



Unconventional and user-friendly sampling techniques of semi-volatile organic compounds present in an indoor environment: An approach to human exposure assessment

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ABSTRACT

The commonly applied solutions used to assess the potential risk of human exposure to semi-volatile organic compounds (SVOCs) are based on the investigation of biological samples collected in an invasive or non-invasive manner. For SVOCs, which are typically introduced to humans through the respiratory system, dermal adsorption, or digestive system, sampling solutions generally used in the indoor environments are classified as active and passive. From the user's perspective, the most convenient method to assess the potential risk is the use of an analytical tool that combines the benefits of passive and non-invasive sampling techniques—use of an unconventional personal sampler such as a silicone wristband, brooch, dog tag, cotton gauze, or viscose wiper. Despite the advantages of this method, the aforementioned techniques require further analytical research owing to the differences in the results of human exposure assessment owing to the lack of standards and unified sampling protocols.

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1. Introduction

Semi-volatile organic compounds (SVOCs) are considered an emerging class of contaminants owing to their ubiquity and negative impact on the environment and human health. SVOCs might be toxic to aquatic environments and could have a chronic toxic effect on the central nervous and reproductive systems in living organisms, such as: thyroid dysfunction, neurological defects, behavioral changes, delayed onset of puberty, predisposition to obesity fetal malformations [1–3]. Furthermore, SVOCs have the proven ability to transport over long distances and undergo bioaccumulation through the trophic chain (in animal tissues). SVOCs are also recognized as important/relevant indoor environment pollutants as relatively high concentrations of them have been reported in almost every element of the indoor environment.

In terms of human exposure and, consequently, the impact on the human body, SVOCs might be introduced to the organism mainly through the digestive system (via polluted food consumption as well as dust, which is a hazard particularly for toddlers and infants) [4,5].

However, when people spend most of their daily time indoors (up to 100% of the day during pandemics), the primary human exposure to SVOCs could be through inhalation or skin rather than food consumption [6,7]. Consequently, the risk of human exposure to SVOCs (and a long-term potential threat to human health) is mainly associated with the indoor environment owing to long exposure time and the wide spectrum of emission sources (such as additives to plastics, textiles, electrical and electronic equipment, floor coverings, furnishings, and other synthetic materials present in indoor elements), causing higher concentrations of pollutants [8–10]. Furthermore, the problem of presence of SVOCs in indoor environments, such as households, apartments, workplaces, and public utilities, has become increasingly important because some of the SVOCs are not chemically bonded to the structure of the material (lack of binding sites on the polymer surface), and could be present both in the gaseous phase and as compounds adsorbed on the surface of particulate matter (house dust, microorganisms, and indoor aerosols). The predicted and indicative transportation pathways of SVOCs (based on compounds classified as flame retardants) into the indoor microenvironment have been described in detail previously [11–13]. Consequently, direct air inhalation, inhalation of re-entrained dust particles, skin contact (dermal sorption), and inadvertent ingestion after hand-to-mouth contact are the dominant pathways of SVOCs into the human body in enclosed spaces [14].

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Following the currently available literature data, it should be noted that in indoor environments, several groups of chemical compounds classified as SVOCs were determined. Their occurrence and content levels in enclosed areas are related to their source of origin (direct emission from indoor material), as well as regular or irregular human activity (cooking, painting, renovation works). The most common SVOCs that might occur in an indoor environment are: (i) polycyclic aromatic hydrocarbons (PAHs), which are emitted indoors from deep oil frying, candle burning, or low-efficiency heating stoves [15,16]; (ii) polychlorinated biphenyls (PCBs), which are mainly derived from electronic devices and floor coverings and have been replaced by polybrominated diphenyl ethers (PBDEs) [17,18]; (iii) PBDEs, which are gradually being phased out and replaced by organophosphate flame retardants (OPDRs); however, they still might be present in textiles, electronic devices, and furniture elements [19,20]; (iv) OPFRs, which are introduced in foams, furniture, textile and personal care products [21,22]; (v) chlorinated paraffins (CPs), which are applied as additives (flame retardants) in paints, adhesives, sealants, plastics, rubbers, and textiles [23,24]. Considering the indoor environment quality (IEQ), the concentration level of the representative SVOCs determined in indoor air might be in the range of pg m^{-3} to several $\mu\text{g m}^{-3}$ and of pg g^{-1} to several mg g^{-1} in house dust samples. In a review paper the examples of presence of SVOCs in consumer and indoor products, has been reported by Lucattini et al. [6].

The identification and assessment of the content level of chemicals classified as SVOCs in indoor air (in a sample of the gaseous phase, condensed phase, or in a sample of particulate matter, such as house dust) might be considered an essential step to estimating and predicting the exposure and, from a future perspective, to assess the potential health risks due to SVOC exposure. Generally, analytes present in gaseous or condensed phases are collected using passive or active/dynamic sampling techniques directly in a defined indoor area, living or working space. Dust samples might be collected manually from indoor surfaces, as well as automatically using pumps equipped with various types of filters. Additionally, some indoor devices, such as air conditioning, vacuum cleaners, personal computers, or cooker hoods, may be considered user-operated dust sampling devices [25–28]. Another important step in assessing the human exposure to SVOCs compounds is the application of biomonitoring, in which the samples of biological materials are collected in an invasive or non-invasive manner, with or without disruption of tissue continuity. This type of research is obliged to receive authorization and approval from the appropriate ethics committee. In the case of invasive solutions, the main object of research contains samples of human tissues, such as liver fractions, adipose tissue, serum, or blood. In general, the entire sampling procedure can be stressful for humans. Regarding non-invasive solutions, samples are collected without disruption of tissue continuity and come directly from the human body, including nails, hair, saliva, urine, and breast milk. The benefits of non-invasive solutions are the sampling process, which is less complicated than in the case of invasive sampling, and prolonged sample storage time prior to the analysis without the loss of information [29]. However, the sampling step does not always consider the presence of primary compounds metabolites. In this case, the selection of the appropriate analytical procedure had a significant influence. General approaches commonly used to assess the human exposure to SVOC in indoor environment are summarized in Fig. 1. More detail information referring to techniques, direct and indirect, commonly used to assess the personal exposure to SVOCs in an indoor environment, pointing out/indicating their advantages and limitations, is presented in Supplementary Materials (Supplementary Section 1). The promising alternative to direct and indirect approaches in estimation of

human exposure to SVOCs seems to be personal passive samplers employing unconventional and user-friendly solutions of analyte samples collection.

This article provides comprehensive, state-of-the-art, unconventional, non-invasive, and user-friendly sampling techniques for selected SVOCs that occur in an indoor environment to estimate the human exposure. The aim of this paper is to highlight the main advantages and limitations of the unconventional techniques of sample collection and to indicate the application potential of both cotton gauze and viscose wipers as wipe techniques for sample collection, and rubbery silicone polymer elements (wristbands, brooches, and dog tags) as personal, useful, and user-friendly passive samplers. This type of approach makes it possible to estimate the daily human exposure to SVOCs from a wide spectrum of micro-environments.

2. Wiping techniques application in SVOCs sampling protocol

The primary example of the use of unconventional and user-friendly sampling approach is the wiping technique. This solution is generally employed as a relatively new approach for collecting SVOCs from flat indoor surfaces and/or inhabitants' hands (skin wipes). The application of this technique is possible because SVOCs can be adsorbed at the surface layer of the material by adhesion of chemical compounds to the surface, as well as when the surface layer is covered with organic material, such as lipids (sebum on skin lipid film). Additionally, this type of sampling solution offers the possibility of directly assessing exposure, mainly from dermal absorption [30]. According to Wang et al. [31], depending on the type of samples collected (i.e., back of the hand or palms), hand/skin wipes can either characterize uptake from indoor/outdoor air and dust (back of the hand), or they assimilate the hand-to-mouth path (e.g., nail biting, smoking, thumb and finger sucking) due to contact with various types of surfaces (palms).

