

Simultaneous determination of semivolatile organic compounds in indoor air by gas chromatography–mass spectrometry after solid-phase extraction

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Abstract

A method is described for simultaneous determination of semivolatile organic compounds (SVOCs) in indoor air by gas chromatography–mass spectrometry (GC–MS). The selected 73 SVOCs were collected using combined adsorbents (quartz fiber filter disk and Empore disk) for 24 h at a 5.0 l/min flow rate. The SVOCs collected were extracted with acetone, concentrated, then analyzed by an internal standard method. Forty compounds (19 plasticizers and flame retardants; 19 insecticides; 1 synergist; and 1 fungicide) among the target SVOCs were determined accurately and precisely. The method of detection limits for these compounds were approximately 0.5 ng/m³ for most of the SVOCs. The collected SVOC samples could be stored for up to 1 month at 4 °C in the refrigerator.

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1. Introduction

Many chemicals are present in indoor air and exposure to them is one of the causes of the ‘sick building syndrome’ and ‘multiple chemical sensitivity’ [1,2]. In general, the airborne concentrations of semivolatile organic compounds (SVOCs), with boiling points from 240 or 260 to 380 or 400 °C [3], seem to be lower than those of volatile organic compounds (VOCs), with boiling points from 50 or 100 to 240 or 260 °C [3], because the vapor pressures of SVOCs are lower than those of VOCs. However, the SVOCs include several pesticides having toxicities on nerve systems and some phthalates having endocrine disrupting effects. Thus, knowing the exposure concentrations to SVOCs is important for evaluating their effects on humans in indoor environments. However, there are few reports concerning SVOC concentrations in indoor air compared with those for VOCs [4–10].

Simultaneous determination of the multiple compounds can be done by chromatographic analysis [11]. Specifically,

gas chromatography–mass spectrometry (GC–MS) is advantageous for identification of unknown components and for separating the objective components from interfering materials.

For the analysis of airborne SVOCs, various sampling procedures have been attempted using filters such as activated carbon fiber filter [12] and glass fiber filter [13] or using solid sorbent tubes packed with XAD-2 [14], silica gel [15], XAD-4 [16], octadecylsilane (ODS) [17], activated carbon [7,18] and polyurethane foam [5,19]. The sampling efficiencies of these adsorbents were compared using several SVOCs by Roper and Wright [20], Gonzalez et al. [21] and Leidy and Wright [22]. Recently, samplers with a combination of a filter (glass-fiber or quartz-fiber) and a secondary solid sorbent [6,9,23–25] have also been employed for sampling of airborne SVOCs, because most SVOCs can exist in air as both aerosols and vapors.

A disk-type filter is more advantageous than a tube-type sorbent for determining trace amounts of compounds in air because it does not restrict the flow rate of the pump. Saito et al. [4] and Matsumura et al. [26] have described analytical methods of organophosphorus compounds in air using a quartz fiber filter disk followed by an ODS filter disk and GC–flame photometric detection.

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In the present study, we tried to simultaneously determine 73 SVOCs (plasticizers, flame retardants, insecticides, fungicides and synergists that are often used in combination with the various insecticides to potentiate the pesticidal effects), which are highly likely to be detected in indoor air, using the above two combined disk-type filters and a GC–MS system.

2. Experimental

2.1. Chemicals

The purchase sources and purities of the standard materials for determination of the SVOCs are shown in Table 1.

The standard materials were used without further purification. Acetone, which was of a grade for pesticide residue and polychlorinated biphenyl analysis, and [²H₁₀] fluoranthene (fluoranthene-d₁₀; molecular formula, C₁₆H₁₀; molecular mass, 212.3; purity, 99.3%) as an internal standard were obtained from Wako Pure Chemical (Osaka, Japan).

2.2. Equipment

A Shimadzu (Kyoto, Japan) GCMS-QP2010 gas chromatograph–mass spectrometer, combined with a Shimadzu AOC-20i auto injector, was controlled with a Fujitsu (Kanagawa, Japan) FM V-6766CL7c computer installed GCMS solution Ver. 2.10 software for instrument control and data

Table 1
Objective SVOCs for determination and purchase sources of standard materials

| SVOC | CAS no. | Molecular formula | Molecular weight | Maker ^a | Purity (%) |
|---|------------|---|------------------|--------------------|------------|
| Plasticizers and flame retardants | | | | | |
| Benzylbutyl phthalate | 85-68-7 | C ₁₉ H ₂₀ O ₄ | 312.4 | W | 99.8 |
| Di(2-ethylhexyl)adipate | 103-23-1 | C ₂₂ H ₄₂ O ₄ | 370.6 | W | 100.6 |
| Di(2-ethylhexyl)phthalate | 117-81-7 | C ₂₄ H ₃₈ O ₄ | 390.6 | W | 99.6 |
| Dicyclohexyl phthalate | 84-61-7 | C ₂₀ H ₂₆ O ₄ | 330.4 | W | 100.0 |
| Diethyl phthalate | 84-66-2 | C ₁₂ H ₁₄ O ₄ | 222.2 | W | 99.7 |
| Diisobutyl phthalate | 84-69-5 | C ₁₆ H ₂₂ O ₄ | 278.3 | W | 99.4 |
| Di- <i>n</i> -butyl phthalate | 84-74-2 | C ₁₆ H ₂₂ O ₄ | 278.3 | W | 99.6 |
| Di- <i>n</i> -heptyl phthalate | 3648-21-3 | C ₂₂ H ₃₄ O ₄ | 362.5 | Al | 97.0 |
| Di- <i>n</i> -hexyl phthalate | 84-75-3 | C ₂₀ H ₃₀ O ₄ | 334.5 | T | 99.6 |
| Dimethyl phthalate | 131-11-3 | C ₁₀ H ₁₀ O ₄ | 194.2 | W | 99.9 |
| Di- <i>n</i> -pentyl phthalate | 131-18-0 | C ₁₈ H ₂₆ O ₄ | 306.4 | T | 99.5 |
| Di- <i>n</i> -propyl phthalate | 131-16-8 | C ₁₄ H ₁₈ O ₄ | 250.3 | K | 99.9 |
| Tributyl phosphate | 126-73-8 | C ₁₂ H ₂₇ O ₄ P | 266.3 | W | 99.9 |
| Tricresyl phosphate | 1330-78-5 | C ₂₁ H ₂₁ O ₄ P | 368.4 | T | 99.7 |
| Triethyl phosphate | 78-40-0 | C ₆ H ₁₅ O ₄ P | 182.2 | W | 99.9 |
| Triphenyl phosphate | 115-86-6 | C ₁₈ H ₁₅ O ₄ P | 326.3 | W | 99.9 |
| Tripropyl phosphate | 513-08-6 | C ₉ H ₂₁ O ₄ P | 224.2 | P | 97.0 |
| Tris(2-butoxyethyl)phosphate | 78-51-3 | C ₁₈ H ₃₉ O ₇ P | 398.5 | Al | 94.0 |
| Tris(2-chloroethyl)phosphate | 115-96-8 | C ₆ H ₁₂ Cl ₃ O ₄ P | 285.5 | W | 100.0 |
| Tris(1,3-dichloro-2-propyl)phosphate | 13674-87-8 | C ₉ H ₁₅ Cl ₆ O ₄ P | 430.9 | T | 95.6 |
| Tris(2-ethylhexyl)phosphate | 78-42-2 | C ₂₄ H ₅₁ O ₄ P | 434.6 | T | 99.5 |
| Insecticides | | | | | |
| Allethrin | 584-79-2 | C ₁₉ H ₂₆ O ₃ | 302.4 | W | 99.2 |
| Bifenthrin | 82657-04-3 | C ₂₃ H ₂₂ ClF ₃ O ₂ | 422.9 | W | 99.6 |
| Carbaryl | 63-25-2 | C ₁₂ H ₁₁ NO ₂ | 201.2 | W | 99.9 |
| Chlorpyrifos | 2921-88-2 | C ₉ H ₁₁ Cl ₃ NO ₃ PS | 350.6 | W | 99.9 |
| Chlorpyrifosmethyl | 5598-13-0 | C ₇ H ₇ Cl ₃ NO ₃ PS | 322.5 | Dr | 99.5 |
| Cyfluthrin | 68359-37-5 | C ₂₂ H ₁₈ Cl ₂ FNO ₃ | 434.3 | Dr | 98.5 |
| Cyphenothrin | 39515-40-7 | C ₂₄ H ₂₅ NO ₃ | 375.5 | R | 96.5 |
| Deltamethrin | 52918-63-5 | C ₂₂ H ₁₉ Br ₂ NO ₃ | 505.2 | Dr | 99.0 |
| Diazinon | 333-41-5 | C ₁₂ H ₂₁ N ₂ O ₃ PS | 304.3 | W | 99.8 |
| Dichlofenthion | 97-17-6 | C ₁₀ H ₁₃ Cl ₂ O ₃ PS | 315.2 | W | 98.4 |
| Dichlorvos | 62-73-7 | C ₄ H ₇ Cl ₂ O ₄ P | 221.0 | W | 98.2 |
| <i>N,N</i> -Diethyl- <i>m</i> -toluamide (DEET) | 134-62-3 | C ₁₂ H ₁₇ NO | 191.3 | W | 96.0 |
| Empenthrin ^b | 54406-48-3 | C ₁₈ H ₂₆ O ₂ | 274.4 | Ea | 95.0 |
| Ethofenprox | 80844-07-1 | C ₂₅ H ₂₈ O ₃ | 376.5 | K | 99.9 |
| Fenitrothion | 122-14-5 | C ₉ H ₁₂ NO ₃ PS | 277.2 | W | 99.9 |
| Fenobucarb | 3766-81-2 | C ₁₂ H ₁₇ NO ₂ | 207.3 | W | 99.8 |
| Fenoxycarb | 79127-80-3 | C ₁₇ H ₁₉ NO ₄ | 301.3 | W | 99.6 |
| Fenthion | 55-38-9 | C ₁₀ H ₁₅ O ₃ PS ₂ | 278.3 | Dr | 95.5 |
| Furamethrin ^b | 23031-38-1 | C ₁₈ H ₂₂ O ₃ | 286.4 | Da | 91.8 |
| Hydramethylnon | 67485-29-4 | C ₂₅ H ₂₄ F ₆ N ₄ | 494.5 | Ac | 99.4 |

