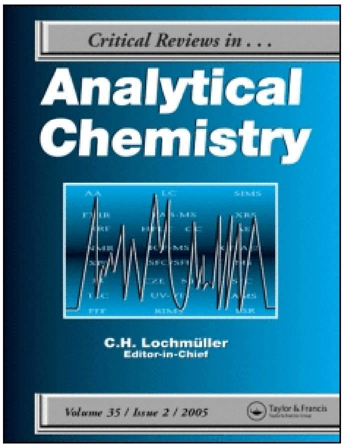

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Elżbieta Dobrzyńska[a]; Małgorzata Pośniak[a]; Małgorzata Szewczyńska[a]; Bogusław Buszewski[b]
[a] Department of Chemical and Aerosol Hazards, Central Institute for Labour Protection—National Research Institute, Warsaw, Poland [b] Department of Environmental Chemistry & Bioanalytics, Faculty of Chemistry, Nicolaus Copernicus University, Toruń, Poland

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Chlorinated Volatile Organic Compounds—Old, However, Actual Analytical and Toxicological Problem

Elżbieta Dobrzyńska,[1] Małgorzata Pośniak,[1] Małgorzata Szewczyńska,[1] and Bogusław Buszewski[2]
[1]*Department of Chemical and Aerosol Hazards, Central Institute for Labour Protection—National Research Institute, Warsaw, Poland*
[2]*Department of Environmental Chemistry & Bioanalytics, Faculty of Chemistry, Nicolaus Copernicus University, Toruń, Poland*

The interest in chlorinated volatile organic compounds is not a new task but still draws the attention of scientists. The role they play in human organism, is an important aspect to consider, since the development of analytical techniques and instrumental solutions gives new possibilities of their application in the analytics of volatile compounds and recognition of properties, so far impossible to achieve. Regarded mostly as xenobiotics, these compounds become a challenge for analysts aiming at sample preparation, which will ensure a high value of the analyte's enrichment factor, its determination on the lowest possible concentration level, without excluding the quality of analytical results. Current contributions review issues of environmental fate of halogenated compounds with a special emphasis on chlorinated volatiles, their toxicity, and bioaccumulation in living organisms. Focusing on analytical techniques, overviews include several sampling, preconcentration, and detection methods exemplified by measurements in air, water, and other matrices, including living organisms (e.g., human breath).

Keywords chlorinated volatile organic compounds, chromatographic methods, CVOCs, detection methods, review, sample preparation

INTRODUCTION

Halogenated organic volatiles represent a tremendous group of compounds, interest-worthy because of their common use, persistence in the environment, and their potential toxicity. Some of these substances are able to induce several adverse health effects into humans, both acute and chronic. In this context, monitoring of such type of compounds in different environments—in water, soil, and air (both ambient and indoor air)—as well as their biomonitoring, seems to be essential and valuable from the human's health point of view.

Several different definitions of volatile organic compounds (VOCs) have been elaborated so far. Some of them were collected last year by Demeestere et al. (1) and covered the definition of Environmental Protection Agency that has defined VOCs as organic compounds contributing to photochemical ozone creation (2), while other source has given a definition of organic chemicals (vapors) as containing carbon atoms and having a normal boiling temperature below 373.15 K at 101 kPa (3). Other sources have considered them as organic compounds having a vapor pressure larger than 13.3 Pa at 25°C (4) or at least 10 Pa at 20°C (5). According to this last term, halogenated volatile organic compounds (HVOCs) have been described by J. Dewulf and co-workers (6) as organic compounds that have a vapor pressure above 10 Pa at 20°C and bear at least one halogen (fluorine, chlorine, bromine, or iodine) atom. HVOCs cover several groups of compounds, such as trihalomethanes (THMs), chlorofluorocarbons (CFCs), chlorinated methanes, ethanes, etc., or hydrofluorocarbons (HFCs), which are not only almost ubiquitous, but present a topic of growing attention. Numerous papers concerning HVOCs cover such issues as their occurrence, properties, significance to the environment and a human being, but also analytical methods.

Therefore, this review is a trial of collecting previous achievements in the range of chlorinated VOCs, which may have an influence on bioaccumulation in tissues, or which are exhaled by living organisms in unchanged form, not being metabolized and principally at extremely low concentration levels. Taking into account the action of these compounds

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Address correspondence to B. Buszewski, Department of Environmental Chemistry and Bioanalytics, Faculty of Chemistry, Nicolaus Copernicus University, 7 Gagarin St., PL 87-100 Toruñ, Poland. E-mail: bbusz@chem.uni.torun.pl

as potential carcinogens or teratogens, this is an effort of contemplation over their toxicity, bioaccumulation, or analytics in the broad sense of this word, including sampling techniques, methods of their detection, and validation.

Physical and Chemical Properties

Physico-chemical properties of halogenated organic compounds have an influence on their fate and behavior in the environment (7). They are also critical in determining their toxicological characteristics and recalcitrance to biodegradation (8). Therefore, a correlation between such properties as an aqueous solubility of compounds, their boiling or melting points, air/water equilibrium partitioning, and many other factors that they exhibit is useful in predicting their behavior, reactions, and activity. The presence of halogen-substituents, in most cases, affects both the chemical and toxicological properties of hydrocarbons (8).