2.1. General stages of analytical protocols using wiping techniques

The wipes used in the sampling protocols are usually prepared based on well-characterized cotton or viscose (in the form of sterile gauze pads or wipes). All analytical procedures described in the literature, in which the wiping technique was introduced, are characterized by several common stages (schematically shown in Fig. 2). More information about the application of wiping techniques and general conditions of analytical protocols (including wiping procedure, pre-cleaning stage, extraction conditions, and concentration ranges of targeted chemicals) for determining the SVOCs representatives from defined surface areas (indoor materials and human skin) is listed in Table 1. At this point, it should be highlighted that the applied SVOCs extraction technique (using Soxhlet or ultrasound bath) is characterized by low selectivity because a wide spectrum of SVOCs might be extracted from the applied wipe. Consequently, after the extraction stage, it is necessary to introduce an analytical protocol using the isolation and/or preconcentration technique, such as the SPE technique with an appropriate sorbent, to narrow the spectrum of collected SVOCs. It is also worth considering fractionating the extract and analyzing it after passing it through various types of SPE sorbents to determine a specific group of compounds classified as SVOCs [32].

2.2. SVOCs representatives collected by wiping techniques

Considering the data presented in Table 1, it can be observed that the wiping technique is mostly employed for the determination of phthalates and PBDEs adsorbed on the surface of human skin on indoor equipment. The parameter that generally describes

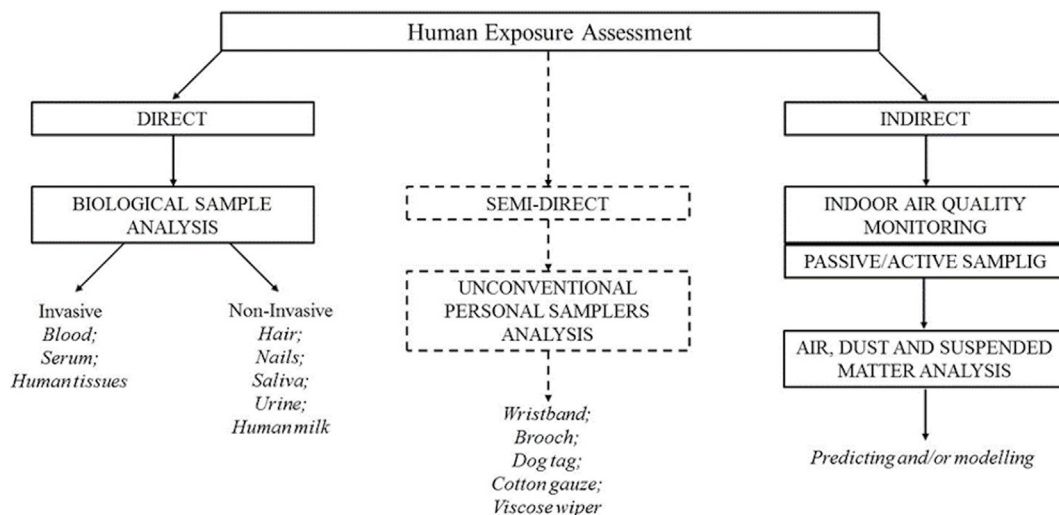


Fig. 1. Analytical approaches used to assess the human exposure to SVOCs.

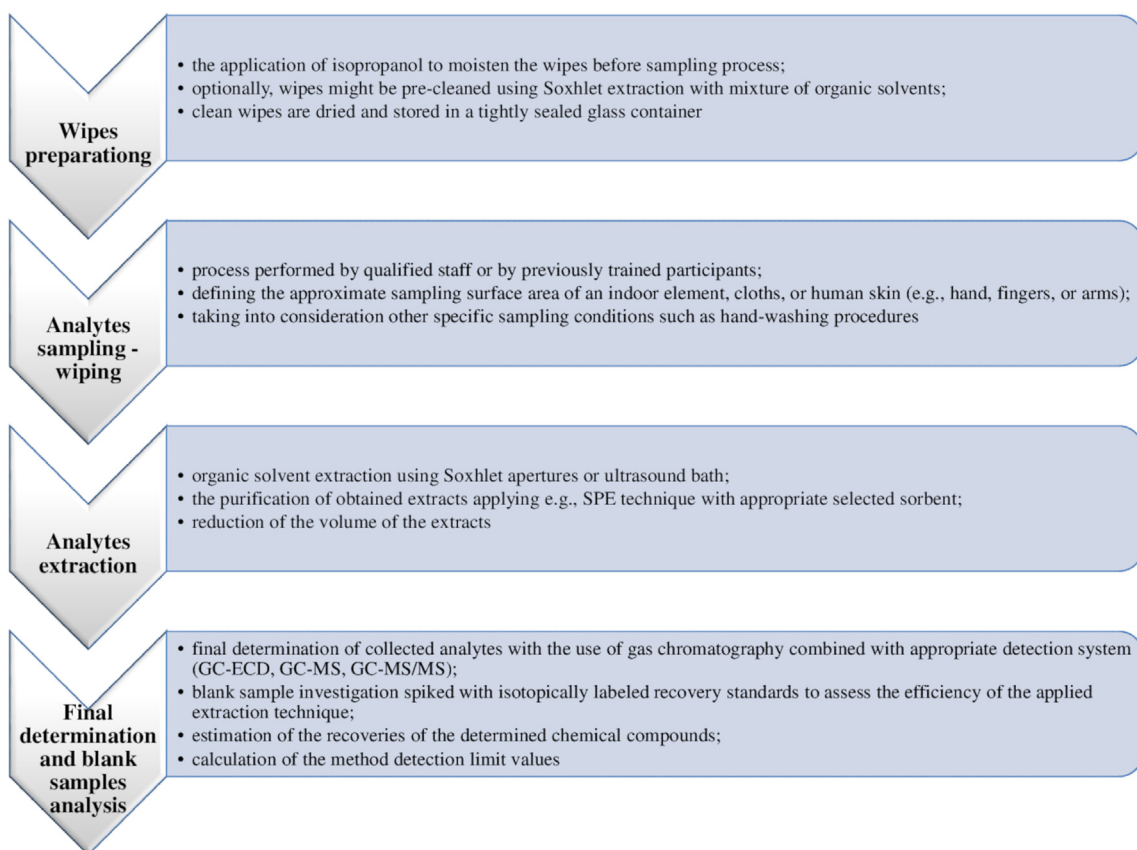


Fig. 2. General stages of analytical protocols used to determine SVOCs by wiping technique.

the applied type of wiping material is the surface area (indoor element or hand area estimated by applying the trapezoid method) from which the samples were collected. There are no specific or restricted conditions to prepare the wipe materials before the sampling process, and the liberation process of the collected SVOCs is not very complicated. For this reason, it should be kept in mind that received analytical information about the amount of adsorbed SVOCs is only the screening information, and the obtained results might be difficult to compare with other results received from a different scientific center. Nevertheless, as was proved by Hoffman

et al. [33] and Hammel et al. [34], the concentration of SVOCs representatives (four OPFR compounds and their metabolites, tris(1,3-dichloroisopropyl) phosphate, tris(1-chloro-2-isopropyl) phosphate, triphenyl phosphate, and monosubstituted isopropylated triaryl phosphate) determined using the wiping technique was significantly correlated with results obtained using different sampling techniques, such as passive sampling and non-invasive sampling of biological material (urine samples).

To demonstrate the application potential of the aforementioned wiping techniques, Esttil et al. [35] investigated four beauty salons in

Table 1
Information on the analytical protocols used to determine the amount of SVOCs in wipe samples.