Table 1 (Continued)

| SVOC | CAS no. | Molecular formula | Molecular weight | Maker ^a | Purity (%) |
|--|-------------|--|------------------|--------------------|------------|
| Imiprothrin ^b | 72963-72-5 | C ₁₇ H ₂₂ O ₄ N ₂ | 318.4 | Ea | 50.0 |
| Malathion | 121-75-5 | C ₁₀ H ₁₉ O ₆ PS ₂ | 330.4 | W | 99.8 |
| Methoprene | 40596-69-8 | C ₁₉ H ₃₄ O ₃ | 310.5 | Dr | 98.0 |
| Metoxadiazone ^b | 60589-06-2 | C ₁₀ H ₁₀ N ₂ O ₄ | 222.2 | Ea | 97.2 |
| Permethrin | 52645-53-1 | C ₂₁ H ₂₀ Cl ₂ O ₃ | 391.3 | Dr | 97.5 |
| Phenothrin | 26002-80-2 | C ₂₃ H ₂₆ O ₃ | 350.5 | Dr | 94.5 |
| Prallethrin ^b | 23031-36-9 | C ₁₉ H ₂₄ O ₃ | 300.4 | Ea | 92.5 |
| Propetamphos | 31218-83-4 | C ₁₀ H ₂₀ NO ₄ PS | 281.3 | Ac | 97.8 |
| Propoxur | 114-26-1 | C ₁₁ H ₁₅ NO ₃ | 209.2 | W | 99.6 |
| Pyridaphenthion | 119-12-0 | C ₁₄ H ₁₇ N ₂ O ₄ PS | 340.3 | W | 100.0 |
| Pyriproxyfen | 95737-68-1 | C ₂₀ H ₁₉ NO ₃ | 321.4 | W | 100.0 |
| Resmethrin | 10453-86-8 | C ₂₂ H ₂₆ O ₃ | 338.4 | Ac | 94.0 |
| Silafuofen | 105024-66-6 | C ₂₅ H ₂₉ FO ₂ Si | 408.6 | W | 96.7 |
| Tetrachlorvinphos | 22248-79-9 | C ₁₀ H ₉ Cl ₄ O ₄ P | 366.0 | W | 99.5 |
| Tetramethrin | 7696-12-0 | C ₁₉ H ₂₅ NO ₄ | 331.4 | Dr | 99.1 |
| Tripropyl isocyanurate ^b | 4015-16-1 | C ₁₂ H ₂₁ N ₃ O ₃ | 255.3 | Ei | 96.3 |
| Synergists | | | | | |
| MGK-264 | 113-48-4 | C ₁₇ H ₂₅ NO ₂ | 275.4 | Ac | 97.4 |
| 2,3,3,3,2',3',3'-Octachlorodipropylether (OCDPE) | 127-90-2 | C ₆ H ₆ Cl ₈ O | 377.7 | R | 99.0 |
| Piperonyl butoxide | 51-03-6 | C ₁₉ H ₃₀ O ₅ | 338.4 | W | 94.3 |
| Fungicides | | | | | |
| 1-Bromo-3-ethoxycarbonyloxy-1,2-diiodo-1-propene (BECDIP) ^b | 52465-53-1 | C ₆ H ₇ O ₃ BrI ₂ | 460.8 | Sa | 99.1 |
| 1-Chloronaphthalene | 90-13-1 | C ₁₀ H ₇ Cl | 162.6 | W | 89.9 |
| 1-(4-Chlorophenyl)-3-iodopropargyl formal (CPIP) ^b | 29772-02-9 | C ₁₀ H ₈ O ₂ ClI | 322.5 | N | 97.0 |
| Chlorothalonil | 1897-45-6 | C ₈ Cl ₄ N ₂ | 265.9 | W | 99.7 |
| Cyproconazole | 94361-06-5 | C ₁₅ H ₁₈ ClN ₃ O | 291.8 | W | 100.0 |
| Dichlofluanid | 1085-98-9 | C ₉ H ₁₁ Cl ₂ FN ₂ O ₂ S ₂ | 333.2 | W | 100.0 |
| Difolatan | 2425-06-1 | C ₁₀ H ₉ Cl ₄ NO ₂ S | 349.1 | W | 98.7 |
| Furmecycloz | 60568-05-0 | C ₁₄ H ₂₁ NO ₃ | 251.3 | R | 98.2 |
| 3-Iodo-2-propynyl- <i>N</i> -butylcarbamate (IPBC) | 55406-53-6 | C ₈ H ₁₂ INO ₂ | 281.1 | Al | 97.0 |
| Pentachlorophenol | 87-86-5 | C ₆ HCl ₅ O | 266.3 | W | 99.5 |
| Thiabendazole | 148-79-8 | C ₁₀ H ₇ N ₃ S | 201.3 | W | 99.6 |
| 2-(Thiocyanomethylthio)benzothiazole (TCMTB) | 21564-17-0 | C ₉ H ₆ N ₂ S ₃ | 238.3 | Su | 99.5 |
| Thiuram | 137-26-8 | C ₆ H ₁₂ N ₂ S ₄ | 240.4 | W | 99.9 |

^a Abbreviations of the manufacturers are as follows: Ac, AccuStandard (New Haven, CT, USA); Al, Aldrich (Milwaukee, WI, USA); Da, Dainihon Jochugiku (Osaka, Japan); Dr, Dr. Ehrenstorfer GmbH (Augsburg, Germany); Ea, Earth Chemical (Tokyo, Japan); Ei, Eiko Kasei (Fukushima, Japan); K, Kanto Chemical (Tokyo, Japan); N, Nagase Kasei (Kyoto, Japan); P, Pfaltz&Bauer (Waterbury, CT, USA); R, Riedel-de Haen (Seelze, Germany); Sa, Sankyo (Tokyo, Japan); Su, Supelco (Bellefonte, PA, USA); T, Tokyo Kasei Kogyo (Tokyo, Japan); W, Wako (Osaka, Japan).

^b These compounds were giveaway samples from the manufacturer and were not available as reagents.

analysis. A sampler and a small suction pump for airborne SVOCs collection were obtained from GL Sciences (Model EMO-47, Tokyo, Japan) and Sibata Scientific Technology (Model MP-Σ500, Tokyo, Japan), respectively. A Hitachi (Tokyo, Japan) Model Himac CF7D centrifuge was used. An ultrasonic bath was purchased from Elma (Transsonic T570, Singen, Germany). A GL Sciences Model Soldry SD905 was used to concentrate the sample solutions.

All the glassware for preparation of the samples and standard solutions used during the experiments were washed with deionized water and acetone and then dried at room temperature.

2.3. Sampling of SVOCs

Airborne SVOCs were collected using the sampler packed with two adsorbents and a small suction pump. A quartz fiber filter disk (Type 2500 QAT-UP, 47 mm diameter, ca.

0.64 mm thickness, Tokyo Dylec, Tokyo, Japan) and an Empore disk (Type C18FF, 47 mm diameter, ca. 0.50 mm thickness, 3 M, MN, USA), which were set in the first and second layer, respectively, in the sampler, were used as adsorbents. Prior to the sampling of airborne SVOCs, the Empore disks were subjected to ultrasonic cleaning five times for 10 min each by 10 ml of acetone per disk, and the quartz fiber filter disks were heated at 400 °C for 4 h by applying the method by Saito et al. [27].

The sampler was fixed using a tripod in the center of the target room at a height of 1.2–1.5 m from the floor, and the SVOCs in the indoor air were collected for 24 h using the suction pump adjusted to a flow rate of 5.0 l/min. The total volume of air passed through the adsorbents resulted in 7.2 m³. This large sampling volume is necessary because many SVOCs exist only trace amounts in indoor air. The temperatures in the room were monitored automatically at 10 min intervals during the sampling of the airborne SVOCs

by using a Sato Keiryoki (Tokyo, Japan) Model SK-L200TH Thermo-Recorder.

After the sampling, the double ends of the sampler were sealed with caps and the entire sampler was wrapped in aluminum foil and transported to our laboratory. The two adsorbents, quartz fiber filter disk and Empore disk, packed in the sampler were removed together into a 10 ml centrifuge tube. The tube was wrapped with aluminum foil and stored at 4 °C in a refrigerator until analysis. A sampler containing the two adsorbents without the SVOC sample was used as a travel blank.

2.4. Target SVOCs

The compounds analyzed were the 73 SVOCs shown in Table 1, namely 21 plasticizers and flame retardants, 36 insecticides, 3 synergists and 13 fungicides. These were compounds which were expected to be detected in indoor air based on information on the use of chemicals [28–30] and our survey of marketed products.

2.5. Mixed SVOC stock solution and internal standard solution

Each stock standard solution of 68 SVOCs except for propetamphos, MGK-264, resmethrin, hydramethynon and thiabendazole was prepared with 10.0 mg/ml of each compound by dissolving it in acetone in 10 ml brown high-airtight vials (Kanto Kagaku, Tokyo, Japan). Solutions of propetamphos, MGK-264, resmethrin and hydramethyl-non were prepared at 5.0 mg/ml, and that of thiabendazole at 2.0 mg/ml, as for the above 68 SVOCs. Aliquots of these stock standard solutions were combined, and the mixed SVOC stock solution of 73 compounds was prepared at 123.5 µg/ml in another 10 ml brown high-airtight vial.

A solution of the internal standard, fluoranthene-d₁₀, was prepared at 100 µg/ml by dissolving the compound in acetone in a 2 ml brown high-airtight vial.

All of these solutions were stored at 4 °C in a refrigerator.

2.6. Standard solutions of SVOCs

The mixed SVOC stock solution was diluted with acetone on each day of analysis at concentrations of 0, 0.12, 0.23, 0.47, 0.94, 1.88, 3.75, 7.50, 15.0 and 30.0 µg/ml. A 0.3 ml portion of each solution was decanted into the vials for the auto-injector combined with the analytical equipment, and the working standard solutions of SVOCs were prepared by adding 3.0 µl of the internal standard solution to each of them using a micro syringe.

2.7. Sample preparation

Acetone, 8.0 ml, was added to the 10 ml centrifuge tube containing two adsorbents, and the SVOCs were extracted by ultrasonication for 15 min and then shaking for 10 min. After

centrifugation (2000 rpm for 10 min) to remove particulate matter, a 5.0 ml of the supernatant was decanted into another brown tube. The extract with 3.0 µl of the internal standard solution was concentrated to 0.3 ml using the Soldry SD905 under a stream of nitrogen gas (flow rate, 150 ml/min per tube; temperature, 30 °C; purity of the gas, >99.999%). The concentrated solution was transferred to the vial of the auto injector.

2.8. Gas chromatography–mass spectrometry

The analytical conditions for GC–MS were as follows: injection mode into the gas chromatograph, splitless; sampling time, 2.0 min; injection amount, 1.0 µl; capillary column, DB-1 (30 m × 0.25 mm i.d., 0.25 µm film thickness, J&W Scientific, CA, USA); column oven temperature, programmed from 60 to 300 °C at 5 °C/min and kept for 10 min at the final temperature; injection port temperature, 300 °C; carrier gas, helium; carrier gas pressure, 68.4 kPa; total flow rate, 20.0 ml/min; column flow rate, 1.14 ml/min; interface temperature, 300 °C; ionization method on the mass spectrometer, electron impact mode (EI); ionization energy, 70 eV; ionization current, 60 µA; ion source temperature, 200 °C; analytical mode, selected ion monitoring (SIM); grouping for ion monitoring, 8 (7.0–19.0, 19.0–23.4, 23.4–26.7, 26.7–28.1, 28.1–30.3, 30.3–34.7, 34.7–40.6, and 40.6–50.0 min). The ions selected for SIM quantification of the compounds are listed in Table 2.

2.9. Calibration

The SVOCs in indoor air were determined by the internal standard method. Their concentrations were calculated by interpolation from the linear least-squares regression line of the multi-level standard curve plot of peak-area ratio (areas SVOCs/area internal standard) versus the concentration of SVOCs in the working standard solutions.

The amounts of each compound in the sample and the travel blank were calculated with the following equation:

$$X = \left[\left[\frac{(A/I_a)}{S} \right] \left(\frac{P}{100} \right) \right] 0.3 \left(\frac{8}{5} \right) 1000 \quad (1)$$

where X (ng) is the amount of SVOCs in the adsorbents; A the peak-area of SVOCs; I_a is the peak-area of the internal standard; S the slope of the calibration curve; P the purity (%) of the SVOCs standard material.

Airborne concentrations of SVOCs were calculated with the following equation:

$$C = \frac{[(X_s - X_b) \times 1000]}{(FT \times 60)} \quad (2)$$

where C (ng/m³) is the airborne concentrations of SVOCs at mean temperature during air sampling; X_s (ng) the amount of SVOCs in the sample; X_b (ng) the amount of SVOCs in the travel blank; F (l/min) the flow rate of the suction pump in sampling; T (h) the sampling time.

