
3	Diethyl phthalate	Cholestane	Acenaphthene-d10
4	Di-n-propyl phthalate	beta-Sitosterol	Anthracene-d10
5	Di-iso-butyl phthalate	Ergosterol	Chrysene-d12
6	Di-n-butyl phthalate	Stigmasterol	Perylene-d12
7	Di-n-pentyl phthalate	Cholesterol	
8	Di-n-hexyl phthalate	24-Ethyl coprostanol	
9	Butyl benzyl phthalate	Campesterol	
10	Dicyclohexyl phthalate	Coprostanone	
11	Di (2-ethylhexyl) phthalate	Epicoprostanol	
12	Di-n-octyl phthalate	Fucosterol	
13		Stigmastanol	

12 mixed PAEs (Table 1) stock standard solutions, 10mg/L, in dichloromethane (CRM47930, QTM PAH Mix) was obtained from Supelco, Bellefonte, PA, USA and 13 mixed Sterols (Table 1) stock standard solutions, 100mg/L, in dichloromethane (CRM47930, QTM PAH Mix) was obtained from Supelco, Bellefonte, PA, USA. Appropriate dilutions of the standard solution with dichloromethane were made to the working solutions. Six internal standards (Table 1) were purchased from Wellington Laboratories (Ontario, Canada), Sigma–Aldrich Japan K.K. (Tokyo, Japan) and Restek (Bellefonte, PA, USA) and were used in a 10 µg/mL hexane solution (IS).

All of solvents used for this research (acetone, dichloromethane, methanol and n–hexane) were pesticide residue analysis purchased from Kanto Chemical Co. (Tokyo, Japan). Sodium sulfate (Na_2SO_4) at grade of 99 % was supplied by Kanto Chemical Co. Quartz fiber filter (QR-100, 203×254 mm) was purchased from Advantec Toyo Kaisha, Ltd. Purified water generated by a Milli-Q system (Milli-Q Biocel, Millipore, USA) was washed with dichloromethane twice before used.

2.2. Sample collection

Air particle samples were collected on the roof (about 8 m in height) of a buildings located at Pham Van Dong street, Cau Giay district, Ha Noi city (AP1, 21° 2'31.94"N and 105°46'53.00"E) and Phu Do town, Tu Liem district, Ha Noi city (AP2, 21° 0'41.79"N and 105°45'58.29"E), respectively. AP1 is represented for busy traffic road in which trucks, coaches, and motorbikes are main fleets, while AP2 is located in a highly populated residential area, which is well known as a handicraft village producing fresh noodles for Ha Noi city. At each sampling location and each day, day and night samples were collected separately (around 10 h for each sample) and continuously 6 days in April 2018 using simultaneously two Kimoto high-volume air sampler system (Model-120H). Air flow was adjusted at the rate of 400 liters per min. The ambient temperature ranged from 20 °C to 22 °C at night time and from 28 °C to 33 °C at day time. Each quartz fiber filter (quartz fiber filter) was wrapped in an aluminum foil enveloped and placed in a lockable polypropylene bag and transferred to the laboratory. The samples were kept in the desiccator for at least 24 hours before being quantified. Then the samples were stored at -20 °C until being analyzed.

2.3. Sample preparation

Dichloromethane has been confirmed to efficiently extract mixtures of chemicals with a broad range of physicochemical properties from solid waste-, water-, and air-sampling media [18]. In addition, it is used to extract compounds registered in the AIQS database (including PAEs and sterols) from water [19] and sediment [17]. Therefore, we used dichloromethane for the extraction PAEs and sterols from the atmospheric particulate matter with some modification. Briefly, half of a quartz fiber filter was cut into small species and placed in a 50 mL of brown centrifuge tube. A mixture of surrogate compounds (1 µg each), which have the same range of broad physico-chemical properties was spiked onto the filter to check the extraction efficiency. Sample was then immersed in 20 ml of dichloromethane and sonicated for 15 min in an ultrasonic bath at 26 ± 2 °C. After that, the sample was centrifuged for 10 min (2000 rpm). The extraction solution was collected into a 50 mL evaporating flask. This extraction procedure was repeated twice with solvent volume of 15 mL each. Combined extraction solution was concentrated to approximately 1 mL using a rotary evaporator, and then 5 mL hexane was added into the extract and further concentrated to 1 mL by using gentle nitrogen stream. The

concentrate was applied to a Na₂SO₄ column to remove water. After adding 1 µg of internal standards to the final concentrate, the 12 PAEs and 13 sterols compounds in the samples were determined and quantified by GC/MS instrument.