Wiping procedure	Pre cleaning – wipe preparation	Extraction	Recovery of extraction	Concentration of targeted groups	Ref.
10 adult participants; Wiping of dominant hand before wash.	Soxhlet extraction: acetone/hexane for 24 h; Saturated with isopropanol	Ultrasound extraction: hexane/acetone (25 mL/15 min - two repetitions); Solvent changing: hexane (volume reduction to 2 mL); Purification: water-deactivated silica column; Elution: hexane (12 mL); hexane/DCM (12 mL); acetone/DCM (12 mL); Volume reduction to 1 mL	Values for matrix spike: PAHs: 71.6 ÷ 103%; PBDEs: 56.9 ÷ 88.5%; nBFRs: 53.6 ÷ 88.4%; OPEs: 85.5 ÷ 115%	Total PAHs (10) range: 0.84 ÷ 11.18 ng cm ⁻² ; Median - 1.37 ng cm ⁻² ; Total PBDEs (12) range: 0.73 ÷ 8.93 ng cm ⁻² ; Median - 2.11 ng cm ⁻² ; Total nBFRs (9) range: 52 pg cm ⁻² ÷ 12.51 ng cm ⁻² ; Median - 1.61 ng cm ⁻² ; Total OPEs (7) range: 2.10 ÷ 96.83 ng cm ⁻² ; Median - 8.99 ng cm ⁻²	[31]
Participants with no skin diseases; Lack of use of skincare products; 7 different skin locations; Wiping performed using gauze pads	Soxhlet extraction: DCM for 4 h; Dried and wetted with isopropanol	Soxhlet extraction: DCM (120 mL/6 h); Extracts concentration to 25 mL; Volume reduction to 300 µL	79 (±9%) ÷ 85 (±9%)	DIBP: 98 ÷ 947 µg m ⁻² ; DBP: 18 ÷ 1865 µg m ⁻² ; DEHP: 200 ÷ 1020 µg m ⁻²	[36]
38 participants; The use of cotton twill wipes on both hands.	Soxhlet extraction: acetone/hexane for 12 h; Purification and drying	Ultrasound extraction: hexane/acetone - three repetitions; Volume reduction of combined extracts to 1 mL	97 (±12%) ÷ 119 (±14%)	TDCPP - geometric mean – 108.3 ng per wipe; TCPP - geometric mean - 45.42 ng per wipe; TPhP – geometric mean - 22.41 ng per wipe; mono-ITP – geometric mean - 120.2 ng per wipe	[34]
Wipes collected by scientist stuff, both hands were wipe from 11 participants	Sterile gauze wipe soaked in isopropanol	Soxhlet extraction: DCM/hexane; Extracts purification: SPE column with Florisil; PBDEs elution: hexane (10 mL); PFRs elution: ethyl acetate (10 mL); Volume reduction of each fraction to 1 mL	63 (±17%) ÷ 91 (±18%)	TDCPP - geometric mean – 84.1 ng per wipe; TPhP - geometric mean – 62.1 ng per wipe; BDE-47 - geometric mean – 18.4 ng per wipe; BDE-99 - geometric mean – 26.0 ng per wipe; BDE-100 - geometric mean – 2.8 ng per wipe; BDE-153 - geometric mean – 1.3 ng per wipe; BDE-154 - geometric mean – 1.0 ng per wipe; BDE-209 - geometric mean – 19.5 ng per wipe.	[33]
Wipe was collected from 33 participants; top and bottom of hand and space between fingers	Sterile gauze pads immersed in isopropanol	Ultrasound extraction: DCM (40 mL/20 min - three repetitions); Purification: deactivated alumina BDEs elution: petroleum ether (50 mL); Volume reduction to 0.5 mL of hexane.	Average value: 50 ÷ 84%	BDE-17 – mean 1.16 ng per wipe BDE-28, 33 - mean 1.35 ng per wipe BDE-47 - mean 72.7 ng per wipe BDE-49 - mean 5.49 ng per wipe BDE-66 - mean 3.07 ng per wipe BDE-85 – mean 1.33 ng per wipe BDE-99 – mean 72.2 ng per wipe BDE-100 – mean 13.2 ng per wipe BDE-138 – mean 0.60 ng per wipe BDE-153 – mean 15.8 ng per wipe BDE-154 – mean 4.88 ng per wipe BDE-183 - mean 0.70 ng per wipe BDE-209 – mean 43.1 ng per wipe	[37]
Toddlers between 1 and 3 years; Wipes collected by trained personnel; the entire surface area of the child's hands from fingers to the wrist			Average value: 102 (±15%)	BDE-17: 0.5 ÷ 3.3 ng per wipe; BDE-28: 0.5 ÷ 14.8 ng per wipe; BDE-47: 2.3 ÷ 923 ng per wipe; BDE-66: 0.2 ÷ 67.8 ng per wipe; BDE-85/155: 0.2 ÷ 27.7 ng per wipe; BDE-99: 3.1 ÷ 1001 ng per wipe; BDE-100: 0.9 ÷ 228 ng per wipe; BDE-153: 0.3 ÷ 35.3 ng per wipe; BDE-154: 0.3 ÷ 46.6 ng per wipe; BDE-183: 1.8 ÷ 2.1 ng per wipe; BDE-209: 4.5 ÷ 283 ng per wipe	[38]
12 nail salon technicians working at four nail salons; Hand wipe samples collected before and after the work shift;	Sterile gauze pads soaked in isopropanol	Lack of data	89.2 ÷ 129%	TPhP concentration: Hand Wipe Average: 0.16 ÷ 4.36 µg per wipe; Hand Wipe Pre: 0.02 ÷ 3.18 µg per wipe; Hand Wipe Post: 0.22 ÷ 7.91 µg per wipe	[35]
College students - 20 male and 10 female; Samples collected from the forehead, back,	Medical gauze pads sonicated	Ultrasound extraction: DCM (50 mL/30 min - three	72.9 ÷ 118.4%	The median concentrations: DIBP: 5.10 × 10 ⁻² ÷ 1.58 × 10 ² µg m ⁻² ;	[39]

Table 1 (continued)

Wiping procedure	Pre cleaning – wipe preparation	Extraction	Recovery of extraction	Concentration of targeted groups	Ref.
both hands, both forearms, both calves, as well as left and right instep	with DCM; Vacuum-dried and soaked in isopropanol.	repetitions); Purification: organic microporous membrane; Volume reduction to 1.0 mL		DBP: $6.24 \div 6.84 \times 10^2 \mu\text{g m}^{-2}$; DMEP: $5.62 \div 7.44 \times 10^2 \mu\text{g m}^{-2}$; DBEP: $14.3 \div 2.02 \times 10^3 \mu\text{g m}^{-2}$; DEHP: $13.3 \div 1.97 \times 10^3 \mu\text{g m}^{-2}$; DnOP: $1.72 \div 5.35 \times 10^3 \mu\text{g m}^{-2}$; DNP: $16.3 \div 5.75 \times 10^3 \mu\text{g m}^{-2}$	
55 adult office workers; Wiping surfaces: palm and back of the hand from wrist to fingertips; computer keyboards and mobile phones	Washing with DCM/acetone; Sterile gauze pads immersed in isopropanol.	Accelerated solvent extraction: DCM/acetone - three repetitions; Volume reduction to 2 mL; Purification: SPE column with Florisil; Analytes elution: DCM (100 mL); DCM/acetone (100 mL); Volume reduction to 0.1 mL of DCM	Hand surface: $90 \div 108\%$; surfaces of electronic devices: $93 \div 108\%$	Mean values (hands): DMP – 0.157 μg ; DEP – 0.837 μg ; DnBP – 16.0 μg ; BBP – 2.34 μg ; DEHP – 381 μg ; DnOP – 2.52 μg Mean values (keyboard): DMP – 0.71 μg ; DEP – 1.98 μg ; DnBP – 41.9 μg ; BBP – 1.92 μg ; DEHP – 415 μg ; DnOP – 5.22 μg Mean values (mobile phones): DMP – 0.63 μg ; DEP – 1.98 μg ; DnBP – 42.5 μg ; BBP – 1.06 μg ; DEHP – 116 μg ; DnOP – 1.54 μg	[40]

BBP - Benzyl butyl phthalate; DBEP - di (2-*n*-butoxyethyl) phthalate; DBP - di(*n*-butyl) phthalate; DCM – dichloromethane; DEHP - Di-2-ethylhexyl phthalate; DEP - Diethyl phthalate; DIBP - di(isobutyl) phthalate; DMEP - di (2-methoxyethyl) phthalate; DMP - Dimethyl phthalate; DnBP - Dibutyl phthalate; DnOP - Di-*n*-octyl phthalate; DNP - dinonyl phthalate; mono-ITP - monosubstituted isopropylated triaryl phosphate; nBFRs - Novel brominated flame retardants; OPEs - Organophosphate esters; PAHs – polycyclic aromatic hydrocarbons; PBDEs - Polybrominated diphenyl ethers; PFRs - Organophosphorus flame retardants; TCPP - tris(1-chloro-2-isopropyl) phosphate; TDCPP - tris(1,3-dichloropropyl) phosphate; TPhP - Triphenyl phosphate.