Table 2
Selected target ions and reference ions (*m/z*) for GC–MS analysis of SVOCs

| SVOC ^a | Target | Reference |
|--------------------------------------|--------|-----------|
| Triethyl phosphate | 99.0 | 155.1 |
| Dichlorvos | 109.0 | 185.1 |
| 1-Chloronaphthalene | 162.1 | 127.1 |
| Tripropyl phosphate | 99.0 | 141.1 |
| Dimethyl phthalate | 163.1 | 77.1 |
| DEET | 119.1 | 190.2 |
| Thiuram | 88.1 | 144.1 |
| Diethyl phthalate | 149.1 | 150.2 |
| Propoxur | 110.1 | 152.2 |
| Fenobucarb | 121.1 | 150.2 |
| IPBC | 165.0 | 182.0 |
| Tributyl phosphate | 99.1 | 155.1 |
| Tripropyl isocyanurate | 214.3 | 56.0 |
| Empenthrin | 123.1 | 91.1 |
| Tris(2-chloroethyl)phosphate | 249.1 | 251.1 |
| Metoxadiazone | 120.1 | 222.2 |
| Pentachlorophenol | 266.0 | 264.0 |
| Di- <i>n</i> -propyl phthalate | 149.1 | 191.2 |
| Propetamphos | 138.0 | 194.0 |
| Chlorothalonil | 266.0 | 268.0 |
| Diazinon | 179.2 | 137.1 |
| BECDIP | 306.9 | 333.0 |
| Furmecyclox | 123.1 | 251.3 |
| Diisobutyl phthalate | 149.1 | 57.1 |
| CPIP | 165.1 | 257.1 |
| Dichlofenthion | 279.1 | 281.1 |
| Carbaryl | 115.1 | 116.1 |
| Chlorpyrifosmethyl | 286.1 | 287.9 |
| Furamethrin | 119.1 | 123.1 |
| OCDPE | 131.9 | 129.9 |
| Fenitrothion | 125.0 | 277.1 |
| Dichlofluandil | 123.1 | 224.1 |
| Di- <i>n</i> -butyl phthalate | 149.1 | 223.2 |
| Malathion | 173.2 | 127.1 |
| Fenthion | 278.1 | 169.1 |
| Chlorpyrifos | 197.0 | 314.1 |
| MGK-264 | 164.1 | 177.1 |
| Thiabendazole | 201.2 | 174.1 |
| Allethrin | 123.2 | 136.2 |
| TCMTB | 180.1 | 238.1 |
| Prallethrin | 123.2 | 105.2 |
| Tetrachlorvinphos | 329.1 | 331.1 |
| Methoprene | 73.1 | 111.1 |
| Di- <i>n</i> -pentyl phthalate | 149.1 | 237.2 |
| Cyproconazol | 222.2 | 138.9 |
| Imiprothrin | 123.1 | 151.2 |
| Tris(1,3-dichloro-2-propyl)phosphate | 75.1 | 381.1 |
| Benzylbutyl phthalate | 149.1 | 206.3 |
| Di- <i>n</i> -hexyl phthalate | 149.1 | 251.2 |
| Difolatan | 79.1 | 80.1 |
| Triphenyl phosphate | 326.2 | 325.2 |
| Resmethrin | 123.1 | 171.1 |
| Piperonyl butoxide | 176.1 | 177.2 |
| Tris(2-butoxyethyl)phosphate | 85.2 | 199.2 |
| Di(2-ethylhexyl)adipate | 129.1 | 147.0 |
| Pyridaphenthion | 340.3 | 199.2 |
| Tetramethrin | 164.2 | 123.1 |
| Fenoxycarb | 116.1 | 186.2 |
| Bifenthrin | 181.2 | 166.2 |

Table 2 (Continued)

| SVOC ^a | Target | Reference |
|--|--------|-----------|
| Tris(2-ethylhexyl)phosphate | 99.1 | 113.2 |
| Dicyclohexyl phthalate | 149.1 | 167.1 |
| Phenothrin | 123.1 | 183.2 |
| Di- <i>n</i> -heptyl phthalate | 149.1 | 265.3 |
| Pyriproxyfen | 136.2 | 226.2 |
| Di(2-ethylhexyl)phthalate | 149.1 | 167.1 |
| Tricresyl phosphate | 368.3 | 367.3 |
| Cyphenothrin | 123.2 | 81.1 |
| Permethrin | 183.1 | 163.1 |
| Cyfluthrin | 163.1 | 226.2 |
| Ethofenprox | 163.1 | 135.1 |
| Silafluofen | 179.2 | 286.2 |
| Deltamethrin | 181.2 | 253.0 |
| Hydramethylnon | 491.4 | 492.4 |
| Fluoranthene-d ₁₀ (internal standard) | 212.3 | 213.3 |

^a Compounds are listed in the order of column retention times.

The compounds, which were mixtures of several isomers such as pyrethroids, were quantitated using the total amounts of peak-areas of the isomers on the basis of the assumption that the sensitivities of all isomers were the same in the detection.

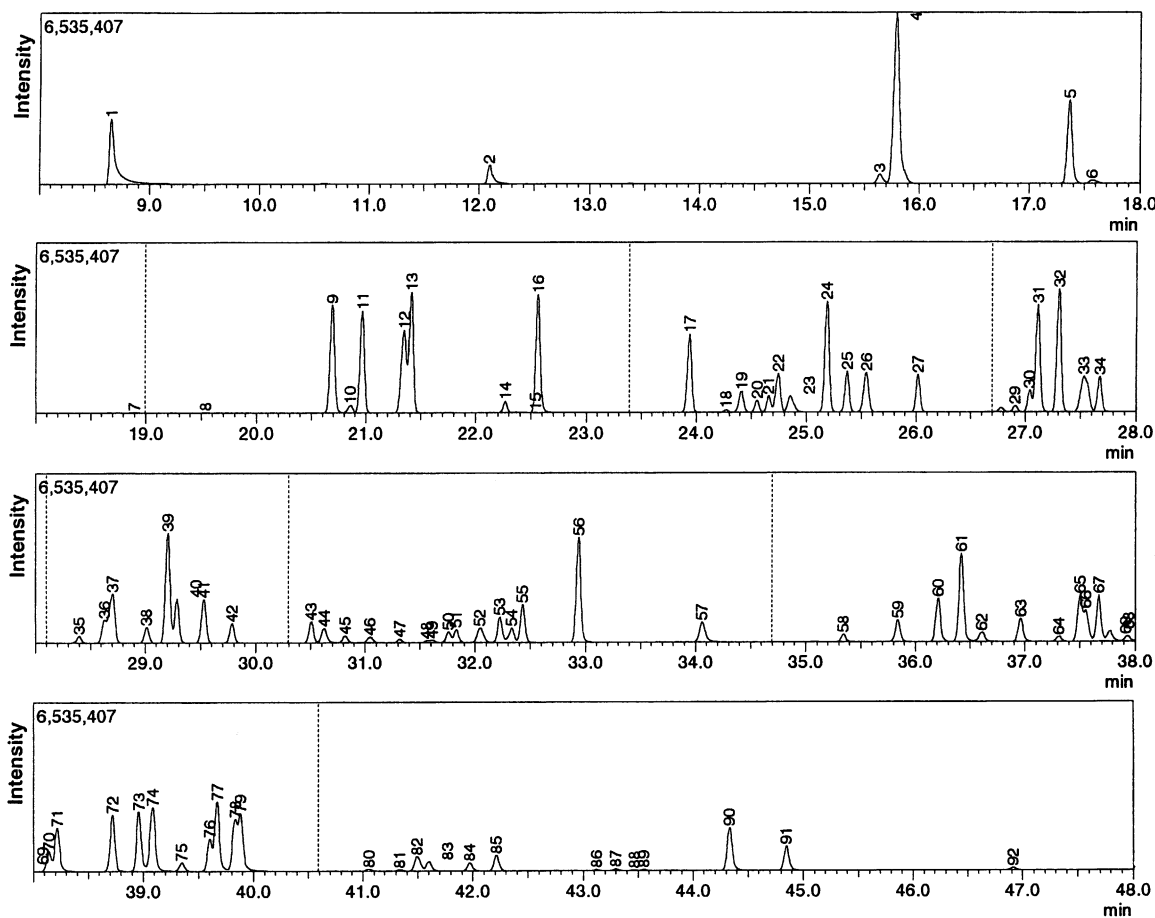
2.10. Storage stabilities of SVOCs in adsorbents

One each of a quartz fiber filter disk and an Empore disk without sampling were inserted into 27 centrifuge tubes. A 60 µl portion of the mixed SVOC stock solution (7.4 µg of each SVOC) was spiked to the adsorbents in these tubes. SVOCs in three tubes were analyzed immediately after preparation. The average concentrations of each compound determined for the three tubes were considered to be those of SVOCs at time zero. The remaining centrifuge tubes were wrapped with aluminum foil, and stored at 4 °C in the refrigerator until analysis. The contents of three samples each were analyzed periodically.

3. Results and discussion

3.1. Chromatography

Total ion chromatogram (TIC) of the standard solution containing 73 SVOCs (15.0 µg/ml each) determined by GC–MS is shown in Fig. 1. All compounds were resolved within 48 min. The multiple peaks based on the isomers appeared on the chromatogram of most of the pyrethroids (empenthrin, furamethrin, allethrin, prallethrin, imiprothrin, resmethrin, tetramethrin, phenothrin, cyphenothrin, permethrin, cyfluthrin, deltamethrin), MGK-264 and tricresyl phosphate. In TIC, the peaks of some SVOCs overlapped with each other (Peak nos. 4, 19, 23, 33, 37, 52, 66, 82 and 84 in Fig. 1), namely, their separation was insufficient. However, the target ions and the reference ions of these SVOCs shown in Table 2 did not exist or only trace