Various physico-chemical properties of HVOCs have been mentioned so far in the literature in the form of tables within the individual studies. However there are also examples that the reported compounds do not have all of their physicochemical properties listed. Such values as, e.g., normal boiling points of halogenated organic compounds collected in a table (9) are helpful in not only predicting their thermodynamic properties but also investigating their fate, starting from their volatilization to abundance or half-life, as it was mentioned above. This can be exemplified by, e.g., a group of hydrofluorocarbons, which have very high volatility at room temperature connected to their low boiling points. They have also low solubility in water, low surface tension, as well as low flammability. This latter property and other factors, such as electrical non-conductivity, ready vaporization, and low toxicity make HFCs to be used as, e.g., fire extinguishers (10).

Hydrophobicity and fat solubility of some halogenated chemicals, like THMs, make them accumulate into fatty substances, exemplified by lipid fraction of blood or milk (11). The stability of organic compounds in the environment is characterized by their half-lifes or times of degradation. Here, in the case of small molecules of volatile chlorinated hydrocarbons (C_1-C_2), high atmospheric stability that they exhibit results in relatively long atmospheric lifetimes (varying from few weeks up to hundreds years). Organohalogen compounds are therefore very persistent in the environment and their half-lifes are, in some cases, of the order of several thousand years (e.g., cases of chloroform or tetrachloromethane) (12, 13).

Source and Environmental Fate of HVOCs

Halogenated compounds enter into the biosphere from both industrial and natural sources. Currently, more than 3800 natural organohalogens, with over 2200 organochlorine compounds, are known (14). K. Ballschmiter (15), describing the formation chemistry of marine natural organohalogens, has concluded that although the wide spectrum of natural volatile organohalogens exist and is rather well established in its qualitative aspects, single new compounds still may be found in the future.

Found in the environment, HVOCs can be classified as biogenic (chloromethane), anthropogenic (e.g., freons) or having anthropogenic precursors, both halogenated and non halogenated, as well as natural (in other words—geogenic), which can be exemplified by specific dioxins in clay (15, 16). Several different types of HVOCs are produced by living organisms, including bacteria, marine plants (sponges, algae), fungi, or even some insects; they are rarely produced by higher animals (although such examples also exist) or formed during abiogenic processes, including e.g., volcanic eruption (14). Fungi can produce, for example, chlorophenols (17), while marine and polar macroalgae form several organoiodine species releasing them into the oceans (18). Chloromethane may be produced by potato tubers and by fungi and lichen (same as chloroform) and has been found (together with other haloalkanes—dichloromethane, chloroform, or carbon tetrachloride) entombed in rocks and minerals. Small amounts of different organohalogens may be released when rocks are crushed, e.g., during mining operations. An extraordinary finding is that six Australian species of termites can produce chloroform, and what is more—up to 1000 times higher than the ambient concentration (14).

Anthropogenic volatile halocarbons, which include chlorofluorocarbons, hydrochlorofluorocarbons, hydrofluorocarbons, and chlorinated solvents, play a key role in a global change phenomena. They are involved in a number of atmospheric reactions, including the destruction of tropospheric and stratospheric ozone (19), although they also remain powerful greenhouse gases (20). Considered as global contaminants, these compounds are released to the environment in large quantities, e.g., chloromethane, the most abundant naturally formed organohalogen. They can be found almost everywhere in the environment, even if in trace amounts. Their presence in water, air, or soil was experimentally confirmed many times. Literature review also brings reports testifying their presence in, e.g., plant leaves (12) or even Antarctic snow (21), because evaporated in warm climate, where they are produced, they can be carried by wind for a long distance to colder climates to be condensed and deposited. Atmospheric transport is one of the main vectors for their transfer far away from the sites where they were produced or used (22). Description and understanding of the main environmental processes driving the global distribution of organochlorine compounds is an important requirement after confirmation of the spread of these compounds throughout the planet. An exemplary scheme representing sources and fate processes in the marine environment is given in Fig 1. However, the mechanisms of incorporation from gas phase to the aquatic, terrestrial, or biogenic compartments and the environmental physico-chemical properties determining their retention in the remote ecosystems are still pending to be clarified. The anthropogenic production, release, and dispersal of organochlorine compounds into natural settings at the earth's surface is a

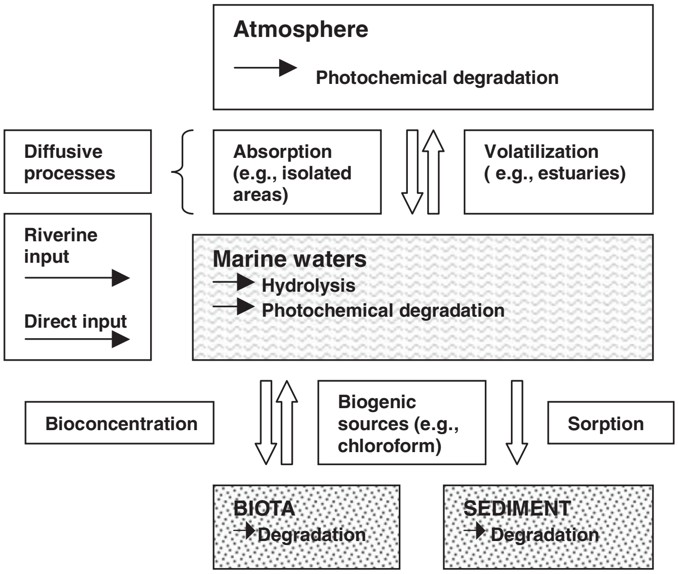

FIG. 1. Schematic representation of sources and fate processes in the marine environment (7).

matter of widespread environmental and epidemiological concern.