2.4. Chromatographic conditions

1 µl of the extract was injected onto the GC/MS, utilizing the sample injector. Capillary column DB5-MS was used for the separation of 12 phthalates and 13 sterols with selected ion monitoring (SIM). Measurement condition of GC/MS was shown in Table 2. The calibration curves for 12 PAEs were made with the concentration of 0.01, 0.02, 0.04, 0.1, 0.2, 0.4, 1.0, 2.0 mg/L and for 13 sterols were 0.01, 0.02, 0.04, 0.05, 0.1, 0.2, 0.4, 0.5, 1.0, 2.0, 5.0, 10.0 mg/L.

2.5. Quality control

Quality controls were performed by blank analysis, surrogate recovery analysis, and performance check standard (PCS) analysis. Laboratory blank samples were examined (one for every batch of 5 samples) by using the same analytical method as that used to examine the air particle samples. When reporting data, blank concentrations have been subtracted from the sample concentrations. Surrogate recovery analysis was used to assess the suitability of the extraction process for the study. Prior to extraction, air particle and blank samples were spiked with surrogate compounds in order to assess the efficiency of extraction processes.

Table 2. Measurement condition of GC-MS.

GC-MS	Shimadzu GCMS-QP 2010 Plus
Column	J&W DB-5 ms (5 % phenyl-95 % methylsilicone) fused silica capillary column, 30 m × 0.25 mm i.d., 0.25 µm film
Column temperature	2 min at 40 °C, °C/min to 310 °C, 4 min at 310 °C
Injector	250 °C
Transfer line	310 °C
Ion source	200 °C
Injector method	splitless, 1 min for purge-off time
Carrier gas	He
Linear velocity	40 mL/min, constant flow mode
Ionization method	EI
Tuning method	target tuning for US EPA method 625
Measurement method	SIM/Scan
Scan range	45 amu to 600 amu
Scan rate	0.3 s/scan

2.6. Statistical analysis

Statistical analysis was performed using Microsoft Excel 2007 (Microsoft Japan, Tokyo, Japan).

3. RESULTS AND DISCUSSION

3.1. Results of evaluating GC-MS performance

To check the operation condition of GC-MS for simultaneous identification and quantification of PAEs and sterols in the sample, we carried out GC-MS instrument tuning, calibration solution analysis and analysis of instrument PCS. The tuning results (Figure 1) showed that all the parameters were satisfied with the standard, such as the ratio of fragment ions m/z 69; m/z 219; m/z 502, peak shape, detector voltage was 1.06 (< 2).

Comparing the analytical results of PCS 1 mg/L (Table 3) with the standard analysis of PCS, the results showed that there is no peak tailing for benzidine and pentachlorophenol and their peak signal and intensity were clear (Figure 2, 3). Mass spectra of trans-nonachlor (Figure 4) were similar to the standard spectra. The decomposition of DDT to DDD was less than 20 %. Concentrations of most compounds in PCS were reached over 90 % of standard values. The PCS analytical results showed that the GC-MS instrument was in good and stable conditions, which are suitable for simultaneous identification and quantification of the organic compounds with AIQS-DB.