| No. | SVOC | R.T. ^a | No. | SVOC | R.T. ^a | No. | SVOC | R.T. ^a |
|-----|-------------------------------|-------------------|-----|---------------------------------------|-------------------|-----|--------------------------------------|-------------------|
| 1 | Triethyl phosphate | 8.65 | 36 | OCDPE | 28.63 | 66 | Resmethrin (2) | 37.56 |
| 2 | Dichlorvos | 12.10 | 37 | Fenitrothion | 28.68 | 67 | Di(2-ethylhexyl) adipate | 37.68 |
| 4 | 1-Chloronaphthalene | 15.78 | 37 | Furamethrin (2) | 28.71 | 68 | Pyridaphenthion | 37.77 |
| 4 | Tripropyl phosphate | 15.80 | 38 | Dichlofluanid | 29.02 | 69 | Tetramethrin (1) | 37.93 |
| 5 | Dimethyl phthalate | 17.37 | 39 | Di-n-butyl phthalate | 29.21 | 70 | Fenoxycarb | 38.14 |
| 9 | DEET | 20.69 | 40 | Malathion | 29.29 | 71 | Tetramethrin (2) | 38.22 |
| 10 | Thiuram | 20.86 | 41 | Fenthion | 29.53 | 72 | Bifenthrin | 38.73 |
| 11 | Diethyl phthalate | 20.97 | 42 | Chlorpyrifos | 29.79 | 73 | Tris(2-ethylhexyl) phosphate | 38.96 |
| 12 | Propoxur | 21.35 | 43 | MGK-264 (1) | 30.51 | 74 | Dicyclohexyl phthalate | 39.09 |
| 13 | Fenobucarb | 21.42 | 44 | Thiabendazole | 30.62 | 75 | Phenothrin (1) | 39.35 |
| 14 | IPBC | 22.27 | 45 | MGK-264 (2) | 30.82 | 76 | Phenothrin (2) | 39.60 |
| 16 | Tributyl phosphate | 22.57 | 46 | Fluoranthene-d10 | 31.04 | 77 | Di-n-heptyl phthalate | 39.67 |
| 17 | Tripropyl isocyanurate | 23.94 | 46 | Allethrin (1) | 31.57 | 78 | Pyriproxyfen | 39.83 |
| 18 | Empenthrin (1) | 24.27 | 49 | Allethrin (2) | 31.61 | 79 | Di(2-ethylhexyl) phthalate | 39.88 |
| 19 | Empenthrin (2) | 24.40 | 50 | Allethrin (3) | 31.76 | 80 | Tricresyl phosphate (1) | 41.06 |
| 19 | Tris(2-chloroethyl) phosphate | 24.41 | 51 | Allethrin (4) | 31.83 | 81 | Cyphenothrin (1) | 41.34 |
| 20 | Empenthrin (3) | 24.56 | 52 | TCMTB | 32.04 | 82 | Cyphenothrin (2) | 41.49 |
| 21 | Empenthrin (4) | 24.66 | 52 | Prallethrin (1) | 32.07 | 82 | Tricresyl phosphate (2) | 41.51 |
| 22 | Metoxadiazone | 24.75 | 53 | Prallethrin (2) | 32.23 | 83 | Cyphenothrin (3) | 41.60 |
| 23 | Pentachlorophenol | 24.85 | 54 | Tetrachlorvinphos | 32.33 | 84 | Permethrin (1) | 41.97 |
| 23 | Empenthrin (5) | 24.89 | 55 | Methoprene | 32.43 | 84 | Tricresyl phosphate (3) | 41.97 |
| 24 | Di-n-propyl phthalate | 25.19 | 56 | Di-n-pentyl phthalate | 32.94 | 85 | Permethrin (2) | 42.21 |
| 25 | Propetamphos | 25.37 | 57 | Cyproconazol | 34.06 | | Tricresyl phosphate (4) ^b | 42.43 |
| 26 | Chlorothalonil | 25.55 | | Imiprothrin (1) ^b | 35.08 | 86 | Cyfluthrin (1) | 43.12 |
| 27 | Diazinon | 26.02 | 58 | Imiprothrin (2) | 35.35 | 87 | Cyfluthrin (2) | 43.30 |
| 29 | BECDIP | 26.91 | 59 | Tris(1,3-dichloro-2-propyl) phosphate | 35.84 | 88 | Cyfluthrin (3) | 43.47 |
| 31 | Furmecycloz | 27.12 | 60 | Benzylbutyl phthalate | 36.21 | 89 | Cyfluthrin (4) | 43.55 |
| 32 | Di-iso-butyl phthalate | 27.31 | 61 | Di-n-hexyl phthalate | 36.42 | 90 | Ethofenprox | 44.33 |
| 33 | CPIP | 27.50 | 62 | Difolatan | 36.61 | 91 | Silafluofen | 44.85 |
| 33 | Dichlofenthion | 27.53 | 63 | Triphenyl phosphate | 36.96 | | Deltamethrin (1) ^b | 46.51 |
| 33 | Carbaryl | 27.57 | 64 | Resmethrin (1) | 37.31 | 92 | Deltamethrin (2) | 46.91 |
| 34 | Chlorpyrifosmethyl | 27.68 | 65 | Piperonyl butoxide | 37.50 | | Hydramethylnon ^b | 47.13 |
| 35 | Furamethrin (1) | 28.40 | 66 | Tris(2-butoxyethyl) phosphate | 37.54 | | | |

Fig. 1. Total ion chromatogram of standard solution (15.0 µg/ml). The superscript letters (a) represent retention time and (b) there are no peak numbers because these peaks were very small. The figure in parenthesis is to distinguish among the isomers of each compound.

Table 3
Slopes of the calibration graphs for determination of SVOCs

| SVOC | Slope | r^2 |
|--------------------------------------|-------|-------|
| Triethyl phosphate | 0.274 | 1.000 |
| Dichlorvos | 0.190 | 1.000 |
| 1-Chloronaphthalene | 0.601 | 1.000 |
| Tripropyl phosphate | 0.704 | 1.000 |
| Dimethyl phthalate | 0.705 | 1.000 |
| DEET | 0.723 | 1.000 |
| Thiuram | 0.150 | 0.998 |
| Diethyl phthalate | 0.687 | 1.000 |
| Propoxur | 0.850 | 1.000 |
| Fenobucarb | 0.825 | 1.000 |
| IPBC | 0.112 | 0.998 |
| Tributyl phosphate | 0.861 | 1.000 |
| Tripropyl isocyanurate | 0.509 | 1.000 |
| Empenthrin | 0.273 | 1.000 |
| Tris(2-chloroethyl)phosphate | 0.167 | 1.000 |
| Metoxadiazone | 0.255 | 1.000 |
| Pentachlorophenol | 0.145 | 0.999 |
| Di- <i>n</i> -propyl phthalate | 0.978 | 1.000 |
| Propetamphos | 0.267 | 1.000 |
| Chlorothalonil | 0.296 | 1.000 |
| Diazinon | 0.180 | 1.000 |
| BECDIP | 0.071 | 0.999 |
| Furmecyclox | 1.051 | 1.000 |
| Diisobutyl phthalate | 1.022 | 1.000 |
| CPIP | 0.143 | 0.998 |
| Dichlofenthion | 0.222 | 1.000 |
| Carbaryl | 0.237 | 1.000 |
| Chlorpyrifosmethyl | 0.308 | 1.000 |
| Furamethrin | 0.552 | 0.999 |
| OCDPE | 0.157 | 1.000 |
| Fenitrothion | 0.180 | 0.999 |
| Dichlofluanid | 0.124 | 0.997 |
| Di- <i>n</i> -butyl phthalate | 1.138 | 1.000 |
| Malathion | 0.184 | 1.000 |
| Fenthion | 0.437 | 1.000 |
| Chlorpyrifos | 0.109 | 1.000 |
| MGK-264 | 0.186 | 1.000 |
| Thiabendazole | 0.300 | 0.999 |
| Allethrin | 0.277 | 1.000 |
| TCMTB | 0.258 | 0.998 |
| Prallethrin | 0.378 | 0.999 |
| Tetrachlorvinphos | 0.258 | 1.000 |
| Methoprene | 0.272 | 1.000 |
| Di- <i>n</i> -pentyl phthalate | 1.209 | 1.000 |
| Cyproconazol | 0.281 | 0.999 |
| Imiprothrin | 0.185 | 0.997 |
| Tris(1,3-dichloro-2-propyl)phosphate | 0.143 | 1.000 |
| Benzylbutyl phthalate | 0.510 | 1.000 |
| Di- <i>n</i> -hexyl phthalate | 1.291 | 1.000 |
| Difolatan | 0.044 | 0.989 |
| Triphenyl phosphate | 0.398 | 1.000 |
| Resmethrin | 0.279 | 1.000 |
| Piperonyl butoxide | 0.646 | 1.000 |
| Tris(2-butoxyethyl)phosphate | 0.109 | 0.997 |
| Di(2-ethylhexyl)adipate | 0.537 | 1.000 |
| Pyridaphenthion | 0.214 | 0.999 |
| Tetramethrin | 0.616 | 1.000 |
| Fenoxycarb | 0.477 | 1.000 |
| Bifenthrin | 0.867 | 1.000 |
| Tris(2-ethylhexyl)phosphate | 0.992 | 0.999 |

Table 3 (Continued)

| SVOC | Slope | r^2 |
|--------------------------------|-------|-------|
| Dicyclohexyl phthalate | 0.856 | 1.000 |
| Phenothrin | 0.524 | 1.000 |
| Di- <i>n</i> -heptyl phthalate | 1.257 | 1.000 |
| Pyriproxyfen | 0.966 | 1.000 |
| Di(2-ethylhexyl)phthalate | 0.715 | 1.000 |
| Tricresyl phosphate | 0.451 | 0.999 |
| Cyphenothrin | 0.465 | 1.000 |
| Permethrin | 0.511 | 1.000 |
| Cyfluthrin | 0.154 | 0.999 |
| Ethofenprox | 1.111 | 1.000 |
| Silafluofen | 0.408 | 1.000 |
| Deltamethrin | 0.087 | 0.998 |
| Hydramethylnon | 0.079 | 0.986 |

^a Correlation coefficient ($n = 10$).

amounts appeared as fragments of mass spectrum peaks that interfered with the determination. Therefore, the present chromatographic method by SIM appears to be satisfactory for the determination of all SVOCs without their affecting each other.

3.2. Calibration

The slopes of the SVOC calibration curves obtained by measurement of the standard solutions are shown in Table 3. For many compounds, the values of the correlation coefficient of the normal linear regression lines were better than 0.9995 ($n = 10$), i.e., these calibration curves were linear over the concentration range 0–30.0 $\mu\text{g}/\text{ml}$, with conversion to 0–2.0 $\mu\text{g}/\text{m}^3$ as airborne concentration when SVOCs were collected for 24 h at a flow rate of 5.0 l/min. However, the calibration curves for thiuram, 3-iodo-2-propynyl-*N*-butylcarbamate (IPBC), pentachlorophenol, 1-bromo-3-ethoxycarbonyloxy-1,2-diiodo-1-propene (BECDIP), 1-(4-chlorophenyl)-3-iodopropargyl formal (CPIP), furamethrin, fenitrothion, 2-(thiocyanomethylthio)benzothiazole (TCMTB), prallethrin, cyproconazol, imiprothrin, tris(2-butoxyethyl)phosphate, pyridaphenthion, tris(2-ethylhexyl)phosphate, cyfluthrin and deltamethrin were quadratic functions. The detected quantities of these compounds tended to decrease at low concentrations. On the other hand, the curves for dichlofluanid, difolatan and hydramethylnon were sigmoid. The absence of linearity of their calibration curves may be explained by previous findings. The organoiodine fungicides, IPBC, BECDIP and CPIP, were relatively susceptible to photoirradiation and decomposed easily through photochemical reactions [31,32]. IPBC was easily decomposed by adsorption in gas chromatograph at the detection level of the electron capture detector [33]. For gas chromatographic analysis of pentachlorophenol, this compound was derivatized to the anisole by reaction with diazomethane [8] or converted to the acetylated compound by acetic anhydride [34] in order to avoid adsorption of the compound at the injection port

Table 4
Amounts of SVOCs detected in adsorbents without sampling (ng)

| SVOC | Mean | S.D. ^a |
|-------------------------------|------|-------------------|
| Diethyl phthalate | 2.0 | 1.7 |
| Diisobutyl phthalate | 0.3 | 0.2 |
| Di- <i>n</i> -butyl phthalate | 5.4 | 4.9 |
| Di(2-ethylhexyl)adipate | 0.2 | 0.2 |
| Tris(2-chloroethyl)phosphate | 0.6 | 0.4 |
| Di(2-ethylhexyl)phthalate | 2.7 | 2.4 |

^a Standard deviation ($n = 10$).

and analytical column. Otake et al. [7] reported that the analysis of phosphates was imprecise when GC–MS was used, even if internal standardization was employed. The gas chromatographic analysis of thermolabile pyrethroids in insecticidal pyrethrum extract and in insecticide formulations was achieved by on-column injection with hydrogen as the carrier gas at high velocities and with short thin-film capillaries in order to avoid thermal degradation [35].

3.3. Contamination of adsorbents and procedure blank during sample preparation

Pre-cleaning of the adsorbents, quartz fiber filter disk and Empore disk, before sampling is mandatory as they are contaminated with various materials at the time of purchase. Therefore, the Empore disks were washed with acetone and quartz fiber filter disks heated at 400 °C were employed for SVOC sampling during the present study. Ten-milliliter centrifuge tubes containing one each of a cleaned quartz fiber filter disk and a heated Empore disk without sampling, were analyzed immediately by the present method. The amounts of SVOCs detected are shown in Table 4. Diethyl phthalate, diisobutyl phthalate, di-*n*-butyl phthalate, di(2-ethylhexyl)phthalate, tris(2-chloroethyl)phosphate and di(2-ethylhexyl)adipate were detected in the adsorbents. All of these compounds were also found at nearly equal levels in the solutions treated only acetone without adsorbents. Therefore, pre-cleaning of the adsorbents was satisfactory and contamination during sample preparation (procedure blank) was the main reason for the detection of these SVOCs. Saito et al. [27] also found di-*n*-butyl phthalate and di(2-ethylhexyl)phthalate as procedure blanks in these adsorbents without sampling. These phthalate esters are ubiquitous as contaminants in the laboratory environment [36–38]. Though the detected amounts of these compounds were low, it was considered necessary to subtract the quantitative values of the compounds found in the travel blank, which was handled and prepared similarly to the sample, for accurate measurements of airborne concentrations.