A tendency to persist in the environment, where HVOCs remain available for bioaccumulation in organisms, and their toxification causing such a contamination is a problematic issue (23). The occurrence of halogenated compounds of unknown origin in an assortment of biota, including humans, indicates a widespread distribution in the environment and because of that constraining the sources and cycling is very important. Natural compounds probably have been present in the environment for longer time periods than those industrially synthesized. In case of compounds derived from industrial activity, their source, mode of production, fate, impact, and whether their emission can or needs to be controlled should be contemplated (24).

Another thing is, that depending on atmospheric conditions due to washing by rain or evaporation from water for long periods of warm weather, HVOCs can display variables in concentrations in air and water (13). Aerial variations of concentration levels of some typical CVOCs in ambient air were reported (25, 27) with a conclusion that, except for the industrial usage or synthesis of analyzed compounds, they depended also on the season of the year or various meteorological factors.

It should be mentioned that the interaction of volatile compounds with soil is often found to be quite important in predicting and interpreting their ultimate fate. Migration of chlorinated solvents in soils, exemplified by chloroform, tri-chloroethylene (TCE), and tetrachloroethylene or perchloroethylene (PCE) largely depends upon their interaction with the soil particles (28). Biological transformation is widely recognized as a critical mechanism in the attenuation of xenobiotics. Under anoxic/anaerobic conditions, chlorinated hydrocarbons can be fortuitously biotransformed via reduction dechlorination to produce a series of lower chlorinated homologs, exemplified by chloroform, which in fact is the daughter product of carbon tetrachloride (29). Biodegradability tasks of chlorinated solvents and other chlorinated aliphatic compounds were comprehensively reviewed (16) 3 years ago, as well as cases of anaerobic biodegradability of, e.g., chlorophenols (30) and will not be a subject of this study.

Apart from natural production, environmental pollution caused by organohalogen compounds also results from their industrial manufacturing and use. These compounds are mostly used as solvents, cleaners, dry-cleaning, and degreasing agents, porogens or polymerization modifiers (17, 31). Thus, they can be found in the proximity of industrial sites, in different environmental forms, in estuary waters, air, or soil. In one Spanish village, different types of organochlorinated compounds were detected in water, which was associated with the activity of a nearby organochlorinated solvent factory (32). Elevated concentrations of different HVOCs detected in the air in the shopping center and the sports center with a swimming pool were associated with chlorinated water and environmental tobacco smoke (33). Occupational exposure to compounds such as chloroform, methylene chloride, and carbon tetrachloride was estimated in chemical laboratories, where the use of solvents was extensive (17).

It should be also emphasized that HVOCs have received special attention as indoor air pollutants, because of their wide use in insect repellents, washing clothes and dishes, in dry cleaning (34), and even their potential appearance during showering or bathing (35, 36). Several examples found in the literature cover tetrachloromethane utilized as a material for chemicals (37), hydrofluorocarbons as refrigerants for air conditioners in cars, and fire suppression agents (10). Chlorobenzenes are used as air fresheners; in the cleaning and degreasing of metal, leather, and wool; as solvents for organic materials, waxes, or rubbers. In some countries, however, the use of such compounds as, e.g., pentachlorobenzene or hexachlorobenzene is now ceased, because of their highly toxic properties, despite their previous use as fungicides.

Toxicity of CVOCs

Halogenated organic compounds are mainly regarded as xenobiotics, resistant to biodegradation, and hence, persistent in the environment. Most of them are toxic or carcinogenic and present potential danger if a human being is exposed to them. Many volatile organochlorine compounds have a harmful effect on the tissues and organs of the human body. However, repeating after Amaral and co-workers (32), an obvious risk to avoid is a generalization between the environmental occurrence and health problems, which in practice may become unproven but assumed, cause-effect assignment. Conversely, the same authors have admitted that any serious approach must be focused on the recognition of a direct link between exposure to specific compounds routes, body burden, and health effects.

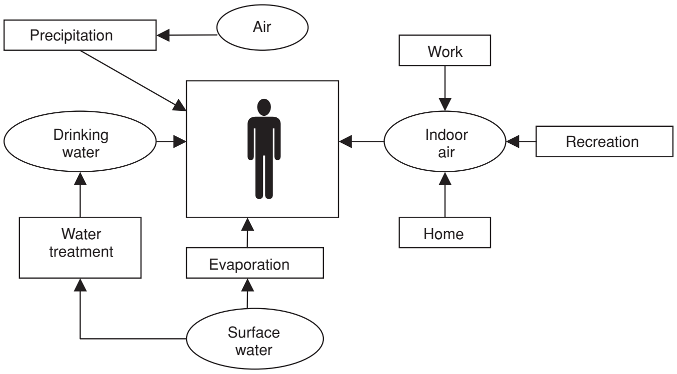

FIG. 2. Potential pathways of human exposure to volatile chlorinated compounds (17).