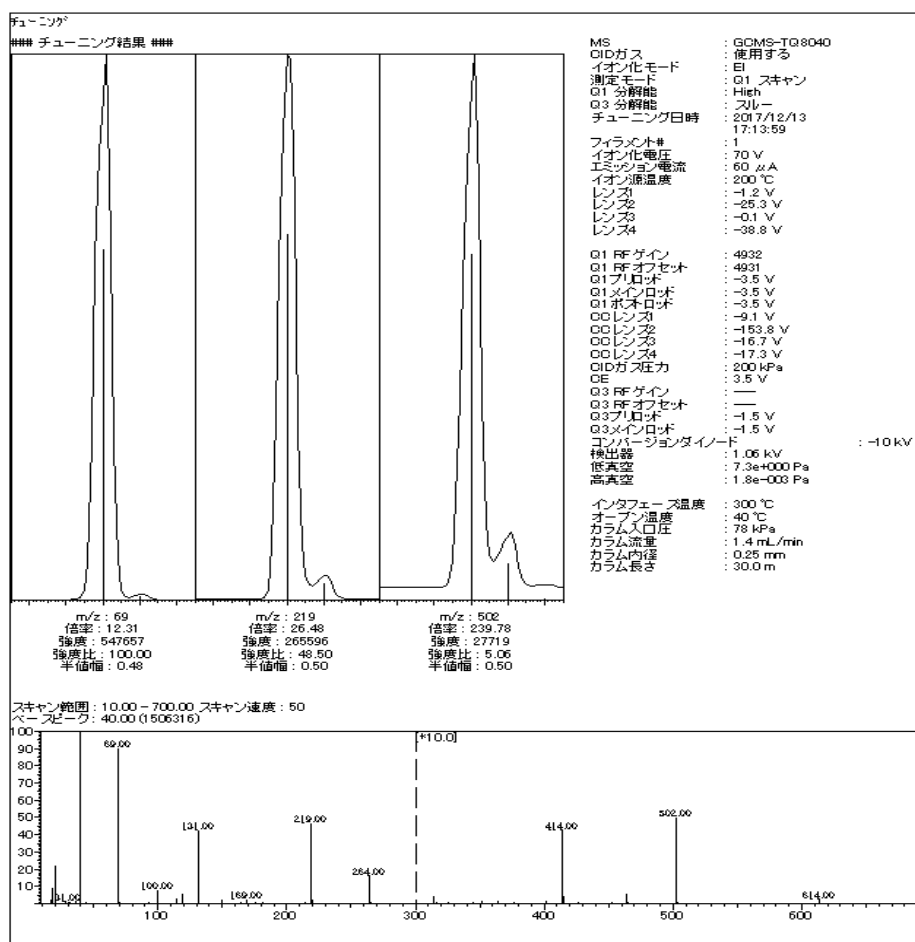


Figure 1. GCMS-TQ8000 tuning results.

Table 3. Analytical results of PCS solution.

No	Compound	Concentration, mg/L	No	Compound	Concentration, mg/L
1	Octanol	1.19	24	2,4-Dinitroaniline	1.27
2	Nitrobenzene	1.11	25	Isofenphos oxon	1.51
3	2,6-Dimethylphenol	1.11	26	Triphenylmethane	1.13
4	2,6-Dimethylaniline	1.09	27	Fluoranthene	0.89
5	2,6-Dichlorophenol	1.19	28	Benzidine	1.1
6	Benzothiazole	1.08	29	Pyrene	0.91
7	2,4-Dichloroaniline	1.14	30	trans-Nonachlor	1.61
8	Dimethyl phthalate	1.05	31	p,p'-DDE	0
9	Acenaphthylene	1.12	32	p,p'-DDD	0.01
10	Acenaphthene	1.14	33	p,p'-DDT	1.1
11	4-Nitrophenol	1.45	34	Thenylchlor	0.99
12	2,4-Dinitrotoluene	1.33	35	Captafol	1.1
13	2,3,5,6-Tetrachlorophenol	1.13	36	Benzo(a)anthracene	0.97
14	Fluorene	0.99	37	Chrysene	0.93
15	Tributyl phosphate	1.61	38	Pyridaben	1.14
16	2,4,6-Trinitrotoluene	1.23	39	Benzo(j&b)fluoranthene	1.01
17	1,2,4,5-Tetrabromobenzene	1.58	40	Benzo(k)fluoranthene	0.89
18	Pentachlorophenol	1.39	41	Quizalofop-ethyl	1.63
19	Tris(2-chloroethyl) phosphate	1.32	42	Benzo(a)pyrene	1.01
20	Chlorothalonil (TPN)	1.51	43	Perylene-d12	1.55
21	Phenanthrene	1.1	44	Azoxystrobin	1.67
22	Anthracene	1.14	45	Indeno(1,2,3-cd)pyrene	1.06
23	DFTPP	0.02	46	Dibenzo(a,h)anthracene	1.05