3.4. Retention and breakthrough of SVOCs in sampling

Portions of 120 µl of the mixed SVOC stock solution (14.8 µg each of SVOCs), with equivalent to 2.1 µg/m³ as airborne concentration, were spiked onto the first layers of

eight samplers in the air-flow. The four samplers (Control) were analyzed immediately, and the other four were analyzed after sampling outdoor atmospheric air from our laboratory for 24 h at the flow rate of 5.0 l/min according to the present method. In these four samplers, one quartz fiber filter disk and two Empore disks, namely a quartz fiber filter disk for the first layer and Empore disks for the second and third layers, were set for the air sampling. In following the sample preparation, the third layer (Sample-1) was treated separately from the first and second layers (Sample-2). Similarly, air sampling was done for 24 h using another four samplers without spiking SVOCs (Blank). The retention efficiencies of SVOCs to the adsorbents and rates of breakthrough of SVOCs in air sampling were calculated with the following equations:

$$\text{retention efficiency (\%)} = \left[\frac{(S2 - B)}{C} \right] 100 \quad (3)$$

$$\text{rate of breakthrough (\%)} = \left[\frac{S1}{(S1 + S2 - B)} \right] 100 \quad (4)$$

where $S1$, $S2$, C and B are the means ($n = 4$) of the peak-area ratio (area SVOC/area internal standard) for each SVOC obtained by analysis of Sample-1, Sample-2, Control and Blank, respectively.

The values of retention efficiencies calculated are shown in Table 5. The values for 1-chloronaphthalene, thiuram, empenethrin, furemecyclo, furamethrin, fenthion, MGK-264, allethrin, prallethrin, methoprene, imiprothrin, difolatan, resmethrin, tetramethrin, phenothrin, cyphenothrin and hydramethylnon were <10% after air sampling for 24 h with a flow rate of 5.0 l/min. These compounds could not be sufficiently collected by the present sampling method. Some of these compounds may be decomposed by daylight during air sampling and other adsorbents may be necessary for their collection. Most of the pyrethroids are photodegraded relatively quickly due to their photolability [39]. Class and Kintrop [15] have also reported that allethrin was decomposed by daylight in an indoor environment. Ramesh and Vijayalakshmi [40] collected allethrin, prallethrin and deltamethrin in air using an airtight syringe and then dissolved them in acetone. Airborne fenthion was collected by using quartz fiber wool followed by activated carbon [23] and resmethrin by using Tenax TA [6]. In these studies, the recoveries of fenthion and resmethrin were 88–93 and 85%, respectively. With the present method, the retention efficiencies for piperonyl butoxide (56%) and propetamphos (74%) were low. That of propetamphos from Tenax TA was also low (76%) [6]. The retention efficiencies for 54 SVOCs except for the above 19 compounds were >85%, and their breakthrough rates were <1% after the air sampling. Therefore, 54 SVOCs except for the above 19 compounds were suggested not to be broken through the adsorbents and to be satisfactorily collected at airborne concentrations of <2.1 µg/m³ in sampling for 24 h at a flow rate of 5.0 l/min.

Table 5
Retention efficiencies of SVOCs for adsorbents in air sampling

| SVOC | Retention efficiency (%) |
|--------------------------------------|--------------------------|
| Triethyl phosphate | 99.4 |
| Dichlorvos | 103.1 |
| 1-Chloronaphthalene | 0.0 |
| Tripropyl phosphate | 98.3 |
| Dimethyl phthalate | 98.1 |
| DEET | 97.7 |
| Thiuram | 0.6 |
| Diethyl phthalate | 97.4 |
| Propoxur | 112.1 |
| Fenobucarb | 100.8 |
| IPBC | 106.2 |
| Tributyl phosphate | 98.8 |
| Tripropyl isocyanurate | 98.8 |
| Empenthrin | 2.8 |
| Tris(2-chloroethyl)phosphate | 101.2 |
| Metoxadiazone | 99.4 |
| Pentachlorophenol | 108.0 |
| Di- <i>n</i> -propyl phthalate | 97.8 |
| Propetamphos | 74.2 |
| Chlorothalonil | 99.9 |
| Diazinon | 96.2 |
| BECDIP | 91.1 |
| Furmecyclox | 0.1 |
| Diisobutyl phthalate | 96.0 |
| CPIP | 104.5 |
| Dichlofenthion | 96.6 |
| Carbaryl | 114.0 |
| Chlorpyrifosmethyl | 98.8 |
| Furamethrin | 2.3 |
| OCDPE | 99.5 |
| Fenitrothion | 97.2 |
| Dichlofluanid | 122.9 |
| Di- <i>n</i> -butyl phthalate | 96.3 |
| Malathion | 100.8 |
| Fenthion | 5.6 |
| Chlorpyrifos | 97.5 |
| MGK-264 | 0.1 |
| Thiabendazole | 93.7 |
| Allethrin | 0.0 |
| TCMTB | 94.9 |
| Prallethrin | 0.4 |
| Tetrachlorvinphos | 91.4 |
| Methoprene | 8.0 |
| Di- <i>n</i> -pentyl phthalate | 94.8 |
| Cyproconazol | 85.9 |
| Imiprothrin | 0.1 |
| Tris(1,3-dichloro-2-propyl)phosphate | 99.2 |
| Benzylbutyl phthalate | 96.1 |
| Di- <i>n</i> -hexyl phthalate | 94.2 |
| Difolatan | 3.7 |
| Triphenyl phosphate | 99.1 |
| Resmethrin | 0.6 |
| Piperonyl butoxide | 55.5 |
| Tris(2-butoxyethyl)phosphate | 97.1 |
| Di(2-ethylhexyl)adipate | 94.2 |
| Pyridaphenthion | 84.7 |
| Tetramethrin | 0.2 |
| Fenoxycarb | 98.3 |
| Bifenthrin | 95.3 |
| Tris(2-ethylhexyl)phosphate | 95.0 |

Table 5 (Continued)

| SVOC | Retention efficiency (%) |
|--------------------------------|--------------------------|
| Dicyclohexyl phthalate | 95.4 |
| Phenothrin | 0.6 |
| Di- <i>n</i> -heptyl phthalate | 93.0 |
| Pyriproxyfen | 92.4 |
| Di(2-ethylhexyl)phthalate | 97.4 |
| Tricresyl phosphate | 97.2 |
| Cyphenothrin | 0.4 |
| Permethrin | 91.1 |
| Cyfluthrin | 96.1 |
| Ethofenprox | 92.8 |
| Silafluofen | 93.8 |
| Deltamethrin | 110.7 |
| Hydramethylnon | 5.7 |

3.5. Desorption from adsorbents

One each of a quartz fiber filter disk and an Empore disk without sampling were inserted into six centrifuge tubes. A 60 μl portion of the mixed SVOC stock solution (7.4 μg each of SVOCs) and 8 ml of acetone were added to these tubes (Sample) and to the other six centrifuge tubes without the adsorbents (Control). Only 8 ml of acetone was added to another 12 centrifuge tubes, six with (S-Blank) and six without (C-Blank) the adsorbents. The 24 samples prepared were analyzed according to the present method. The desorption efficiencies of SVOCs from the adsorbents in the extraction process were calculated using the following equation:

$$\text{desorption efficiency (\%)} = \left[\frac{(S - B_s)}{(C - B_c)} \right] 100 \quad (5)$$

where S , C , B_s and B_c are the means ($n = 6$) of peak-area ratio (area SVOC/area internal standard) for each SVOC obtained by analysis of Sample, Control, S-Blank and C-Blank, respectively. The samples spiked with 6.0 μl of the mixed SVOC stock solution (0.74 μg each of SVOCs) were examined in the same manner as above.

The values of the desorption efficiencies calculated are shown in Table 6. The desorption efficiencies for the SVOCs except for thiabendazole were approximately 100%, which indicates complete desorption from the adsorbents, in the spiked examinations of both 7.4 and 0.74 μg each of the SVOCs. Thiabendazole was demonstrated to be difficult to determine accurately as its desorption efficiency from the adsorbents was low, with 77 and 56% being in the spiked examinations of 7.4 and 0.74 μg , respectively.

On the basis of above results, we concluded that 20 SVOCs, namely 1-chloronaphthalene, thiuram, empenthrin, propetamphos, furmecyclox, furamethrin, fenthion, MGK-264, thiabendazole, allethrin, prallethrin, methoprene, imiprothrin, difolatan, resmethrin, piperonyl butoxide, tetramethrin, phenothrin, cyphenothrin and hydramethylnon, among the selected 73 SVOCs could not be determined by the present method. In addition, the accurate quantitation of IPBC, pentachlorophenol, BECDIP, CPIP, fenitrothion,

Table 6
Desorption efficiencies of SVOCs from adsorbents (%)

| SVOC | 7.4 μg^{a} | 0.74 μg^{a} |
|--------------------------------------|------------------------------|-------------------------------|
| Triethyl phosphate | 101.7 | 94.5 |
| Dichlorvos | 101.5 | 98.5 |
| Tripropyl phosphate | 103.7 | 96.6 |
| Dimethyl phthalate | 102.9 | 96.5 |
| DEET | 99.7 | 97.7 |
| Diethyl phthalate | 103.7 | 98.3 |
| Propoxur | 97.4 | 90.5 |
| Fenobucarb | 98.0 | 95.4 |
| IPBC | 103.7 | 99.7 |
| Tributyl phosphate | 102.2 | 98.0 |
| Tripropyl isocyanurate | 101.8 | 96.7 |
| Tris(2-chloroethyl)phosphate | 100.7 | 103.0 |
| Metoxadiazone | 100.4 | 100.4 |
| Pentachlorophenol | 106.0 | 120.9 |
| Di- <i>n</i> -propyl phthalate | 102.4 | 98.0 |
| Chlorothalonil | 106.4 | 104.0 |
| Diazinon | 99.1 | 98.6 |
| BECDIP | 100.0 | 98.0 |
| Diisobutyl phthalate | 101.6 | 98.1 |
| CPIP | 101.6 | 100.8 |
| Dichlofenthion | 100.1 | 96.9 |
| Carbaryl | 97.3 | 98.7 |
| Chlorpyrifosmethyl | 101.5 | 97.5 |
| OCDPE | 100.3 | 102.1 |
| Fenitrothion | 102.9 | 103.7 |
| Dichlofluanid | 108.9 | 116.5 |
| Di- <i>n</i> -butyl phthalate | 101.4 | 100.6 |
| Malathion | 101.5 | 101.4 |
| Chlorpyrifos | 98.7 | 97.0 |
| Thiabendazole | 76.5 | 55.8 |
| TCMTB | 99.1 | 104.0 |
| Tetrachlorvinphos | 99.6 | 104.1 |
| Di- <i>n</i> -pentyl phthalate | 101.2 | 100.6 |
| Cyproconazol | 100.8 | 106.4 |
| Tris(1,3-dichloro-2-propyl)phosphate | 99.6 | 102.3 |
| Benzylbutyl phthalate | 101.9 | 105.2 |
| Di- <i>n</i> -hexyl phthalate | 101.0 | 102.9 |
| Triphenyl phosphate | 100.4 | 102.3 |
| Tris(2-butoxyethyl)phosphate | 100.3 | 112.2 |
| Di(2-ethylhexyl)adipate | 98.1 | 102.0 |
| Pyridaphenthion | 102.0 | 108.2 |
| Fenoxycarb | 100.4 | 109.7 |
| Bifenthrin | 100.1 | 103.8 |
| Tris(2-ethylhexyl)phosphate | 97.6 | 105.0 |
| Dicyclohexyl phthalate | 100.5 | 101.9 |
| Di- <i>n</i> -heptyl phthalate | 100.8 | 103.5 |
| Pyriproxyfen | 101.3 | 104.7 |
| Di(2-ethylhexyl)phthalate | 100.8 | 105.8 |
| Tricresyl phosphate | 100.3 | 108.1 |
| Permethrin | 100.9 | 107.8 |
| Cyfluthrin | 104.0 | 114.3 |
| Ethofenprox | 101.9 | 112.9 |
| Silafuofen | 100.9 | 109.5 |
| Deltamethrin | 109.0 | 110.2 |

^a The amounts of SVOCs spiked to adsorbents. They are 1.0 $\mu\text{g}/\text{m}^3$ and 0.1 $\mu\text{g}/\text{m}^3$, respectively, as airborne concentrations.