Occupational or environmental exposure to chemicals, such as HVOCs, may induce various diseases in humans and may lead to major public health problems. The scheme of potential pathways of human exposure to volatile organohalogen compounds found in a paper of Z. Polkowska et al. (17) is presented in Fig 2. Repeating after Amorim et al. (38), the health risks resulting from occupational exposure to such chemical agents require the attention of governments and the companies that produce or use these substances in their industrial processes and who are responsible for controlling exposure to them. Correlation between environmental chemical agents and diseases is not a simple task. Chemical substances that exist mainly in the gas phase at room temperature are eliminated unchanged, principally through the lungs (38). The increased or changed concentration of one or more components in exhaled air can be directly related to the disease. This can be exemplified by tetrachloroethylene used in dry cleaning shops. Metabolized by humans only in few percents to trichloroacetic acid, the compound is mainly excreted unchanged in exhaled air. Interest in determination of breath's constituents as disease markers has been increased in the last few years (39) and can become a practical tool in the assessment of occupational or environmental exposure to potentially toxic chemicals. Monitoring exposure based on biomarkers allows the evaluation of individual and group hazards and the early detection of exposure to hazardous chemicals, significantly reducing their effects on health (38).

The compounds of interest can be also metabolized and eliminated with, e.g., biological fluids. Toxic or carcinogenic effects of chemicals taken up by the organism may result from the compounds themselves or from metabolites thereof. Its toxic activity in different organs depends on the concentration, and the time it remains at the site of action. It has an influence on the distribution between blood and tissues, rates of transport by the bloodstream, biotransformation, and at last its excretion from the body (40). Furthermore, complex interaction between human organism, and the environment should be considered, which is especially important when there is a long period between exposure and manifestation of disease. Indicators of biological exposure, since it has not been possible to establish biomarkers for many chemical substances that present a biological interaction with the human organism, may allow estimation of the internal dose before the toxic effects are manifested. Therefore, the goal of biomarker research and application is to prevent disease by reducing exposure to hazardous agents through the early identification of exposure and response (38). Chemical analysis of, e.g., breath gases can provide valuable information related to the state of health and well-being of the examined person, because breath analysis is based on the equilibrium between alveolar air and pulmonary capillary blood. Single substances or sets of exhaled markers can be analyzed in order to establish correlations between the chemical composition of breath and patients' clinical conditions as a convenient and safe complementary method to blood and urine sampling (41). This, consequently, could help in diagnosis, of such illnesses as lung cancer, tuberculosis or certain other diseases (42, 43).

Volatile compounds are known to influence the airways by induction of inflammatory responses and asthmatic symptoms; their primary route of exposure is inhalation. Chlorinated organic solvents, which constitute a big part of volatile organohalogen derivatives, are well known to disturb the central nervous system and induce changes in the parenchymal organs, especially liver and kidneys, but may also accelerate allergic diseases (44). Body fat is, in that case, the most important body compartment for fat soluble solvents. Focusing on occupational exposure to these compounds, its pathway follows its solubility in blood; tissue should be also taken into account. Body fluids and physical work load affect the blood flow and alveolar ventilation and therefore will affect the amount of solvent inhaled as well as absorbed through the blood and delivered to the liver (45). One such solvent example is tetrachloroethylene; population and occupational exposure it could pose (e.g., in dry-cleaning) was associated with the risk of neurotoxic effects, even with the risk of such a complex disease as schizophrenia (46). In the case of chlorinated ethenes, the primary effects of chronic exposure are mainly liver and kidney damage, as well as damage to the nervous system. These compounds are, however, also thought to be mutagenic and the metabolic oxidation to corresponding epoxides is the key step in their metabolism (8). Recently, the reason of concern is exposure to mixtures of chemicals. In a comprehensive review concerning toxicity of chemical mixtures containing chlorinated compounds, different test methods were discussed and the toxicity was thought to be an extensive property of a chemical since it is a function of amount or concentration (47).

Some compounds, exemplified by hydrofluorocarbons, are not toxic to humans at air exposure levels up to a few percent. In that case, possible exposure may occur only via inhalation from accidental leaks from the refrigeration system or medical delivery system for treatment of asthma (10). What is more, the most common hydrofluorocarbons have very low potentials of bioaccumulation in the environment.