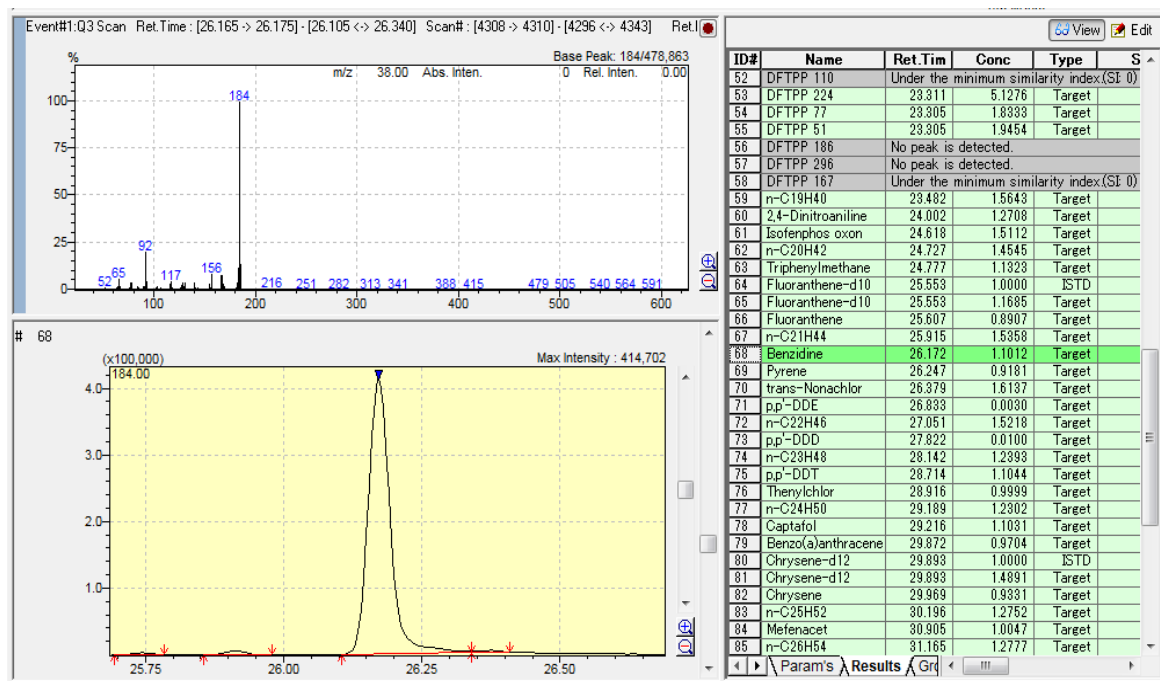


Figure 2. Peak shape of benzidine.