Table 7
Calibration curves calculated as quadratic functions for 13 SVOCs

| SVOC | A | B | R ^a |
|------------------------------|---------|-------|----------------|
| IPBC | 0.0016 | 0.063 | 0.998 |
| Pentachlorophenol | 0.0013 | 0.105 | 1.000 |
| BECDIP | 0.0007 | 0.052 | 0.999 |
| CPIP | 0.0019 | 0.087 | 0.998 |
| Fenitrothion | 0.0013 | 0.141 | 0.999 |
| Dichlofluanid | -0.0005 | 0.137 | 0.995 |
| TCMTB | 0.0035 | 0.154 | 0.999 |
| Cyproconazol | 0.0025 | 0.207 | 1.000 |
| Tris(2-butoxyethyl)phosphate | 0.0019 | 0.054 | 1.000 |
| Pyridaphenthion | 0.0015 | 0.169 | 0.999 |
| Tris(2-ethylhexyl)phosphate | 0.0094 | 0.711 | 0.999 |
| Cyfluthrin | 0.0016 | 0.106 | 0.999 |
| Deltamethrin | 0.0011 | 0.055 | 0.999 |

Calibration curve: $y = Ax^2 + Bx$.

^a Correlation coefficient.

dichlofluanid, TCMTB, cyproconazol, tris(2-butoxyethyl)phosphate, pyridaphenthion, tris(2-ethylhexyl)phosphate, cyfluthrin and deltamethrin were difficult as their calibration curves were not linear. Quantification of these 13 SVOCs was attempted in the following examinations for precision and accuracy and storage stability using the calibration curves calculated as quadratic functions ($y = Ax^2 + Bx$). The values of A and B for the equations in each compound are shown in Table 7.

The retention efficiencies and the desorption efficiencies for the remaining 40 SVOCs among the selected 73 SVOCs were satisfactory at the concentrations studied. The 40 compounds could be sufficiently separated from each other by the present chromatographic method, and the calibration curves of the compounds were linear over the concentration range of 0–2 $\mu\text{g}/\text{m}^3$ as the airborne concentrations.

3.6. Detection limits

The Ministry of Health, Labour and Welfare of the Japanese Government recommends that the concentration of the detection limit of a chemical in indoor air is calculated from the quantitative value of the standard solution of the minimum concentration needed to construct the calibration curve. On the other hand, the detection limit for a chemical, which is detected from the contamination of adsorbents and the procedure blank during sample preparation, is calculated from the results of analysis of the adsorbents without sampling. In both examinations, more than five samples are prepared and analyzed. The standard deviations of the quantitative values are calculated for each chemical, and the detection limits are defined as being three times the standard deviations [41].

Each standard solution of 0.12 $\mu\text{g}/\text{ml}$ SVOC concentration ($n = 10$) was prepared by diluting the mixed SVOC stock solution and analyzed according to the present method. The detection limit of each SVOC was calculated by conversion to the airborne concentration when

air sampling was done for 24 h at a flow rate of 5.0 l/min. The detection limits of diethyl phthalate, diisobutyl phthalate, di-*n*-butyl phthalate, di(2-ethylhexyl)phthalate, di(2-ethylhexyl)adipate and tris(2-chloroethyl)phosphate were also calculated from the results shown in Table 4 because these compounds were found as procedure blanks in the analysis of the adsorbents without sampling. The detection limits calculated from this table were as follows: 0.7 ng/m³ for diethyl phthalate, 0.1 ng/m³ for diisobutyl phthalate, 2.0 ng/m³ for di-*n*-butyl phthalate, 1.0 ng/m³ for di(2-ethylhexyl)phthalate, 0.1 ng/m³ for di(2-ethylhexyl)adipate and 0.2 ng/m³ for tris(2-chloroethyl)phosphate. The values of the detection limits of the 40 compounds except for the 13 SVOCs, whose calibration curves were not linear, are shown in Table 8. The detection limits for diisobutyl phthalate, tris(2-chloroethyl)phosphate and di(2-ethylhexyl)adipate

were from the results of analysis of the standard solutions since the values were higher than those calculated from Table 4. The detection limits of airborne SVOCs were demonstrated to be 0.1–2.0 ng/m³. Most of the SVOCs were detectable at concentrations of more than 0.5 ng/m³ in air. The detection limits of di-*n*-butyl phthalate and di(2-ethylhexyl)phthalate that were detected in the procedure blanks were higher than those of other SVOCs.

3.7. Precision and accuracy

The precision and accuracy of the method were demonstrated by repeated analysis of the sample spiked authentic standard. Portions of 60 µl of the mixed SVOC stock solution (7.4 µg each of SVOCs) were spiked to the first layers of five samplers in the air-flow. The adsorbents in the samplers were analyzed after sampling outdoor air for 24 h at a flow rate of 5.0 l/min (Sample). Similarly, air sampling was done for 24 h using three other samplers without spiking SVOCs (Blank), and the samples obtained were also determined by the present method. The airborne concentrations of SVOCs in each 'Sample' were calculated using the above Eqs. (1) and (2). The means of the amounts of SVOCs found in three 'Blank' were used instead of X_b in the Eq. (2). The precision of this method was evaluated by the relative standard deviations (R.S.D.) in studies with replicate assays ($n = 5$), and the accuracy of the method was evaluated by the error of the assayed samples relative to their spiked concentrations. Furthermore, the samplers spiked with 60 µl aliquots of the solutions, which were diluted to the concentrations of 10.0 and 3.3 µg/ml from the mixed SVOC stock solution, were examined in the same manner as above (spiked amounts: 0.60 µg and 0.20 µg each of SVOCs, respectively).

The precision and accuracy of the present method for the determination of 53 SVOCs are shown in Table 9. Pentachlorophenol was not detected in the sample spiked with 0.20 µg of the compound. The R.S.D. values of di-*n*-butyl phthalate and di(2-ethylhexyl)phthalate were more than 20% in the samples spiked with 0.20 µg of the compounds. The R.S.D. values in many SVOCs tended to increase at low concentrations of the compounds. However, the R.S.D. values except for the above three compounds were mostly <10%, which indicates good reproducibility, for all concentrations of each compound. These findings suggested that precise determination is possible at airborne concentrations of 27 ng/m³ to 1.0 µg/m³ by sampling for 24 h.

Pentachlorophenol and dichlofluanid could not be accurately determined at airborne concentrations of less than ca. 0.1 µg/m³ as the relative error values were higher than 30% in the samples spiked with 0.60 µg of the compounds. The values for the remaining 51 SVOCs were approximately <10% in the samples spiked with 7.4 µg and 0.60 µg of the compounds. In the study of 0.20 µg spiking, the values for many SVOCs were also <10%, although those for BECDIP, CPIP, fenitrothion, di-*n*-butyl phthalate, TCMTB, di(2-ethylhexyl)phthalate, cyfluthrin and

Table 8
Detection limits of airborne SVOCs

| SVOC | (ng/m ³) |
|--------------------------------------|----------------------|
| Triethyl phosphate | 0.6 |
| Dichlorvos | 0.5 |
| Tripropyl phosphate | 0.3 |
| Dimethyl phthalate | 0.4 |
| DEET | 0.4 |
| Diethyl phthalate | 0.7 |
| Propoxur | 0.4 |
| Fenobucarb | 0.4 |
| Tributyl phosphate | 0.1 |
| Tripropyl isocyanurate | 0.3 |
| Tris(2-chloroethyl)phosphate | 0.4 |
| Metoxadiazone | 0.7 |
| Di- <i>n</i> -propyl phthalate | 0.4 |
| Chlorothalonil | 0.5 |
| Diazinon | 0.2 |
| Diisobutyl phthalate | 0.3 |
| Dichlofenthion | 0.3 |
| Carbaryl | 0.3 |
| Chlorpyrifosmethyl | 0.4 |
| OCDPE | 0.2 |
| Di- <i>n</i> -butyl phthalate | 2.0 |
| Malathion | 0.2 |
| Chlorpyrifos | 0.3 |
| Tetrachlorvinphos | 0.2 |
| Di- <i>n</i> -pentyl phthalate | 0.4 |
| Tris(1,3-dichloro-2-propyl)phosphate | 0.2 |
| Benzylbutyl phthalate | 0.3 |
| Di- <i>n</i> -hexyl phthalate | 0.3 |
| Triphenyl phosphate | 0.4 |
| Di(2-ethylhexyl)adipate | 0.4 |
| Fenoxycarb | 0.1 |
| Bifenthrin | 0.3 |
| Dicyclohexyl phthalate | 0.4 |
| Di- <i>n</i> -heptyl phthalate | 0.3 |
| Pyriproxyfen | 0.3 |
| Di(2-ethylhexyl)phthalate | 1.0 |
| Tricresyl phosphate | 0.1 |
| Permethrin | 0.2 |
| Ethofenprox | 0.3 |
| Silafuofen | 0.4 |