San Francisco (California, USA), which focused on assessing the personal exposure to triphenyl phosphate (TPhP) of nail salon workers. During the studies, three different types of samples were collected: (i) air samples collected by a personal air sampler working in a dynamic located near the breathing zone; (ii) hand wipe samples collected pre-shift and post-shift using sterile gauze pads; and (iii) urine samples collected from cups at the workplace prior to workers' first-day shift. It was shown that, the geometric mean of investigated TPhP collected by personal active air sampler ranged from 2.94 to 21.9 ng m³. As for the unconventional sampling technique, the geometric mean of TPhP ranged from 0.17 to 4.36 μg per sample. The authors did not perform a comparative statistical analysis of the database obtained by active and unconventional sampling techniques, probably due to differences in the units in which the results were presented. Regarding the data obtained from investigations of biological material, the authors noticed that there is a correlation between urinary diphenyl phosphate (DPhP) concentrations (ranged from 0.11 to 6.32 $\mu\text{g dm}^3$) and post-shift hand wipe TPhP concentrations (ranged from 0.22 to 7.91 $\mu\text{g dm}^3$). This correlation suggests that a dermal route may be a primary exposure pathway for TPhP in the investigated indoor environment, and the wiping technique might be successfully used for screening studies to assess personal dermal exposure to selected SVOCs [35].

2.3. Exposure assessment using wiping techniques

From the perspective of users/residents/volunteers, the wiping sampling technique is convenient, simple to implement, practical, and most importantly non-invasive. Nevertheless, considering this sampling technique for SVOCs, the analytical information obtained and analytical procedures used are subject to certain limitations. In particular, the sample size and number of investigation participants (population) were considered. In all demonstrated cases, the

common denominator was a relatively small sample size. It is mainly associated with difficulties in recruiting appropriate volunteers characterizing a specific type of population. Additionally, using the wiping technique, only defined body areas were sampled. The obtained analytical information were screened rather than correlated with the whole human organism. To obtain more accurate exposure assessment, it is recommended to perform the hand wiping more frequently [31,36]. According to Gong et al. [36], dermal adsorption of chemical compounds is determined by the gradient (more correctly, the fugacity concentration) between the human skin surface and human blood in the dermal capillaries. For this reason, dermal absorption is associated with a time-dependent content level specified as “determined mass of analytes per cubic meter” on the skin surface. In contrast, techniques such as skin wiping or hand rinsing only measure the surface level (“determined mass of analytes per area”) [35]. This information can be observed by analyzing the data listed in Table 1, where information about the concentration level of defined SVOCs is defined as the mass of analytes per wipe or mass of analytes per sampling/wipe area. Consequently, this creates a problem when comparing the research results obtained in various research centers. An additional issue that should be considered as a limitation of the sampling technique is the type of sampling material applied. It is highly recommended to use commercially available sterile cotton gauze pads or viscose wipers rather than self-made wipes. This is mainly related to the necessity to have relatively uniform dimensions of the material used and a uniform structure, while ensuring adequate cleanliness of the material before starting the sampling process.

3. Rubbery silicone polymer personal passive samplers

Rubbery silicone polymer - polydimethylsiloxane (PDMS) - is described in the literature as a highly hydrophobic, chemically

inert, thermally stable, and nonbioaccumulative material. The physicochemical properties and sorption abilities of PDMS were described in detail by Yates et al. [41], Seethapathy and Górecki [42] and Okeme et al. [43]. The application of rubbery silicone polymers in studies associated with IEQ and personal exposure to SVOCs is a relatively new approach. Silicone materials in the form of wristbands, brooches, or sheets are gaining popularity as commercially available or homemade user-friendly individual/personal passive samplers. The advantages of silicone bands include their low price, easy preparation of the sampler before exposure, high chemical and physical resistance to exposure conditions, and being unobtrusive and well tolerated by users, especially children. Silicone bands and brooches have been successfully used to characterize personal exposure to a wide variety of chemicals in different indoor conditions and populations. The application of silicone wristbands and other similar sampling solutions based on PDMS offers the possibility of receiving screening information about exposure from multiple micro-environments over a multiday time period, as well as receiving data about individual exposures from multiple routes. Furthermore, rubbery silicone polymer samples might be considered as a potential alternative solution or complement approach to the complexity of large-scale biomonitoring endeavors – potentially highly beneficial solutions for epidemiological investigations, for example, by assessing exposure to EDCs [44].

3.1. Silicone personal sampler in the form of wristband

Silicone personal samplers in the form of wristbands were introduced by O'Connell et al., in 2014 [45]. The authors performed an investigation to prove that the mentioned material, which is commonly used in commercially available wristbands (in various colors and forms), might be properly adapted to act as a convenient personal passive sampler. Candidates for personal silicone samplers were fully characterized by performing studies associated with modification of the commercially available wristband for analytical purposes (sampling stage), evaluating the pre-cleaning and storage conditions before starting sampling campaigns, infusion, setting up the conditions of the wristband exposure and extraction of collected analytes, and ultimately developing an appropriate qualitative and quantitative final determination procedure. To check the possibility of using the investigated personal passive samplers, field studies were carried out with the contribution of a selected group of participants - roofers working with hot asphalt and potentially exposed to PAHs. The samplers were worn by the participants for both a single day (approximately 8 h) and a representative workweek (32–39 h). The authors stated that during the investigations, 49 different compounds were identified, including 25 PAHs, consumer and personal care products, pesticides, and phthalates. Considering the obtained results, the authors concluded that silicone wristbands might be introduced to analytical practice and personal exposure monitoring research as sensitive personal sampling devices [45]. Since then, various personal applications and forms of rubbery silicone polymer passive samplers have been used to evaluate personal exposure to a wide spectrum of chemicals, including PBDEs, novel BFRs, PAHs, OPEs, PCBs, phthalates, and pesticides [46].

Other applications of silicone wristbands were described by Hammel et al. [44] and are associated with the use of silicone wristbands as a convenient sampler to assess personal exposure to brominated flame retardants (PBDEs) and novel BFRs. Additionally, the authors wanted to prove that the application of a silicone wristband during the sampling stage of analytes and obtained results of personal human exposure might be comparable to biomarker measurements (serum biomarkers). The investigated cohort consisted of 30 adult participants who had lived in their

homes for at least one calendar year. Considering the obtained results, it was noticed that in both wristband samples) and in serum samples (ng per gram of the lipid), BDE-47 was the most abundant compound with geometric means of 55.9 (ng per gram of the band) and 6.80 (ng per gram of the lipid), respectively. Additionally, the authors assessed the correlation between the results obtained from the silicone wristbands and serum samples for six of the measured PBDEs. Spearman's correlation coefficient analysis revealed a statistically significant relationship between data from silicone wristbands and serum samples for PBDE-47, PBDE-99, and PBDE-100. Considering the obtained results and performing statistical analysis, the authors concluded that silicone wristbands worn by the participants for seven days, might be able to capture relevant personal exposures to defined PBDEs [44].