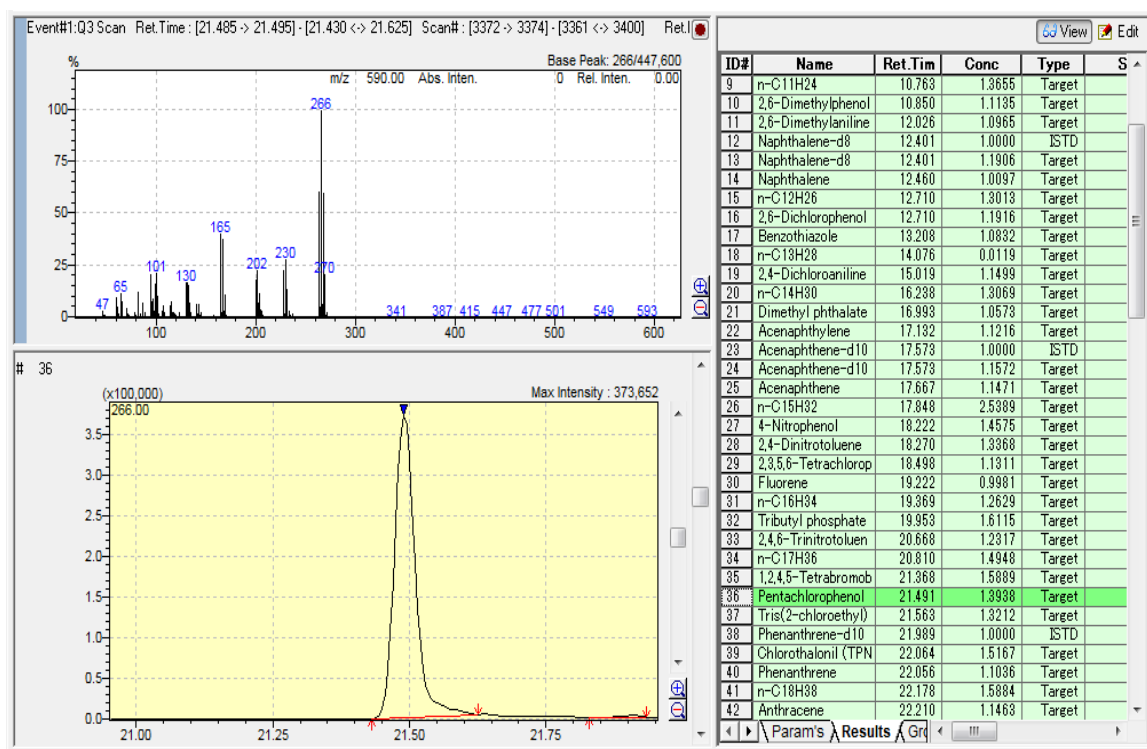


Figure 3. Peak shape of pentachlorophenol.

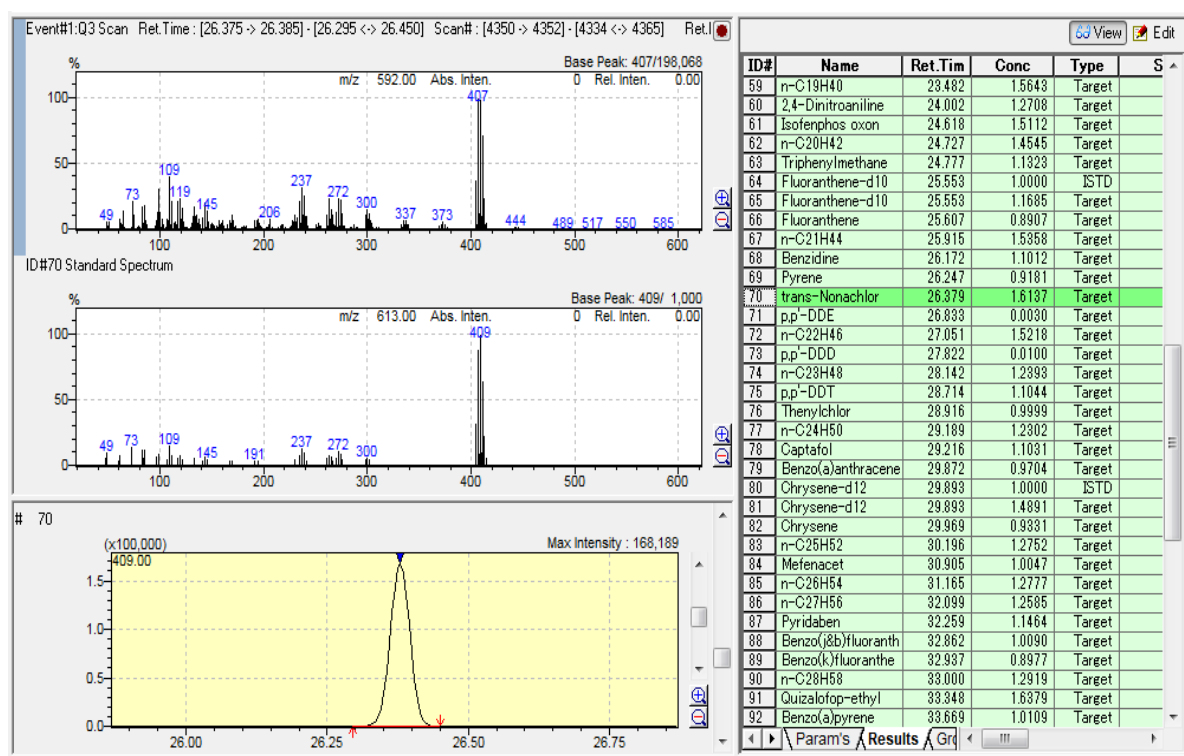


Figure 4. Mass spectra of trans-nonachlor.

3.2. Results of surrogate analysis and calibration curves

3.2.1. Results of surrogate analysis

Table 4. Recoveries of surrogate compounds (n = 24).