Trihalomethanes (THMs), commonly known as by-products of water chlorination, which is the most common and the most important disinfection method all over the world, are associated with the risk of cancer (48, 49), adverse reproductive outcomes, or even spontaneous abortion (50). They include chloroform, bromoform, chlorodibromomethane, or bromodichloromethane. Since these compounds can be taken into human bodies (51) by inhalation, dermal absorption, or orally (swallowing of water), their exposure to man has been widely investigated. The toxicity and carcinogenicity of THMs have been so far extensively studied on rats and mice (52), resulting in a statement that as individuals they have been shown to cause an increase in tumours in these animals, and although they are not strongly genotoxic, the risk to man must be assessed carefully. Growing awareness of the importance of trace amounts of THMs in chlorinated water has placed heavy demands on the ability to determine these compounds at very low concentration levels, which, in fact, may be useful to further analysis of their exposure routes. THMs were detected in drinking (50, 53–56) and in swimming pool water (57), due to the adverse health effects they could cause. To evaluate the health effects in people attending indoor swimming pools, biological fluids were also studied and several examples were related to the detection of trihalomethanes in blood, breath (58), and urine (59) of professional swimmers, and in human milk (11). G. Fantuzzi and his collaborators have studied occupational exposure to these compounds in trainers, reception attendants, and other people working in the indoor swimming pools (60), because of their possible long-term exposure. Although the measured environmental levels inside the swimming pool were generally low, results indicated by biological monitoring have shown higher levels of THMs than the general population. Correlation between selected THMs and some other volatile organohalogen compounds' levels in drinking water and human urine was also investigated (61). Results of the last year's study, on the assessment of exposure to THMs in pregnant women (36), has indicated that individual THM uptake is dominated by inhalation and dermal absorption during showering, swimming in the pool, and bathing. On the other side, the study of McCulloch (62) from 2003 has shown, that the quantities of chloroform in foodstuff and drinking water are not problematic for human ingestion and current environmental concentrations do not present an ecotoxicological risk.

Studies of another possible carcinogen, trichloroethylene (TCE), were also carried out in blood and solid tissues of selected animals (63). These studies were found to be useful in medical monitoring of TCE exposure, as well as in pharmacokinetic and pharmacodynamic studies pertaining to TCE carcinogenesis.

From a perspective of the human's health condition, there is still a lot to be done. Too little attention is paid on studying levels of pollutants, which may enter the human body during different kinds of activities, including occupational tasks.

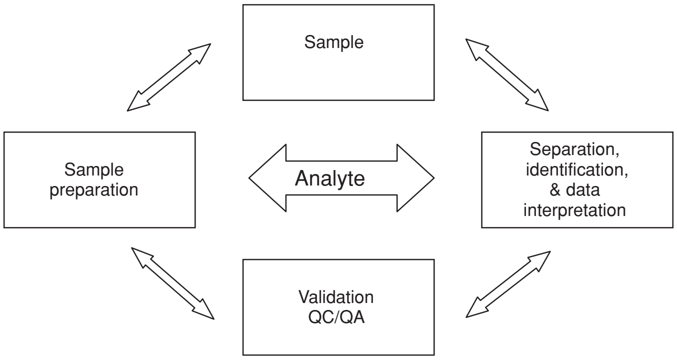

FIG. 3. Schematic representation of the analytical process.

ANALYTICS OF CVOCS

Because of high volatility, HVOCs easily reach the atmosphere and become nearly ubiquitous. Based on the fact, that they are able to cause a serious danger to the environment and owing to their manifold use in industry and everyday life, analysis of such compounds in water, soil, or air is of great importance (64).

The presence of volatile chlorinated xenobiotics in the environment requires careful consideration of different analytical strategies for their qualitative and quantitative determination, depending on the sample matrix, in which HVOCs must be determined. Significance of a matrix usually connected with much higher concentrations of interfering compounds is one of the difficulties that the analyst must face. Some kinds of matrices may cause troubles in the sample preparation step, such as the most complicated matrix to analyze—air (65). In this context, the crucial step is sampling, usually followed by pre-concentration in order to achieve the detection limits of commonly applied analytical techniques. A schematic representation of the whole analytical process is given in Fig. 3.

Sampling, Preconcentration, Isolation, and Determination Techniques

Sampling in air, in the case of volatile compounds, is carried out mainly with the application of canisters (mostly made from boron glass or stainless steel), plastic bags (Teflon, Tedlar), pumped sorbent tubes, diffusive samplers, and semi-continuous on-line air stream sampling or cryogenic trapping (66–68).

The canister sampling technique is well-suited for light hydrocarbons, however, there is a risk for irreversible losses due to wall adsorption increases with increasing boiling point and polarity of analytes. The stability of a compound in air within a canister was found to be affected by a complex interaction of factors from the physico-chemical properties of the compound to the characteristics of the canister surface including temperature, pressure, and air humidity (69). Analysts can obtain very low blank levels with canister sampling. Another advantage is the possibility of storing samples for several weeks without changes in sample composition. Canister bottles are, however, heavy, which limits the transportation, and expensive. The sample may contain water, and its remove before the analysis leads to evaporative losses of the less volatile compounds. This latter limitation can be largely overcome by trapping the analytes on solid sorbents (66). Examples of canister sampling cover the use of so-called SUMMA polished canisters or newly developed fused-silica-lined (FSL) canisters. The first type means that its internal surface has been passivated using the SUMMA process that combines an electro-polishing step with chemical deactivation to produce a chemically inert surface, while the FSL canister has a thin fused-silica layer which is chemically bonded to the metal interior surface in order to reduce surface activity (6). A SUMMA canister was used to collect breath in order to analyze trace levels of volatile chlorinated compounds—dichloromethane, chloroform, methylchloroform, or tetrachloroethylene (70). Such canisters were also used for sampling in 32 different locations in Perth (Australia) in both indoor and ambient air to collect volatile organic compounds including chlorinated solvents (33). It must be emphasized that canister sampling is not a preconcentration technique and the concentrations found in air are usually too low for analytical instrumentation; therefore, they require additional preconcentration methods, e.g., cryogenically or by sorption (68). The cryogenic sampling also has some disadvantages. Although it prevents the generation of artifacts caused by sorbent materials, which doesn't mean that their formation won't occur, it has to deal with water interference (68) even more than sorbent sampling, which will be described below.