3.2. Silicone dog tag sampler

A relatively new analytical approach using silicone materials as a sampling device is military-style dog tags, which were mainly used to investigate the PAH exposure of firefighters in the Kansas City, Missouri metropolitan area [47]. Firefighters were instructed to wear the previously prepared (according to the procedure published by Anderson et al. [48] with slight modifications) silicone dog tags on an elastic necklace around the neck underneath fire-fighting personal protective equipment during the next 30 on- and off-shift days. Dog tags were placed around their neck during all daily activities including eating, showering, and sleeping. When the tags were not worn, they were stored in PTFE bags. The studies were performed in two stages: the 1st stage was associated with the quantification of 63 parent and alkylated PAHs, defined as documented fire-fighter exposure factors; 2nd stage - linked to the screening studies, included the analysis of 98 PAHs, 124 flame retardants, 185 industrial-related chemicals, 773 pesticides, 76 personal care products, 14 phthalates, and 260 polychlorinated biphenyls, dioxins, and furans. According to the authors, 45 PAHs were detected at least once in 110 of the investigated dog tags, and 21 PAHs were detected in half of the analyzed samples. Additionally, there was a lack of two identical dog tags with similar PAH exposure profile characteristics. As for the multi-screening studies, the obtained data display the presence of a clear difference between the estimated target analyte concentrations of on- and off-duty tags, as well as between firefighters' exposures at high and low fire call volume departments (parameter defined by the average number of fire calls per month and types of fires) in the investigated city. Because of the performed research, the authors conclude that some of the detected analytes (excluding PAHs), such as phthalates or DEHP, are currently classified as possible carcinogens. Additionally, the authors observed a relationship between the number of fire attacks that took place during the study and increasing PAHs dog tag concentrations. In their most recent work, the authors described the use of a developed military-style silicone dog tag to assess exposure to potential endocrine-disrupting chemicals (pEDCs) [47,49].

3.3. General stages of analytical procedures applying silicone personal samplers

Fig. 3 presents the general stages of the analytical procedures, in which the various approaches of rubbery silicone polymer are used as a sampling element for SVOCs. To carry out the entire analytical procedure using silicone samplers properly, an appropriate and practical guide developed by Anderson et al. [48] containing all necessary information on the use of silicone samplers was provided. The authors planned to establish a framework for protocols and potential applications of rubbery silicone polymer personal passive



Fig. 3. Main stages of analytical procedures applied to determine SVOCs by rubbery silicone polymer personal passive samplers.

samplers by highlighting the following issues: (i) appropriate preparation (pre-cleaning process) of the applied silicone personal sampler that ensures a simple and relatively easy quantitative determination of SVOCs; (ii) estimation of the stability of the collected analytes on a silicone passive sampler during transportation and storage; and (iii) assessment of the stability of the silicone sampler – air partitioning coefficients for investigated SVOCs [50]. At this point, it should be mentioned that, according to the literature, silicone passive obeys first-order kinetics. Silicone passive samplers in the form of personal wristbands are expected to accumulate analytes at rates comparable to the physicochemistry of individual analyses [50–52]. Each analyte is characterized by individual uptake rate in the silicone material, which may change with the surrounding microenvironment conditions, such as temperature or humidity. Taking into account the issues described in the mentioned guide, there are several articles related with the rubbery silicone polymer samplers applied to determine SVOCs and to assess potential personal exposure. The general information about the applied type of silicone sampler, sampling conditions, and basic parameters of analytical procedures used for the determination of the SVOCs representatives collected on personal samplers is listed in Table 2. Analyzing the data listed in Table 2, it can be observed that rubbery silicone polymer personal passive samplers are currently used to determine organophosphate and halogenated flame retardants (OPFRs and PBDEs), PAHs, pesticides, and plasticizers.

3.4. Problems and challenges in a personal exposure assessment using silicone samplers

Passive samplers in the form of silicone wristbands were characterized by the highest frequency of use. Their popularity has reached such a high level that a guide dedicated only to the analytical approach in the context of using silicone wristbands has been developed. A paper published by Travis et al. [53] contains valuable

information about the workflow for the identification of unknown contaminants collected by silicone wristband personal samplers using a GC-MS and innovative employment of GC/Orbitrap™ MS for unknown organic contaminants that might be introduced during exposure studies. Waclawik et al. [54] presented a valuable review of the analytical considerations associated with the application of silicone wristbands to track personal exposure to harmful chemicals. The authors clearly presented and discussed a wide spectrum of factors that should be considered when comparing the application of silicone wristbands and biomonitoring techniques in a personal exposure assessment process. Additionally, three main aspects were described and discussed: (i) an overview of the application of silicone wristbands as personal passive samplers to assess human exposure to harmful compounds; (ii) discussion (strong and weak aspects) on the selected stages of analytical protocols used to obtain information about human exposure to harmful compounds; and (iii) a comparison of the information obtained using silicone wristbands about human exposure with the data obtained by analyzing different biological (urine and blood) and environmental (air and settled dust) samples [54].

Generally, the sampling period is between five and seven consecutive days, which might be considered too short an exposure time of the applied silicone samplers (and, consequently, collection) in the case of SVOCs (especially, when in some cases it was only 72 h). The entire sample preparation stage is a very time- and solvent-consuming process. In part, a consequence of this is that the obtained recovery values of determined SVOCs from applied types of rubbery silicone polymer personal passive samplers are characterized by a very large spread (in some cases, even from approx. 50 up to 140%). Noteworthy is that the obtained research results are presented in different units: the mass of analytes per gram, mass of analytes per wristband mass of analytes per gram per day, and mass of analytes per cubic meter. This causes significant difficulties in comparing the obtained results between different populations, the

Table 2

Information on the stages of analytical procedures used to determine the amount of selected SVOCs in personal silicone passive samplers.