No	Compound	Average	RS
1	3,3'-Dichlorobenzidine-d6	0	0
2	2-Fluorophenol	36.9	11.0
3	1,2-Dichlorobenzene-d4	66.1	5.15
4	4-Chloroaniline-d4	32.1	24.6
5	BisphenolA-d14	75.5	9.08
6	2,4-Dichlorophenol-d3	82.6	6.30
7	p-Terphenyl-d14	85.8	3.76
8	C20D42	86.9	5.18
9	Benzophenone-d10	100	4.38
10	4-Nonylphenol-d4	102	4.25
11	Tris(2-	105	5.51
12	4,4'-DDT-13C12	107	4.22
13	Pentachlorophenol-13C6	131	6.56

^a One micro gram of each surrogate was added to the samples.

^b Relative standard deviation.

The analytical results of surrogate compounds (Table 4) showed that, good recoveries (75-131 %) were obtained for 9 out of 13 surrogate compounds except for volatile or basic compounds (2-fluorophenol, 1,2-dichlorobenzene-d4, 4-chloroaniline-d4, and 3,3'-dichlorobenzidine-d6), which evaporated or react with acidic compounds during pretreatment [18, 20]. Pentachlorophenol-13C6 showed high recovery rates (over 113 %, average 131 %), which probably due to the matrix effect [20]. Relative standard deviations (RSD) of surrogates were mostly below 11 % (Table 4) except for 4-chloroaniline-d4, confirming that sample analyses were acceptably precise. With the high recovery rates of surrogate analysis, it is confirmed that this method is capable for extraction of organic compounds in air particles.

3.2.2. Calibration curves

A calibration curve for 12 PAEs was made with the concentrations of 0.01, 0.02, 0.04, 0.1, 0.2, 0.4, 1.0, 2.0 mg/L and for 13 sterols was 0.01, 0.02, 0.04, 0.05, 0.1, 0.2, 0.4, 0.5, 1.0, 2.0, 5.0, 10.0 mg/L. All calibration curves of 12 PAEs and 13 sterols had good linearity with correlation coefficient values of over 0.995.

3.3. Analytical results of air particles samples

3.3.1. Analytical results of PAEs in air particles samples

Analytical results of PAEs in 24 air particle samples in two survey locations (Table 5, 6) showed that five out of 12 PAEs were detected. Three PAEs (di2-ethylhexylphthalate, di-n-butyl phthalate and di-iso-butyl phthalate) which are common used in industrial application were detected in all samples. Total concentration of these compounds was contributed 94 % of the total PAEs concentrations in 22 out of 24 air particles samples. The total PAEs concentrations in 24 samples were in the range of 52.5-228ng/m³.

There was no significant difference between the average concentrations of total PAEs in air particles at day (89.7 ng/m³) and night (68.7 ng/m³) at AP1. While at AP2, the concentrations of total PAEs in air particles in the nighttime (155.3 ng/m³) were much higher than those in the daytime (74.3 ng/m³). This probably due to the burning of material containing plastic for Bun production which usually occurred at night in Phu Do village that released PAEs into the air and air particles. Five PAEs were detected in most of air particles samples collected from AP1 and AP2, except DEP was detected in only 2 out of 12 samples at AP2. DEHP and DBP concentrations at AP2 (DEHP, 15.5-58.13 ng/m³; DBP, 19.6-76.3 ng/m³) were at elevated level as in Tainjin, China (DEHP, 98.923 ng/m³; DBP, 12.90 ng/m³) [21] and central of Paris, France (DEHP, 18.9 ng/m³) [22].

The detected PAEs are considered to be endocrine disrupters [23] and have high cancer potential [24]. Especially, DEHP is one of 33 toxic organic compounds in the aquatic environment reported by European Commission (Decision No. 2455/2001/EC dated on November 20th, 2001). Therefore, the high concentrations of DEHP, DBP and DiBP detected in all air particles samples in this study is likely to pose a risk to human health.



Table 5. PAEs concentration in air particles collected at AP1 – Pham Van Dong road.