Biological fluids, such as urine (which is also a complex and complicated matrix, as it tends to foam can cause troubles with the choice of methods for sample preparation) are suitable for determination of volatiles in this medium (61). In this context, sample pre-treatment is an important analytical operation prior to instrumental analysis. It helps not only to achieve low detection limits, but also to clean up the sample matrix (71). This step mainly focuses on isolation and preconcentration of the analytes, especially of those existing in relatively low levels in the sample. Methods for isolation and enrichment of compounds are strictly associated with such factors as the kind of analytes, their polarity, volatility, stability, and solubility in water or in organic solvents, etc. (13).

The biggest part of sampling procedures and the compounds' enrichment before chromatographic analysis is based on the physical adsorption on properly selected sorbents. The adsorption of molecules is a physical adherence process of molecules to the surface of adsorbent. There is a number of important characteristics describing an ideal sorbent, including total chemical inertness towards the adsorbed compounds, low background, stability on storage, no influence by humidity, large adsorption capacity, and total desorption capacity for a maximum number of compounds. When considering the complexity of different atmospheres with regard to the physical condition of air as well as large variations in the presence of numerous compounds with different chemical and physical properties, it is obvious that no single adsorbent possesses the required characteristics for all applications. Selecting a proper adsorbent can be therefore a difficult task. Commercially available adsorbents, employed for the determination of VOCs in air, may be divided into two major classes: carbon based-adsorbents, such as graphitized carbon or carbon molecular sieves, and synthetic polymers (72). Factors such as porosity, represented by pore size, and distribution, volume or specific surface, play an important role in the selection of sorbents for specific compounds (see Table 1). Four important criteria listed by Dewulf and Langenhove (73) also consider avoidance of breakthrough of the analytes, as well as artifacts formation, water vapor sorption, and the fact that sorbents must be kept free of contaminants before and after sampling. A number of papers describe the applicability of different adsorbents with regard to adsorption for selected compounds under various conditions. For the adsorption of airborne organohalogen compounds, sorbents such as Tenax TA (74), Tenax GC (75), carbon molecular sieves (Carbosieve G) (76), or zeolites and granulated activated carbons (77) were applied. The most commonly used adsorbents in ambient air analysis were previously reviewed several times (65, 67, 78, 79). There is still a need for additional descriptive studies in this field, as the complexity of atmospheres and the sample treatment in addition to the selection of compounds might strongly influence the outcome of the studies. Some disadvantages of such a sampling procedure cover possible losses during storage, which may lead to underestimation of atmospheric concentrations. This is especially important in occupational field studies, where the tubes are usually stored for a period of time prior to laboratory analysis (72). There is also a possibility of artifacts formation, generated in different ways by the sorbent sampling technique. What is more, there is no universal sorbent available for the sampling of HVOCs in the wide range of their volatility or molecular masses. That is the reason for placing several sorbents into one tube for the range of analyzed gases, which could be possible by the application of the so-called multi-bed adsorption tube; the scheme is presented in Fig. 4.

This solution was successfully practiced in VOCs' sampling and enrichment (80, 81). Several VOCs, including trichloroethylene, were, e.g., sampled from air on this type of multisorbent tube composed of Carbopack B, Carbopack C, and Carbosieve S III, followed by thermal desorption and GC/MS (82).

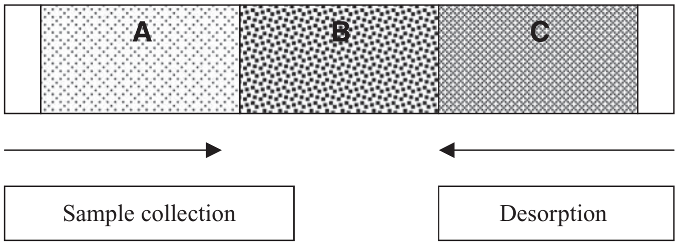

FIG. 4. Multi-bed adsorption tube scheme (79), where A, B, and C stand for different adsorbents with various specific surface area (A = small, B = middle, C = large).