Population	Silicone sampler type	Pre cleaning	Extraction and clean up protocol	Recovery	Concentration of targeted groups	Ref.
10 adult contestants (3 female and 7 male) 20–60 years old	<ul style="list-style-type: none"> One silicone brooch – dimensions: 5.1 cm × 8.9 cm, 0.1 cm thickness, attached to a lapel or shirt in the breathing zone – exposed surface area – 50 cm²; Black silicone wristband wear on the wrist of the dominant hand (weight approx. 5 g); Study duration - 72 h 	<ul style="list-style-type: none"> Brooches: Soxhlet extraction: acetone/hexane for 24 h Wristbands: Two 24-h Soxhlet extractions: 1st - EtOAc/hexane; 2nd - EtOAc/MeOH; 	<ul style="list-style-type: none"> Brooches: <ul style="list-style-type: none"> ASE: hexane/acetone (100 °C/1500/10 min – three static cycles; Wristbands: <ul style="list-style-type: none"> Ultrasound extraction: acetone/hexane (30 mL/2h - left in solvent for 12 h (twice); Volume reduction and solvent changing into hexane; Extraction and fractionation – 1st SPE column with neutral alumina, neutral silica, Florisil, anhydrous sodium sulphate (elution with DCM and EtOAc, volume reduction to 1.0 mL; 2nd similar composition of SPE column – Florisil replaced by sulfuric acid-silica gel (elution with DCM, volume reduction to 1.0 mL). 	<ul style="list-style-type: none"> Brooches: <ul style="list-style-type: none"> PAHs: 45.5 ± 119%; PBDEs: 64.8 ± 90.2%; nBFRs: 66.0 ± 112.0%; OPEs: 73.2 ± 95.6%. Wristband: <ul style="list-style-type: none"> PAHs: 58.7 ± 96.1%; PBDEs: 59.5 ± 98.4%; nBFRs: 70.5 ± 103.0%; OPEs: 47.5 ± 80.9% 	<ul style="list-style-type: none"> Brooches: <ul style="list-style-type: none"> ΣPAHs (10 compounds) – 46 ± 207 ng per brooch; ΣPBDEs (12 compounds) – 0.30 ± 37 ng per brooch; ΣnBFRs (9 compounds) – 1.1 ± 166 ng per brooch; ΣOPEs (7 compounds) - 119 ± 6739 ng per brooch Wristbands: <ul style="list-style-type: none"> ΣPAHs (10 compounds) – 184 ± 2368 ng per wristband; ΣPBDEs (12 compounds) – 47 ± 480 ng per wristband; ΣnBFRs (9 compounds) – 27 ± 1165 ng per wristband; ΣOPEs (7 compounds) – 1090 ± 10 084 ng per wristband 	[31]
31 participants from Italy and 40 participants from France.	<ul style="list-style-type: none"> Silicone wristband - dimensions: 20 cm × 1.2 cm × 0.2 cm thickness. Study duration - 5 days 	<ul style="list-style-type: none"> Soxhlet extractions: 1st - EtOAc/hexane; 2nd - EtOAc/MeOH; 	<ul style="list-style-type: none"> Ultrasound extraction: acetone/hexane (30 mL/2h) left in solvent for 12 h (twice); Volume reduction and dilution to 4 mL of hexane; Extraction and fractionation - 1st SPE column packed with neutral alumina; neutral silica; Florisil and anhydrous sodium sulphate (elution with DCM and with EtOAc; volume reduction to 1 mL of hexane); 2nd similar composition of SPE column - Florisil replaced by sulfuric acid-silica gel (elution with DCM, volume reduction to 0.5 mL of hexane). 	<ul style="list-style-type: none"> For determined compounds: 54 ± 103% 	<ul style="list-style-type: none"> Italy: <ul style="list-style-type: none"> ΣPAHs (18 compounds) – 13 ± 55 ng g⁻¹; ΣPBDEs (39 compounds) – 1 ± 14 ng g⁻¹; ΣnBFRs (10 compounds) – 0.95 ± 140 ng g⁻¹; ΣOPEs (25 compounds) - 177 ± 2100 ng g⁻¹; France: <ul style="list-style-type: none"> ΣPAHs (18 compounds) – 24 ± 310 ng g⁻¹; ΣPBDEs (39 compounds) – 1.6 ± 200 ng g⁻¹; ΣnBFRs (10 compounds) – 1.0 ± 590 ng g⁻¹; ΣOPEs (25 compounds) - 176 ± 3700 ng g⁻¹ 	[59]
10 participants between 18 and 50 years old - 5 males and 5 females, non-smokers;	<ul style="list-style-type: none"> Black silicone wristbands – dimensions: approx. 1.2 cm × 20 cm × 0.2 cm, and weighed 4.98 ± 0.02 g; Study duration - 7 days 	<ul style="list-style-type: none"> Soxhlet extractions: 1st - EtOAc/hexane; 2nd - EtOAc/MeOH; 		<ul style="list-style-type: none"> Average ranges: <ul style="list-style-type: none"> PBDEs: 66 ± 141%; OPEs: 58 ± 103%; NFRs: 70 ± 100%; PAHs: 57 ± 102%. 	<ul style="list-style-type: none"> Determined compounds: <ul style="list-style-type: none"> ΣPBDEs – 28.4 ± 412 ng per wristband; ΣNFRs – 40.7 ± 625 ng per wristband' ΣOPEs – 2440 ± 9580 ng per wristband; ΣPAHs – 76.2 ± 1240 ng per wristband 	[60]
5 office workers	<ul style="list-style-type: none"> Silicone brooch (strip) – dimensions: 9 cm × 5.5 cm; thickness 0.1 cm; the exposed surface area – 50 cm²; sampler equipped with aluminum housing; Study duration - 7 days 	<ul style="list-style-type: none"> ASE: 1st - EtOAc; 2nd - acetone/hexane, 	<ul style="list-style-type: none"> Extraction in stationary shaker: ACN (30 min), left to soak overnight; Volume reduction to 1 mL; Reconstituting extract into acetone/isoctane (0.5 mL). 	<ul style="list-style-type: none"> Target compounds: 60 ± 120% 	<ul style="list-style-type: none"> Median values: <ul style="list-style-type: none"> Phthalates: <ul style="list-style-type: none"> DEHP – 465 ng m⁻³; DiBP – 423 ng m⁻³; DEP – 283 ng m⁻³; DnBP – 219 ng m⁻³; BzBP – 17 ng m⁻³; OPEs: <ul style="list-style-type: none"> TCPP-1 – 283 ng m⁻³; TCPP-2 – 125 ng m⁻³; TCPP-3 – 93 ng m⁻³; TCEP – 34 ng m⁻³; TDCPP – 17 ng m⁻³ 	[58]
30 adult participants	<ul style="list-style-type: none"> Commercially available silicone wristbands purchased in a single size and black color; Study duration - 7 days. 	<ul style="list-style-type: none"> Soxhlet extractions: 1st - EtOAc/hexane; 2nd - EtOAc/MeOH; 	<ul style="list-style-type: none"> Sonication extraction: hexane/acetone (10 mL) - tree times; Volume reduction to 1.0 mL; SPE extraction and fractionation – column with Florisil; 1st fraction elution: hexane (8 mL), 2nd fraction elution: EtOAc (10 mL); Purification: the use of deactivated acid silica gel; Volume reduction to 1 mL 	<ul style="list-style-type: none"> For all of determined compounds: 51.2 ± 141% 	<ul style="list-style-type: none"> Geometric mean for determined PBDEs ranged from 0.10 to 55.9 ng g⁻¹ for PBDE-17 and PBDE-47, respectively; Geometric mean for determined novel BFRs ranged from 0.098 to 43.0 ng g⁻¹ for OBIND and EH-TBB, respectively 	[44]
92 children aged 3–5 years old (36% female and 64%	<ul style="list-style-type: none"> Silicone wristbands – dimensions: width: 1.3 cm; inner diameter: 5.8 cm; average weight - 	<ul style="list-style-type: none"> Soaked in EtOAc, hexane and MeOH 	<ul style="list-style-type: none"> Extraction: EtOAc (100 mL/2h) - two times; 	<ul style="list-style-type: none"> Average values: for SPE 	<ul style="list-style-type: none"> Determined compounds (mean ± SD) <ul style="list-style-type: none"> ΣOPFRs - 93 ± 151 ng/g/day 	[46]

Table 2 (continued)