Phthalate esters	Day-time						Night-time						Min-Max, Mean	SD, %		
	1	2	3	4	5	6	7	8	9	10	11	12				
Dimethyl phthalate	1.28	1.83	1.43	0.36	0.50	0.21	0.21-1.83, 0.94	0.66	1.40	1.06	0.24	0.20	0.12	0.27	0.12-1.40, 0.54	0.54
Diethyl phthalate	2.44	2.49	2.30	30.1	3.61	1.73	1.73-30.1, 7.11	11.28	2.42	1.86	20.2	3.40	1.68	1.15	1.15-20.2, 5.12	7.43
Di-iso-butyl phthalate	26.0	31.0	27.0	39.6	33.2	28.8	39.6-26.0, 30.93	4.99	28.4	19.7	34.1	22.3	23.1	21.5	19.7-34.1, 24.85	5.39
Di-n-butyl phthalate	24.3	28.4	23.5	36.1	27.1	23.5	23.5-36.1, 27.15	4.83	26.7	17.6	28.3	17.5	18.2	16.4	28.3-16.4, 20.78	5.26
Bis(2-ethylhexyl) phthalate	24.9	23.9	21.1	31.0	22.8	18.3	18.3-31.0, 23.67	4.28	21.6	14.7	23.5	15.0	16.6	13.2	13.2-23.5, 17.43	4.15
Total, ng/m ³	78.9	87.6	75.3	137	87.1	72.5	72.5-137, 89.73	23.95	80.5	55.0	106	58.5	59.7	52.5	52.5-106, 68.7	20.81

Table 6. PAEs concentration in air particles collected at AP2 – Phu Do village.

Phthalate esters	Day-time							Night-time								
	13	14	15	16	17	18	Min-Max, Mean	SD, %	19	20	21	22	23	24	Min-Max, Mean	SD, %
Dimethyl phthalate	0.21	0.17	0.18	0.34	0.43	0.00	0.0-0.43, 0.22	0.15	0.13	0.47	0.23	1.85	0.00	0.75	0.0-1.85, 0.57	0.68
Diethyl phthalate	1.41	0.00	0.00	0.00	0.00	0.00	0.0-1.41, 0.24	0.58	0.66	0.00	0.00	0.00	0.00	0.00	0.0-0.66, 0.11	0.27
Di-iso-butyl phthalate	27.4	26.3	24.2	31.4	44.7	23.8	24.2-44.7, 29.63	7.87	23.5	58.0	56.4	74.7	64.2	92.9	23.5-92.9, 61.62	23.02
Di-n-butyl phthalate	22.4	22.2	22.2	26.2	35.5	20.4	20.4-35.5, 24.82	5.57	19.6	47.3	44.7	63.0	53.5	76.3	19.6-76.3, 50.73	19.13
Bis(2-ethylhexyl) phthalate	15.5	18.3	19.6	20.4	24.7	18.3	15.5-24.7, 19.47	3.06	15.9	46.0	37.2	51.0	45.5	58.1	15.9-58.1, 42.28	14.64
Total, ng/m ³	66.9	66.9	66.1	78.3	105	62.5	66.1-105, 74.28	15.97	59.9	152	139	190	163	228	52.5-228, 155.3	56.44

3.3.2. Analytical results of sterols in air particles samples

Analytical results of sterols in 24 air particles samples in two survey locations (Table 7,8) showed that 7 out of 13 sterols were detected, in which cholesterol and beta-sitosterol were detected in all the samples, following by coprostanol, coprostannone (96 %), and stigmastanol (83 %). The total sterol concentrations in the air particle samples were in the range of 3.57-52.6 ng/m³ (average 12.5 ng/m³) with the number of detections ranged from 4 to 7 (average 5). Total sterol concentrations in air particles samples collected at AP1 and AP2 were low (< 9.30 ng/m³). By contrast, the total sterols concentrations in air particles samples collected in night-time at AP2 were at elevated level (24.5 ng/m³) with the total concentrations of cholesterol and beta-sitosterol contributed over 70 % of the total sterols concentration. In addition, Simoneit et al. (1999) and Nolte et al. (2001) indicated that cholesterol is usually detected at elevated levels due to the cooking and phytosterols (β -sitosterol, stigmasterol, campesterol) are detected in air particles [25, 26], which generated by burning wood and biomass [23, 26]. Therefore, the elevated level of sterol concentrations in the night-time at AP2 is probably related to the cooking activities and Bun production of local residents.