TABLE 1
Characterization of adsorbent materials commonly used for adsorptive enrichment and thermal desorption in air analysis (65)

Adsorbent	Particle size (mesh)	Sampling range	T_{max} (°C)	Spec. surface area (m^2/g)	V_g H_2O 20°C (ml/g)	Density (g/ml)
Carbon molecular sieves						
Carboxen 563	20/45	C2–C5	>400	510	778	0.53
Carboxen 564	20/45	C2–C5	>400	400	276	0.60
Carboxen 569	20/45	C2–C5	>400	485	257	0.58
Carboxen 1000	60/80	C2–C5	>400	1200	418	0.44
Carboxen 1001	60/80	C2–C5	>400	500	234	0.61
Carboxen 1003	40/60	C2–C5	>400	1000	79	0.46
Carbosieve SIII	60/80	C2–C5	>400	820	378	0.61
Carbosphere	60/80	C2–C5	>400	1000	779	–
Graphitized carbon blacks						
Carbotrap F	20/40	>C20	>400	5	–	0.66
Carbotrap C	20/40	C12–C20	>400	10	–	0.72
Carbotrap Y	20/40	C12–C20	>400	25	–	0.42
Carbotrap X	20/40	C3–C5	>400	250	–	0.41
Carbograph 5	20/40	C3–C5	>400	560	–	–
Porous organic polymers						
Chromosorb 106 (styrene/divinylbenzene)	60/80	Small molecules	250	750	173	–
Tenax TA poly-(2,6-diphenyl-)-*p*-phenylenoxide	60/80	C7–C26	350	35	39	0.25
Miscellaneous						
Tenax GR (30% graphite, 70% Tenax)	35/60	–	350	–	92	–
Activated carbon (coconut charcoal)	20/40	C2–C5	220	1070	1454	0.44

Apart from placing few sorbents in one tube, Harper (78) has also paid attention to novel sorbents applicable to the analysis of VOCs as a way of continuing research in sorbent sampling.

To guarantee an accurate determination of volatile compounds in air, not only complete enrichment but also complete, fast desorption is necessary. The compounds of interest are extracted from air by adsorption or chemical reaction with sorbent surface. The analyst should take into account the way the analytes are released from selected sorbents, possibly both by thermal desorption and solvent extraction. Both methods have been commonly applied for extracting and isolating volatile and semivolatile compounds from various matrices. Chlorinated derivatives of methane, ethane, ethylene, and propane in air samples were trapped on porous carbon sorbent prepared by pyrolysis of saccharose in the presence of silica gel and desorbed by carbon disulfide and n-pentane (83). Chloromethanes, 1,1,1-trichloroethane, trichloroethene, and tetrachloroethene were extracted with n-pentane from activated carbon (64). The passive sampler consisted of an activated charcoal and a porous PTFE tube was applied for collection of ten volatile organohalogen compounds, both indoor and outdoor (34). The compounds of interest were extracted with toluene by mechanical shaking and determined by GC-ECD. Moreover, it was found to be a simple cheap, and highly sensitive method for the determination of the 24-hour average volatile organohalogen compounds concentration. An exemplary chromatogram is given in Fig. 5. The same method was applied for the comparative analysis of CVOCs, including chloroform, 1,1,1-trichloroethane, tetrachlorocarbon, trichloroethylene, tetrachloroethylene, and p-dichlorobenzene in the indoor air of selected urban dwellings in Japan and Sweden (84).

Thermal desorption, contrary to solvent desorption, enables not only releasing analyzed compounds from the bed, but also direct introduction of the substance onto the gas chromatography column, with the assumption that both the analyte and the selected adsorbent are thermally stable. Compared to solvent desorption, sample treatment is kept to a minimum and the sensitivity is superior because no sample dilution is required, often allowing total sample exploitation (72), although the costs of analysis are higher. Thermal desorption is commonly chosen for air monitoring ranging from the indoor to outdoor, through to workplace air. But it may be also a good choice for analysis of soil, food, or pharmaceuticals.

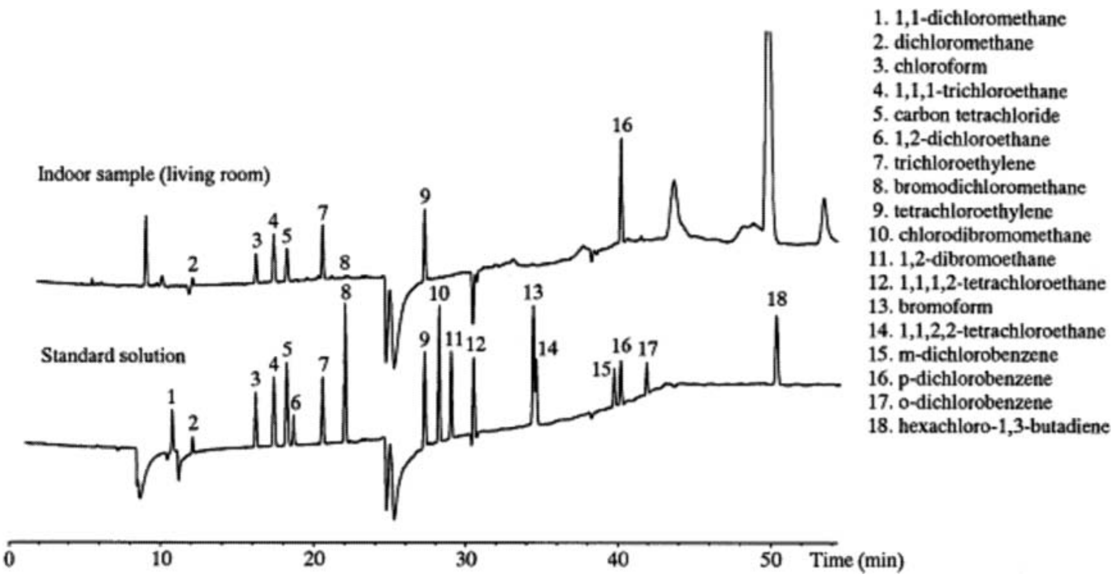

FIG. 5. Exemplary gas chromatogram of volatile organohalogen compounds in air (34).