Population	Silicone sampler type	Pre cleaning	Extraction and clean up protocol	Recovery	Concentration of targeted groups	Ref.
male) recruited through preschools	4.64 ± 0.03 g Study duration - 7 days		<ul style="list-style-type: none"> Extracts combining and volume reduction to 300 µL; Addition of 3 mL of ACN; SPE column with 500 mg C18, pre-rinsed with ACN (6 mL); Elution: ACN (9 mL); Solvent change and volume reduction to 0.5 mL (hexane) 	technique: BDEs - 98 ± 7.3%; OPFRs - 103 ± 6.5%; BFR flame retardants - 101 ± 8.6%, Range for laboratory standards: 24 ÷ 90%.	ΣBDEs - 4.49 ± 5.59 ng/g/day ΣBFRs 8.08 ± 5.62 ng/g/day	
24 children aged 6.0 – 7.8 year attending first grade in 9 elementary schools	Commercially available silicone wristband. Silicone samplers placed on wrists and wear continuously during play, wash, and sleep Study duration - 7 days	Extraction in rotatory shaker: 1st - EtOAc/hexane; 2nd - EtOAc/MeOH (twice);	<ul style="list-style-type: none"> Extraction: EtOAc (25 mL/2h) – two times; Combining extracts and volume reduction to 300 µL; Addition of ACN (3 mL); SPE column with of 500 mg C18 pre-rinsed with ACN; Elution: ACN (6 mL); Solvent change to isoctane 	For target analytes: 50 ÷ 122%	Determined compounds (median and maximum value): ΣOPFRs 1020 and 12 300 ng per gram of wristband; ΣPBDEs 3.00 and 433 ng per gram of wristband; ΣPCBs - 0.52 and 8.35 ng per gram of wristband	[61]
56 firefighters	The silicone dog tags – dimensions: 6.0 cm long × 2.5 cm wide × 0.3 cm thick; approx. weight - 5.4 g; Study duration - the 30 on– and off-shift days	Vacuum oven conditioned at 300 °C for 12 h at 0.1 Torr;	<ul style="list-style-type: none"> Extraction: EtOAc (50 mL) – two times; Combining extracts and volume reduction to 1 mL; SPE extraction by Cleanert S C18 using ACN; Solvent change to isoctane 	PAHs: 40 ÷ 117%	PAHs detected in over 75% of the dog tags (mean ± SD): 2-ethylnaphthalene - 78.5 ± 63.6 pmol per gram of tag; 1,4-dimethylnaphthalene - 33.0 ± 24.0 pmol per gram of tag; 1,5-dimethylnaphthalene - 21.4 ± 22.8 pmol per gram of tag; 1,2-dimethylnaphthalene - 56.7 ± 48.6 pmol per gram of tag; Dibenzothiophene - 19.7 ± 11.4 pmol per gram of tag; 2-methylanthracene - 43.3 ± 28.0 pmol per gram of tag	[47]
30 adult participants (16 males and 14 females)	Silicone wristbands - dimensions: 200 mm long × 12 mm wide × 2 mm thick; weight - 5.33 g; Study duration - 5 days during all daily activities	Solvent extraction: 1st - EtOAc/hexane; 2nd - EtOAc/MeOH;	<ul style="list-style-type: none"> Extraction in overhead shaker: EtOAc (40 mL/30 min) – two times; Volume reduction to 200 µL; Dilution with 400 µL of mobile phase (water/MeOH and ammonium acetate) and adjusted to 1 mL with MeOH. 	Lack of data	The cumulative concentration of 31 LC-amenable pesticide residues - 9.1 ÷ 2217.8 ng g ⁻¹	[62]
22 pregnant women	Silicone wristbands dimensions: 1.3 cm width; inner diameter: 6.4 cm; weight – 5.67 g; Study duration - all waking hours, from drop-off to pick-up 48 h later	Solvent extraction: 1st - EtOAc/hexane (three times); 2nd - EtOAc/MeOH (two times)	<ul style="list-style-type: none"> Extraction in orbital shaker: EtOAc (100 mL/2 h) – two times; Volume reduction to 1 mL 	PAHs: 56 ÷ 93%	51 PAHs representatives were detected. Reported highest values: phenanthrene - 228 ng per wristband; naphthalene - 87 ng per wristband; fluorine - 74 ng per wristband	[63]
45 e-waste workers, recruited from three e-waste recycling facilities	<ul style="list-style-type: none"> Single silicone brooch sampler – dimensions: 9 cm length × 5.5 cm width × 0.1 cm thickness; surface area - 49.5 cm²; Soaking in MeOH (24 h) Small silicone band – dimensions: 16 cm length × 3 cm width × 0.1 cm thickness; surface area - 48 cm²; Large silicone band – dimensions: 18 cm length × 4 cm width × 0.1 cm thickness; surface area - 72 cm²; Study duration - a full-day work shift with sampling times varying between 6 and 10 h	Soxhlet extraction: EtOAc (72h); Soaking in MeOH (24 h)	<ul style="list-style-type: none"> Extraction by shaking and soaking: ACN (30 mL); Volume reduction to 0.5 mL; Purification: the use of Teflon syringe filters; Extracts reconstitution: 0.5 mL in isoctane 	NHFRs, PBDEs, OPEs: 70 ÷ 117%	<ul style="list-style-type: none"> Brooches: geometric mean (ng dm⁻² h⁻¹): NHFRs - 0.10 ÷ 58; PBDEs - 0.1 ÷ 957; OPEs - 0.3 ÷ 204; Wristband: geometric mean (ng dm⁻² h⁻¹): NHFRs - 0.10 ÷ 53; PBDEs - 0.1 ÷ 1360; OPEs - 0.2 ÷ 182 	[64]
35 participants (ages ranged between	Two sized silicone wristbands – average weight: large sampler:		<ul style="list-style-type: none"> Extraction: EtOAc (100 mL) – two times 	For target pesticides:	<ul style="list-style-type: none"> From 26 of detected pesticides, the highest 	[65]

(continued on next page)

Table 2 (continued)

Population	Silicone sampler type	Pre cleaning	Extraction and clean up protocol	Recovery	Concentration of targeted groups	Ref.
15 and 63) -men and women from farming families	4.8 ± 0.1 g; small sampler: 4.3 ± 0.1 g; Study duration - up to 5 days.	Conditioning at 280–300 °C (48 h)	• Combining extracts and volume reduction to 1 mL	Average value: 66%; Median value: 68%; The range: 11 ÷ 124%	concentration was noted for deltamethrin – 4.2 µg per gram of wristband	

ACN – acetonitrile; ASE – Accelerated Solvent Extraction; BFRs – brominated flame retardants; BzBP – Benzylbutyl phthalate; DCM – dichloromethane; DEHP – di (2-ethylhexyl) phthalate; DEP – diethyl phthalate; DiBP – di isobutyl phthalate; DnBP – di-*n*-butyl phthalate; EH-TBB – 2-ethylhexyl-2,3,4,5-tetrabromobenzoate; EtOAc – Ethyl acetate; MeOH – methanol; NFRs – novel flame retardants; NHFRs – novel halogenated flame retardants; OBIND – Octabromotrimethylphenylindane; OPEs – organophosphate esters; OPFRs – organophosphate flame retardants; PAHs – polycyclic aromatic hydrocarbons; PBDEs (BDEs) – polybrominated diphenyl ethers; PTFE – polytetrafluoroethylene; SD – standard deviation; SPE – solid phase extraction; TCEP – tris (2-chloroethyl) phosphate; TCPP-1 – tris (1-chloro-2-propyl) phosphate; TDCPP – tris (1,3-dichloro-2-propyl) phosphate.

same populations in different indoor environments, or even between studies conducted in different countries/scientific centers on the same population in the same indoor environment. The lack of a uniform system for presenting the results forces the necessity to convert them into one form and may also affect the interpretation of the obtained results. This issue is particularly related to the results presented in the form of the mass of the analyte per wristband. Although in several cases, the dimensions of the bands and their weights are not given (as well as the source of their purchases), so there is no guarantee that the material is homogeneous in its entire structure. This may lead to a situation in which the wristbands purchased from the same distributor or manufacturer may differ from each other in terms of homogeneity (as well as color, mass, thickness, and additives introduced during the manufacturing process), which may affect the differences in the obtained results (sorption capacity of selected silicone samplers). Nevertheless, in the case of differences between the amounts of compounds collected by the silicone passive sampler for different participants, this problem can be solved. A more important issue to solve is the assessment and proper calculation of personal exposure based on the air concentrations of SVOC. Therefore, more developed and time-consuming research should be performed, mainly associated with the characterization of the uptake rate/sampling rate of applied types of rubbery silicone polymer personal passive samplers for estimating personal exposure to SVOCs. It is possible to overcome this problem by calibrating the potential sampling element by introducing labeled chemicals (performance reference chemicals - PRCs) directly to the structure of a silicone passive sampler (e.g., wristband) before its field and personal application – a common, but time-consuming investigation performed under laboratory conditions to estimate the sampling/uptake rate of a passive sampler prepared based on synthetic materials to collect analyte samples from aquatic or gaseous media [55,56]. However, the selection of potential chemicals that might be considered as PRCs should consider their impact on the human body; they should be considered generally safe for the human body. Sedláčková et al. [57] performed the research assessed the silicone material – air partition coefficient based on the uptake kinetics of selected SVOCs. Modeling investigations were carried out in an indoor environment using 0.5 mm thick silicone sheets with a total surface area of 300 cm² exposed for 56 days. The results were compared to the concentrations of selected SVOCs in indoor air determined using an active sampling technique. Interpretation of model developed basing on mass transfer theory and consideration of the obtained data gives a possibility to assume that air sampling rate might be considered as a function of compound's molecular volume [57].