Coprostanol is an indicator of fecal pollution [27] and that a ratio of coprostanol to cholesterol (> 0.2) indicates sewage or human feces (> 0.3). In this study, the ratios of coprostanol to cholesterol were < 0.24 at all sampling sites. Although most of the recent studies has shown that the origins of sterols in air and air particles are derived from burning of plant biomass, cooking and other natural sources [11]. However, the analytical results of coprostanol to cholesterol ratios in air particles samples can also show that the origin of sterol in air particles in Ha Noi may be from untreated waste of the local pig farms in AP2, which were observed during sampling period. Untreated waste from local pig farms is discharged directly into the environment, then the waste is absorbed into the dust and fly into the air. However, an in-depth study is needed to determine the origins of sterols in air particles in Ha Noi. This is the first study of sterol analysis in air particles in Viet Nam and provides the new and important data for scientists to further studies on sterol pollution in air particles in the future.

Table 7. Sterols concentration in air particles samples collected at AP1 – Pham Van Dong road.

Sterols	Day-time								Night-time			
	1	2	3	4	5	6	7	8	9	10	11	12
Coprostanol	0.73	0.86	0.86	1.42	0.87	0.00	0.75	0.86	1.58	0.51	0.46	0.22
Cholesterol	4.61	5.36	3.96	7.05	3.81	2.28	5.63	4.47	9.21	2.57	2.27	2.40
Coprostannone	0.21	0.24	0.21	0.33	0.26	0.12	0.23	0.25	0.44	0.17	0.16	0.20
Campesterol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.31	0.79	0.38	0.00	0.00
Stigmasterol	0.00	0.62	0.00	1.34	0.00	0.34	1.08	0.88	3.05	0.80	0.00	0.00
beta-Sitosterol	1.43	2.37	1.40	2.86	0.86	0.83	2.06	2.31	5.74	1.91	0.78	0.06
Stigmastanol	0.57	0.57	0.44	0.62	0.00	0.00	0.75	0.75	1.00	0.24	0.35	0.19
Total, ng/m ³	7.56	10.0	6.87	13.6	5.81	3.57	10.5	9.83	21.8	6.57	4.03	3.07

Table 8. Sterols concentration in air particles samples collected at AP2 – Phu Do village.

Sterols	Day-time						Night-time					
	13	14	15	16	17	18	19	20	21	22	23	24
Coprostanol	0.47	0.39	0.59	0.59	0.46	0.38	0.42	1.53	0.79	0.67	1.65	1.35
Cholesterol	6.37	3.68	3.83	8.40	11.5	3.49	3.78	10.6	7.59	11.9	27.5	39.8
Coprostanone	0.00	0.19	0.19	0.25	0.18	0.18	0.08	0.18	0.14	0.35	0.53	0.63
Campesterol	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.38	0.26	0.00	1.14	1.25
Stigmasterol	0.30	0.00	0.00	0.51	0.66	0.00	0.00	2.33	1.49	0.00	3.11	3.75
beta-Sitosterol	0.71	0.58	1.06	1.67	1.16	0.51	0.25	3.62	3.23	1.90	6.16	4.44
Stigmastanol	0.00	0.29	0.21	0.17	0.54	0.26	0.30	0.67	0.91	0.00	1.06	1.43
Total, ng/m ³	8.04	5.14	5.88	11.6	14.5	4.81	4.83	19.3	14.4	14.8	41.1	52.6

4. CONCLUSIONS

The automated identification and quantification system with a GC-MS database (AIQS-DB) was applied successfully for simultaneous analysis of phthalate esters and sterols in air particles in Ha Noi. The calibration of the used GC-MS instrument results showed that it was in suitable condition for analysis of PAEs and sterols. The linearity of calibration curves of PAEs and sterols were good. This method is quick, simple and cost-effective. As a result, this analytical method was applied to analyze the occurrence of 12 PAEs and 13 sterols in air particles in Ha Noi.

In addition, the preliminary study on the occurrence of PAEs and sterols in 24 air particles samples collected in two typical areas of Hanoi showed that 5 out of 12 PAEs and 7 out of 13 sterols were detected. The concentrations of DEHP, DBP and DiBP were highest, contributed 94 % of the total detected PAEs concentration, which may pose a serious risk to human health. Cholesterol and beta-sitosterol were frequently detected at elevated levels in all the samples and accounted more than 70 % of the total detected sterols concentration at Phu Do village. This result demonstrated that high population density and the Bun production at the night-time were considered to be the main contributor to sterols inputs in the air particles in Hanoi. The primary results obtained from this study will be the new and important data for the management authorities to propose appropriate solutions and countermeasures to improve air quality in Viet Nam, particularly in urban areas.

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