Table 9
Precision and accuracy of the present analytical method

| SVOC | 7.4 µg ^a | | 0.60 µg ^a | | 0.20 µg ^a | |
|---|---------------------|-------------------|----------------------|-------------------|----------------------|-------------------|
| | R.S.D. ^b | R.E. ^c | R.S.D. ^b | R.E. ^c | R.S.D. ^b | R.E. ^c |
| Triethyl phosphate | 3.5 | 9.4 | 4.8 | 8.0 | 5.2 | 11.4 |
| Dichlorvos | 4.1 | 8.4 | 4.8 | 5.9 | 3.7 | 12.2 |
| Tripropyl phosphate | 2.4 | 12.4 | 4.1 | 1.2 | 5.5 | 1.6 |
| Dimethyl phthalate | 2.7 | 5.8 | 4.5 | 9.9 | 4.6 | 7.0 |
| DEET | 2.9 | 6.2 | 3.5 | 4.8 | 4.4 | 7.1 |
| Diethyl phthalate | 2.9 | 2.9 | 4.4 | 7.4 | 7.1 | 9.0 |
| Propoxur | 3.5 | 2.6 | 2.7 | 9.7 | 4.6 | 8.1 |
| Fenobucarb | 2.9 | 4.4 | 3.4 | 6.0 | 4.5 | 5.9 |
| IPBC ^d | 3.6 | 0.7 | 4.8 | 5.0 | 7.6 | 6.3 |
| Tributyl phosphate | 3.1 | 5.1 | 3.7 | 2.2 | 5.2 | 7.4 |
| Tripropyl isocyanurate | 1.9 | 5.9 | 3.6 | 9.6 | 4.0 | 5.6 |
| Tris(2-chloroethyl)phosphate | 1.3 | 1.3 | 4.4 | 4.1 | 2.6 | 1.5 |
| Metoxadiazone | 3.3 | 0.2 | 3.0 | 5.5 | 3.8 | 10.6 |
| Pentachlorophenol ^d | 1.7 | 12.1 | 12.3 | 79.5 | — ^e | — ^e |
| Di- <i>n</i> -propyl phthalate | 2.7 | 2.9 | 4.0 | 8.2 | 4.0 | 10.8 |
| Chlorothalonil | 1.8 | 11.0 | 2.3 | 10.3 | 2.4 | 9.0 |
| Diazinon | 3.7 | 4.9 | 3.2 | 1.5 | 10.5 | 1.9 |
| BECDIP ^d | 2.9 | 0.6 | 2.1 | 5.6 | 3.3 | 20.0 |
| Diisobutyl phthalate | 3.5 | 1.6 | 3.8 | 9.7 | 4.5 | 11.1 |
| CPIP ^d | 3.4 | 4.1 | 3.2 | 10.3 | 10.7 | 57.2 |
| Dichlofenthion | 1.9 | 1.7 | 3.8 | 2.7 | 5.1 | 3.8 |
| Carbaryl | 3.9 | 5.5 | 3.9 | 3.0 | 3.9 | 11.5 |
| Chlorpyrifosmethyl | 2.6 | 8.0 | 3.8 | 3.6 | 1.6 | 8.1 |
| OCDPE | 3.1 | 0.7 | 2.7 | 7.4 | 4.2 | 12.5 |
| Fenitrothion ^d | 3.3 | 0.1 | 2.9 | 3.2 | 8.5 | 30.0 |
| Dichlofluamid ^d | 2.3 | 18.9 | 6.1 | 30.0 | 7.7 | 35.5 |
| Di- <i>n</i> -butyl phthalate | 3.7 | 2.9 | 8.9 | 4.9 | 24.0 | 19.0 |
| Malathion | 2.3 | 3.8 | 2.7 | 11.3 | 10.6 | 13.6 |
| Chlorpyrifos | 3.3 | 3.5 | 3.5 | 5.0 | 8.3 | 6.4 |
| TCMTB ^d | 5.4 | 2.5 | 7.4 | 1.3 | 5.3 | 46.5 |
| Tetrachlorvinphos | 4.7 | 0.9 | 6.2 | 6.8 | 10.5 | 5.0 |
| Di- <i>n</i> -pentyl phthalate | 2.0 | 0.9 | 2.7 | 0.3 | 3.0 | 8.9 |
| Cyproconazol ^d | 2.8 | 9.0 | 7.6 | 8.4 | 7.2 | 7.4 |
| Tris(1,3-dichloro-2-propyl)phosphate | 3.2 | 1.0 | 6.4 | 2.0 | 5.9 | 5.5 |
| Benzylbutyl phthalate | 3.6 | 2.6 | 4.7 | 8.7 | 10.2 | 6.6 |
| Di- <i>n</i> -hexyl phthalate | 3.3 | 1.4 | 4.3 | 3.8 | 4.3 | 4.2 |
| Triphenyl phosphate | 3.7 | 6.8 | 5.3 | 7.7 | 8.7 | 3.4 |
| Tris(2-butoxyethyl)phosphate ^d | 4.2 | 5.0 | 7.0 | 10.2 | 12.3 | 8.6 |
| Di(2-ethylhexyl)adipate | 3.7 | 0.4 | 6.6 | 5.0 | 9.9 | 6.9 |
| Pyridaphenthion ^d | 3.4 | 8.2 | 7.0 | 1.2 | 8.4 | 7.7 |
| Fenoxycarb | 8.6 | 0.2 | 8.6 | 4.9 | 8.0 | 9.9 |
| Bifenthrin | 4.1 | 1.5 | 5.5 | 2.4 | 5.8 | 4.9 |
| Tris(2-ethylhexyl)phosphate ^d | 4.0 | 7.3 | 7.6 | 1.4 | 10.7 | 12.0 |
| Dicyclohexyl phthalate | 4.2 | 0.6 | 5.0 | 1.9 | 4.1 | 4.6 |
| Di- <i>n</i> -heptyl phthalate | 5.4 | 0.8 | 8.3 | 6.8 | 7.5 | 4.1 |
| Pyriproxyfen | 6.2 | 0.7 | 10.0 | 5.5 | 6.9 | 9.9 |
| Di(2-ethylhexyl)phthalate | 6.2 | 0.4 | 8.3 | 11.0 | 24.7 | 18.5 |
| Tricresyl phosphate | 7.6 | 7.9 | 9.9 | 2.8 | 9.5 | 7.0 |
| Permethrin | 7.4 | 1.6 | 13.8 | 7.5 | 9.7 | 9.3 |
| Cyfluthrin ^d | 7.0 | 0.5 | 10.9 | 12.5 | 13.2 | 19.8 |
| Ethofenprox | 9.5 | 2.4 | 7.8 | 4.7 | 8.5 | 9.4 |
| Silafuofen | 9.6 | 2.6 | 7.5 | 5.5 | 7.3 | 7.8 |
| Deltamethrin ^d | 9.2 | 8.7 | 11.3 | 1.9 | 10.8 | 42.4 |

^a The amounts of SVOCs spiked onto the adsorbents. They were 1.0 µg/m³, 84 and 27 ng/m³, respectively, as airborne concentrations.

^b The R.S.D.s in the studies with assays of five spiked samples (%).

^c The error of assayed samples relative to their spiked concentrations (%).

^d They were quantitated using the calibration curves shown in Table 7.

^e Not detected.

Table 10
Stabilities of SVOCs in adsorbents at 4 °C

| SVOC | Storage time (days) | | | | | | | |
|--------------------------------------|---------------------|----------|-----------|-----------|----------|-----------|-----------|-----------|
| | 1 | 2 | 4 | 7 | 11 | 16 | 22 | 31 |
| Triethyl phosphate | 101 (3) | 98 (6) | 99 (2) | 101 (6) | 104 (11) | 92 (3) | 94 (5) | 94 (5) |
| Dichlorvos | 100 (3) | 97 (7) | 99 (4) | 103 (7) | 103 (11) | 97 (7) | 98 (4) | 92 (4) |
| Tripropyl phosphate | 104 (3) | 99 (7) | 100 (0.8) | 102 (4) | 106 (10) | 95 (3) | 94 (4) | 94 (5) |
| Dimethyl phthalate | 98 (4) | 93 (7) | 95 (2) | 97 (4) | 108 (9) | 94 (2) | 96 (5) | 101 (6) |
| DEET | 98 (3) | 93 (6) | 92 (0.7) | 96 (3) | 103 (9) | 93 (3) | 93 (3) | 94 (4) |
| Diethyl phthalate | 98 (4) | 94 (6) | 94 (0.2) | 97 (3) | 107 (8) | 94 (2) | 94 (3) | 97 (4) |
| Propoxur | 100 (2) | 96 (7) | 97 (3) | 102 (6) | 109 (6) | 100 (6) | 94 (2) | 96 (4) |
| Fenobucarb | 100 (2) | 95 (7) | 94 (0.4) | 96 (2) | 107 (7) | 92 (4) | 90 (2) | 92 (4) |
| IPBC | 110 (14) | 110 (21) | 112 (17) | 112 (14) | 97 (10) | 115 (20) | 111 (11) | 104 (9) |
| Tributyl phosphate | 108 (3) | 104 (6) | 105 (2) | 108 (3) | 112 (8) | 102 (3) | 97 (2) | 99 (4) |
| Tripropyl isocyanurate | 101 (3) | 95 (7) | 98 (2) | 97 (4) | 108 (8) | 93 (3) | 94 (4) | 105 (7) |
| Tris(2-chloroethyl)phosphate | 104 (1) | 100 (5) | 103 (0.3) | 102 (3) | 110 (4) | 101 (1) | 100 (0.4) | 101 (3) |
| Metoxadiazone | 99 (2) | 95 (6) | 94 (0.4) | 97 (2) | 105 (4) | 94 (2) | 92 (2) | 92 (2) |
| Pentachlorophenol | 101 (3) | 99 (7) | 103 (7) | 100 (5) | 90 (10) | 94 (6) | 97 (3) | 96 (2) |
| Di- <i>n</i> -propyl phthalate | 98 (3) | 94 (6) | 95 (0.7) | 98 (2) | 107 (7) | 96 (2) | 95 (2) | 97 (4) |
| Chlorothalonil | 103 (2) | 99 (5) | 101 (1) | 101 (3) | 110 (4) | 101 (1) | 98 (3) | 101 (3) |
| Diazinon | 104 (2) | 101 (6) | 104 (0.8) | 104 (3) | 114 (6) | 102 (2) | 100 (2) | 103 (4) |
| BECDIP | 101 (2) | 97 (5) | 97 (4) | 96 (3) | 100 (3) | 93 (6) | 92 (3) | 91 (1) |
| Diisobutyl phthalate | 99 (2) | 94 (6) | 93 (0.3) | 95 (2) | 109 (6) | 94 (2) | 91 (1) | 94 (3) |
| CPIP | 107 (7) | 107 (12) | 107 (10) | 104 (6) | 96 (7) | 103 (12) | 103 (7) | 97 (6) |
| Dichlofenthion | 105 (2) | 100 (6) | 103 (0.6) | 103 (3) | 112 (5) | 99 (2) | 97 (2) | 101 (4) |
| Carbaryl | 101 (2) | 97 (5) | 99 (3) | 100 (1) | 99 (3) | 102 (6) | 96 (2) | 93 (0.6) |
| Chlorpyrifosmethyl | 105 (1) | 101 (5) | 103 (0.6) | 101 (3) | 108 (4) | 98 (0.8) | 98 (0.8) | 97 (3) |
| OCDPE | 102 (3) | 99 (6) | 95 (4) | 94 (1) | 103 (2) | 92 (4) | 90 (0.5) | 91 (2) |
| Fenitrothion | 103 (4) | 100 (6) | 98 (5) | 97 (3) | 106 (2) | 97 (4) | 93 (4) | 90 (2) |
| Dichlofluandil | 104 (2) | 100 (8) | 98 (3) | 101 (3) | 113 (2) | 99 (1) | 90 (2) | 92 (4) |
| Di- <i>n</i> -butyl phthalate | 97 (3) | 91 (5) | 92 (1) | 93 (2) | 106 (4) | 94 (2) | 91 (1) | 92 (0.8) |
| Malathion | 106 (2) | 104 (5) | 105 (2) | 105 (3) | 116 (2) | 105 (2) | 102 (1) | 96 (2) |
| Chlorpyrifos | 103 (2) | 100 (5) | 102 (0.9) | 102 (2) | 111 (4) | 102 (1) | 100 (0.9) | 100 (2) |
| TCMTB | 108 (8) | 110 (10) | 109 (11) | 99 (2) | 92 (12) | 106 (8) | 109 (12) | 105 (14) |
| Tetrachlorvinphos | 107 (2) | 103 (4) | 107 (2) | 104 (3) | 114 (1) | 110 (2) | 107 (2) | 101 (0.2) |
| Di- <i>n</i> -pentyl phthalate | 101 (1) | 96 (3) | 96 (1) | 97 (2) | 109 (1) | 99 (1) | 94 (3) | 93 (0.4) |
| Cyproconazol | 105 (5) | 106 (4) | 107 (5) | 105 (2) | 116 (2) | 113 (1) | 110 (4) | 107 (3) |
| Tris(1,3-dichloro-2-propyl)phosphate | 104 (3) | 101 (2) | 100 (3) | 101 (2) | 109 (2) | 106 (1) | 101 (5) | 98 (3) |
| Benzylbutyl phthalate | 104 (2) | 99 (1) | 96 (2) | 95 (2) | 104 (2) | 98 (1) | 94 (4) | 93 (2) |
| Di- <i>n</i> -hexyl phthalate | 103 (2) | 98 (0.9) | 96 (2) | 95 (2) | 105 (1) | 98 (1) | 94 (4) | 93 (2) |
| Triphenyl phosphate | 111 (2) | 105 (3) | 108 (2) | 103 (5) | 111 (2) | 106 (4) | 107 (3) | 102 (2) |
| Tris(2-butoxyethyl)phosphate | 105 (10) | 104 (6) | 107 (7) | 102 (0.4) | 116 (7) | 128 (4) | 122 (10) | 120 (10) |
| Di(2-ethylhexyl)adipate | 105 (3) | 100 (1) | 96 (2) | 95 (2) | 105 (2) | 98 (2) | 93 (5) | 92 (3) |
| Pyridaphenthion | 111 (6) | 107 (4) | 115 (6) | 103 (8) | 110 (5) | 110 (8) | 111 (7) | 109 (8) |
| Fenoxycarb | 115 (9) | 113 (8) | 108 (9) | 101 (3) | 103 (11) | 111 (4) | 109 (11) | 108 (12) |
| Bifenthrin | 106 (3) | 102 (1) | 101 (3) | 98 (3) | 109 (2) | 103 (3) | 100 (5) | 98 (3) |
| Tris(2-ethylhexyl)phosphate | 104 (10) | 104 (7) | 103 (7) | 101 (0.6) | 110 (7) | 120 (3) | 111 (10) | 109 (8) |
| Dicyclohexyl phthalate | 105 (2) | 99 (1) | 96 (2) | 94 (2) | 106 (2) | 98 (2) | 92 (4) | 92 (3) |
| Di- <i>n</i> -heptyl phthalate | 105 (3) | 100 (2) | 97 (3) | 93 (3) | 106 (4) | 101 (2) | 96 (6) | 98 (5) |
| Pyriproxyfen | 108 (5) | 105 (4) | 101 (5) | 98 (2) | 102 (6) | 104 (1) | 100 (7) | 98 (6) |
| Di(2-ethylhexyl)phthalate | 99 (4) | 92 (1) | 90 (2) | 91 (2) | 98 (3) | 92 (3) | 90 (5) | 91 (5) |
| Tricresyl phosphate | 103 (5) | 109 (4) | 113 (7) | 99 (11) | 113 (7) | 112 (8) | 108 (8) | 95 (8) |
| Permethrin | 108 (5) | 104 (4) | 103 (5) | 97 (5) | 107 (6) | 109 (3) | 106 (8) | 104 (9) |
| Cyfluthrin | 109 (9) | 105 (9) | 103 (9) | 93 (7) | 104 (11) | 112 (2) | 111 (13) | 109 (18) |
| Ethofenprox | 109 (7) | 105 (5) | 101 (6) | 91 (7) | 107 (9) | 106 (3) | 103 (10) | 103 (12) |
| Silafuofen | 108 (7) | 104 (4) | 103 (7) | 93 (8) | 101 (8) | 109 (4) | 108 (10) | 108 (12) |
| Deltamethrin | 109 (9) | 103 (6) | 102 (9) | 101 (8) | 105 (12) | 112 (0.7) | 106 (11) | 109 (18) |