4. Concluding remarks and future perspectives

There is no doubt that the use of cotton gauze pads, viscose

wipers, and rubbery silicone polymer materials may be considered as key elements of the analytical procedure for the determination of SVOCs in the gaseous phase. By obtaining this type of information and making appropriate assumptions, it is possible to assess personal exposure to multiple SVOCs. In the case of rubbery silicone polymer personal passive samplers, depending on their placement on the human body (or clothing), it is possible to estimate the human exposure to harmful SVOCs through dermal contact or inhalation. Mentioned unconventional sampling techniques might be successfully considered as an alternative solution for active sampling techniques as well as for the invasive sampling applied in indoor biomonitoring investigations. Additionally, the results associated with the personal exposure assessment to selected SVOCs performed using wiping techniques or rubbery silicone polymer materials are similar and do not significantly differ from the results obtained with conventional sampling techniques, such as dust or urine samples [66]. According to Anderson et al. [48] and research performed by Kile et al. [46], another advantage is the possibility of storing silicone polymer passive samplers for a long period of time after exposure without significant loss of analytes. Nevertheless, the most important limitation of wiping techniques in human exposure assessment to SVOCs is the obtained information is screening, very general and based on a cross-sectional, single time-point sample [36].

From the user's point of view, it is a very convenient solution because the mentioned personal passive samplers do not interfere with their daily activities, habits, and wellbeing, and might be operated by the participants themselves (after a short instruction process). However, considering the analytical procedure applied for the determination of SVOCs, in which unconventional sampling protocol is introduced, several issues should be highlighted. The limitations are mainly related to the sampling and analyte extraction because, in almost every case, the conditions of the final determination stage are very similar and mostly based on chromatographic techniques coupled with mass spectrometry (MS detectors). One of the key parameters that should be considered is the physicochemical characteristics of the applied material, especially in the case of passive silicone samplers. However, solutions such as silicone wristbands use commercial products that are available in the market, and they can have different parameters (characteristics), such as different additives, dye/pigment, extruded, or sizes (which could affect the sampling area). Additionally, even if the final silicone products (silicone wristbands) are delivered by the same supplier, the basic raw material (silicone) may come from different producers, where different additives are used. For this reason, it is possible that the personal sampler might be inadequately homogeneous and, consequently, potentially affect the sorption abilities/behavior. A possible solution to overcome this drawback is characterizing the material structure, which will be concerned with basic physicochemical research such as: (i) Fourier

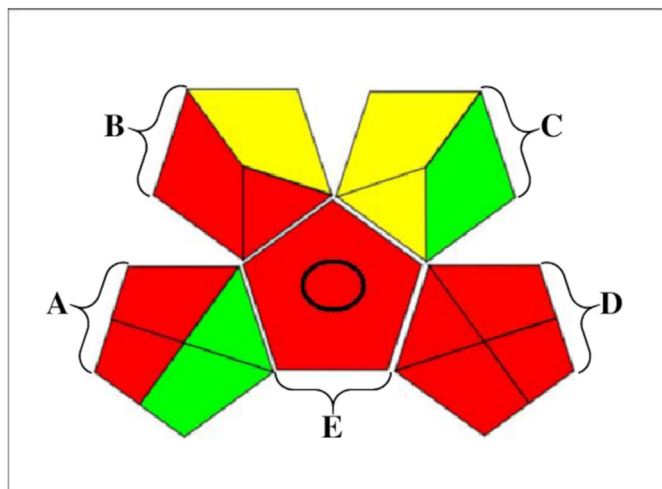


Fig. 4. The overall result of GAPI analysis of the green profile of the analytical procedures for personal exposure assessment to SVOCs using silicone wristbands: element A – sample handling; element B – sample preparation; element C – solvents/reagents; element D – Instrumentation; element E – general method type.

transform infrared spectrometry (FT-IR analysis) to define the homogeneity of the supplied sampling material, presence of the main types of bonds, and also to compare materials obtained from different supplies; (ii) SEM analysis - to obtain information about the surface characteristics of the applied material and to determine the differences in homogeneity and surface morphology; (iii) BET adsorption analysis to determine the sorption isotherms and assess the specific surface area ($\text{m}^2 \cdot \text{g}^{-1}$) of a material; (iv) Barrett-Joyner-Halenda (BJH) analysis to assess the pore area, pore size, and specific pore volume of the investigated material. The material characteristics of personal samplers could reduce the number of variables derived from variations in the selected sampler material and thus contribute to better interpretation of the obtained results. Nevertheless, it should be kept in mind that this approach will significantly increase the time and cost of the entire procedure.

Each time a new type of sorption material or sampling device is introduced in the analytical procedure, particularly in the case of unconventional solutions, a good laboratory practice is to determine their sorption abilities for selected SVOCs by assessing the sorption capacity. An example of this type of modeling research carried out under laboratory conditions in a stationary emission chamber was described in detail by Saini et al. [30] and Rauert et al. [12]. Information about the sorption capabilities can be obtained by performing static (without an air flow rate) and dynamic (with the defined air flow rate) sorption tests. Considering the sorption abilities of unconventional personal passive samplers, it is recommended to assess the equilibrium parameters (sorption isotherms and kinetic parameters) by applying the Freundlich and Langmuir linear isotherm models. Even though in the case of silicone used as a passive sampling device, the compound diffusivity into the polymers might be estimated using first-order kinetics, this type of research should be carried out because of the differences in the basic materials used as passive samplers [67]. In addition, the silicone or cotton gauze – air partitioning coefficients for the investigated SVOCs should be estimated.

Focusing on the next factor that causes several limitations—analyte extraction process—the issue is mainly related to the applied extraction technique as well as the type and volume of organic solvents used during the extraction and extraction purification stages. Following the principles of green analytical chemistry, it is strongly recommended to reduce the number of sample preparation stages and volume of organic solvents, as well

as to use less time, labor, and energy-consuming extraction techniques. To better visualize the issue associated with the green aspect of the analytical procedure used to assess personal exposure to SVOCs using unconventional sampling techniques, the green analytical procedure index (GAPI) was employed (details demonstrated by Plotka-Wasyłka [68]). This type of tool designed for the evaluation of the analytical procedure involves five general elements: (A) sample collection, preservation, transport, and storage (bottom left part of the pictogram); (B) sample preparation (top-left part of the pictogram); (C) reagents and compounds used (top right part of the pictogram); (D) instrumentation (bottom right part of the pictogram); and (E) quantification and general type of applied analytical method (middle part of the pictogram) [68]. Fig. 4 shows a typical graph of the GAPI analysis performed for the analytical procedures in which silicone wristbands were used at the sampling stage.

Following the data shown in Fig. 4, it can be observed that, in general, the most urgent points of the investigated analytical procedures, excluding instrumentation, consider the sample preparation process and applied reagents and compounds. In the aforementioned steps of the analytical procedures, only the green point is related to the safety hazard of the applied reagents (according to the National Fire Protection Association). The remaining yellow and red colors are related to the use of a significant number of solvents, the type of solvent (mainly acetone, hexane, or ethyl acetate), and the extraction technique performed in a Soxhlet apparatus or by shaking, less often with the use of ASE. Moreover, after extraction, it is often necessary to clean the extracts using SPE tubes filled with solid sorbents. Unfortunately, the introduction of this stage generates additional organic and solid waste (yellow color in the top-left part of the pictogram). It was concluded that, in terms of analytical aspects, the application of the described unconventional sampling techniques requires further research, mainly because of the differences in the results of human exposure caused by the lack of general straightforward standards and unifying sampling and final determination protocols.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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