The concentration of each compound just before storage (time: 0) was set at 100% (each compound: 7.4 µg). The values are means for three samples. Figure in parenthesis is standard deviation.

deltamethrin were more than 18%. For di-*n*-butyl phthalate and di(2-ethylhexyl)phthalate, among the eight compounds, the variation of their amounts detected in the procedure blank seems to be one of the reasons for the high values of the R.S.D. and relative error at lower concentrations. For the remaining six compounds, the calibration curves were not linear and they were quantitated using the calibration curves calculated as quadratic functions. The disagreement of the simulation curves with the measured values at low concentrations of the standard solutions for calibration was considered to be the reason for the high relative error values with 0.20 µg spiking. With this spiking, the measured values in all of the six compounds were lower than their concentrations calculated from the spiked amounts. The 43 SVOCs, with the exception of the above 10 compounds, could be determined accurately at airborne concentrations of 27 ng/m³ to 1.0 µg/m³.

3.8. Storage stability

The stabilities of 53 SVOCs in the adsorbents at 4 °C were examined, and the results are shown in Table 10. For all of the SVOCs, no degradation was observed over one month. The samples were not demonstrated to be contaminated during storage periods by ubiquitous phthalates in the indoor air of the laboratory because there was no increase of di-*n*-butyl phthalate, di(2-ethylhexyl)phthalate or other chemicals over the observation periods. These results show that the samples can be stored for up to one month at 4 °C protected from light in the refrigerator until analysis.

4. Conclusions

Among the 73 SVOCs shown in Tables 1, 19 compounds, namely most of the pyrethroids (empenethrin, furamethrin, allethrin, prallethrin, imiprothrin, resmethrin, tetramethrin, phenothrin and cyphenothrin), 1-chloronaphthalene, thiuram, furmecycloz, fenthion, MGK-264, methoprene, difolatan, hydramethylnon, piperonyl butoxide and propetamphos could not be collected sufficiently by the present sampling method. The desorption efficiency of thiabendazole from the adsorbents was unsatisfactory. Therefore, they could not be determined by the present method.

Quantification of IPBC, pentachlorophenol, BECDIP, CPIP, fenitrothion, dichlofluanid, TCMTB, cyproconazol, tris(2-butoxyethyl)phosphate, pyridaphenthion, tris(2-ethylhexyl)phosphate, cyfluthrin and deltamethrin was attempted using the calibration curves calculated as quadratic functions because the curves were not linear. However, most of these compounds could not be determined accurately at low concentrations in air.

The remaining 40 compounds displayed linear calibration curves over the airborne concentration range of 0–2 µg/m³. These compounds could be determined accurately and precisely at the concentrations studied, though the reproducibil-

ity and accuracy of the values measured for di-*n*-butyl phthalate and di(2-ethylhexyl)phthalate were poor at low concentrations because they were detected as procedure blanks. Most of the 40 compounds were detectable at concentrations of more than 0.5 ng/m³ in air. In addition, the samples collected SVOCs could be stored for up to one month at 4 °C protected from light in the refrigerator until analysis.

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References

- [1] M. Miyata, K. Oono, *Allergol. Immunol.* 6 (1999) 970.
- [2] S. Torii, Shikku Hausu Shoukougun, Tokuma Shoten, Tokyo, 1997.
- [3] World Health Organization, Indoor Air Quality, Organic Pollutants, Report on WHO-meeting, EURO Reports and Studies 111, WHO Regional Office for Europe, Copenhagen, 1989.
- [4] I. Saito, A. Onuki, H. Seto, S. Uehara, *Jpn. Soc. Atmos. Environ.* 38 (2003) 78.
- [5] C.G. Wright, R.B. Leidy, H.E. Dupree Jr., *Bull. Environ. Contam. Toxicol.* 40 (1988) 561.
- [6] K.S. Roinestad, J.B. Louis, J.D. Rosen, *J. AOAC Int.* 76 (1993) 1121.
- [7] T. Otaka, J. Yoshinaga, Y. Yanagisawa, *Environ. Sci. Technol.* 35 (2001) 3099.
- [8] A.J. Dobbs, N. Williams, *Environ. Pollut. (Ser. B)* 6 (1983) 271.
- [9] N.K. Wilson, J.C. Chuang, C. Lyu, *J. Expos. Anal. Environ. Epidemiol.* 11 (2001) 449.
- [10] S. Yoshida, S. Taguchi, S. Fukushima, *J. Health Sci.* 46 (2000) 104.
- [11] J. Sherma, *Anal. Chem.* 61 (1989) 153R.
- [12] K. Kawata, A. Yasuhara, *Bull. Environ. Contam. Toxicol.* 52 (1994) 419.
- [13] A. Gudehn, B. Kolmodin-hedman, *J. Chromatogr.* 387 (1987) 420.
- [14] D.T. Williams, C. Shewchuck, G.L. Lebel, N. Muir, *Am. Ind. Hyg. Assoc. J.* 48 (1987) 780.
- [15] T.J. Class, J. Kintrup, *Fresenius J. Anal. Chem.* 340 (1991) 446.
- [16] J.N. Seiber, D.E. Glotfelty, A.D. Lucas, M.M. McChesney, J.C. Sagebiel, T.A. Wehner, *Arch. Environ. Contam. Toxicol.* 19 (1990) 583.
- [17] I. Saito, N. Hisanaga, M. Gotoh, T. Matsumoto, Y. Takeuchi, *Bull. Environ. Contam. Toxicol.* 37 (1986) 664.
- [18] K. Kawata, A. Yasuhara, *Chemosphere* 25 (1992) 821.
- [19] M.C. Marquez, F.J. Arrebola, F.J.E. Gonzalez, M.L.C. Cano, J.L.M. Vidal, *J. Chromatogr. A* 939 (2001) 79.
- [20] E.M. Roper, C.G. Wright, *Bull. Environ. Contam. Toxicol.* 33 (1984) 476.
- [21] F.J.E. Gonzalez, M.L.C. Cano, J.L.M. Vidal, M.M. Galera, *J. AOAC Int.* 80 (1997) 1091.
- [22] R.B. Leidy, C.G. Wright, *J. Environ. Sci. Health B24* (1991) 367.
- [23] K. Kawata, H. Mukai, A. Yasuhara, *J. Chromatogr. A* 710 (1995) 243.
- [24] X. Guardino, J. Obiols, M.G. Rosell, A. Farran, C. Serra, *J. Chromatogr. A* 823 (1998) 91.
- [25] E.R. Kennedy, M.T. Abell, J. Reynolds, D. Wickman, *Am. Ind. Hyg. Assoc. J.* 55 (1994) 1172.
- [26] T. Matsumura, M. Hamada, K. Ito, M. Ando, A. Isozaki, *J. Soc. Indoor Environ. Jpn.* 1 (1998) 11.

- [27] I. Saito, A. Onuki, H. Seto, M. Takeuchi, E. Tsuchiya, J. Ozawa, K. Nakaaki, *J. Soc. Indoor Environ. Jpn.* 2 (1999) 54.
- [28] S. Uemura, H. Kawamura, M. Tsuji, S. Tomita, S. Maeda, *Nouyaku Dokusei no Jiten*. Sanseido, Tokyo, 1988.
- [29] The Society for the Research of Household Insect Pests, Japan, *Kaoku Gaichu Jiten*, Inoueshoin, Tokyo, 1995.
- [30] *The Chemical Daily*, 13398 no Kagaku Shouhin, Tokyo, 1998.
- [31] D.H. Lee, K. Tsunoda, M. Takahashi, *Mokuzai Gakkaishi* 37 (1991) 261.
- [32] D.H. Lee, K. Tsunoda, M. Takahashi, *Mokuzai Gakkaishi* 37 (1991) 76.
- [33] H. Nakashima, I. Matsunaga, N. Miyano, M. Kitagawa, *J. Health Sci.* 46 (2000) 459.
- [34] T. Meissner, F. Schweinsberg, *Toxicol. Lett.* 88 (1996) 237.
- [35] T.J. Class, *J. High Resolut. Chromatogr.* 14 (1991) 48.
- [36] V.B. Stein, T.A. Amin, R.S. Narang, *J. Assoc. Off. Anal. Chem.* 70 (1987) 721.
- [37] J.A. Singmaster III, D.G. Crosby, *Bull. Environ. Contam. Toxicol.* 16 (1976) 291.
- [38] S.C. Leung, B.Y. Giang, *Bull. Environ. Contam. Toxicol.* 50 (1993) 528.
- [39] L.O. Ruzo, in: D.H. Hutson, T.R. Roberts (Eds.), *Progress in Pesticide Biochemistry*, vol. 2, Wiley, New York, 1982, p. 1.
- [40] A. Ramesh, A. Vijayalakshmi, *J. Environ. Monit.* 3 (2001) 191.
- [41] *Pharmaceutical and Food Safety Bureau of the Ministry of Health, Labour and Welfare, A Notice (IYAKU-828)*, Japanese Government, Japan, 2001.