Due to Dettmer and Engewald (65), adsorptive enrichment in combination with thermal desorption and capillary gas chromatography is a well accepted technique in ambient air analysis. The authors confirmed that the crucial step is the best selection of sorbents according to the compounds to be sampled; there is still a lot to be done within this task, especially in the analysis of non-polar compounds.

In the case of water analysis, certain hydrophobic microporous materials—various molecular sieves—have been tested to have an adsorption affinity for CVOCs in the liquid phase (85). These studies suggested that hydrophobicity alone cannot explain differences in sorption capacity of hydrophobic organic compounds from water.

Methods of both isolation and determination of volatile organohalogen compounds in water samples were previously reviewed in 1996 by Biziuk and Przyjazny (13). The authors emphasized the role of sample pretreatment as an essential step of trace analysis and concluded that water analysis for organic pollutants should be carried out by analytical experts only. Among many techniques before the isolation, separation, and final determination of different groups of pollutants, the authors described headspace methods, liquid-liquid extraction (LLE), methods based on sorption on solid sorbents, solid phase extraction (SPE), solid phase microextraction (SPME), or membrane extraction techniques.

Review of the last five years (1) concerning the analysis of VOCs covers mainly sampling and preconcentration techniques of low-concentration VOCs in air and water matrices. The authors browsed through more than 220 papers concentrating on techniques, which comply with sensitivity of the different types of analytical instruments. They have reported numerous applications of multi-bed adsorption in order to achieve high breakthrough volumes and further thermal desorption of HVOCs' enriched sorbents or SPME, according to the current tendency in integrated sampling-extraction-sample introduction methods or membrane extraction. Focusing on water analysis, the authors (1) have given examples of direct aqueous injection (DAI), solvent extraction including commonly known, but rather time-consuming LLE, and steam distillation extraction. They have also drawn attention to the three types of solvent microextraction overcoming its limitations, which are: single drop microextraction (SDME), liquid phase microextraction (LPME), or newly developed dispersive liquid-liquid microextraction (DLLME) applied to the enrichment of, e.g., trihalomethanes or chlorobenzenes. In this group, DAI, in fact, eliminates the sample pretreatment step but can not be commonly applied, because of the incompatibility with most of the stationary columns and FID detector. Many more examples are given for the SPME of different types of volatile compounds, varying from volatile halocarbons to carbonyl compounds in aqueous samples. Finally, headspace techniques, both static and dynamic, and membrane extraction are good alternatives for such types of enrichment techniques that have been mentioned.

Literature review brings us to the conclusion that the most common preconcentration techniques include headspace techniques, purge and trap (P&T), and SPME.

The P&T technique could be a method of choice for extracting and concentrating VOCs from almost every matrix. This method has been used for preconcentration of HVOCs in water (usually applied in combination with gas chromatography [GC]). It is based on purging the compounds from water with a stream of inert gas and subsequently trapping them directly on a sorbent or cold trap prior to analysis (86). There are a lot of reports concerning P&T concentration in the HVOCs analysis in water samples, even fully automated P&T coupled on-line with GC-MS for monitoring different VOCs in surface water (87). However, analyzing volatile compounds in various matrices using a P&T concentrator can be a demanding task because of many variables to be considered. In order to achieve better limits of detection, several modifications of this method were developed. Trace analysis of 24 volatile halogenated organic compounds in seawater was carried out by purge and trap continuous flow system in combination with gas chromatography combustion isotope ratio mass spectrometry (P&T-GC-C-irMS) (86). A group of Italian researchers has applied a modified purge and trap injection system coupled to gas chromatography with mass spectrometric detection (PTI-GC-MS) by using a cold trap to the trace analysis of volatile halogenated hydrocarbons and trihalomethanes in mineral water (commercially bottled), tap water, surface, and ground water receiving concentration levels varying from ng/L to μg/L (88). The same method was successfully applied also to the analysis of chloroform, trichloroethane, tetrachloromethane, trichloroethylene, and tetrachloroethylene in Italian, German, and Antarctic snow (21). Developed, automated on-line P&T GC with a dry electrolytic conductivity detection method allowed for monitoring of trihalomethanes in drinking water (89).

The headspace techniques, reviewed in details by B. Kolb (90), utilize the distribution of analytes between liquid and gaseous phase. The analytes in a liquid sample are thus determined by measuring their concentrations in gaseous phase being in thermodynamic equilibrium with the sample (13). Those three previously described methods of sample preparation have been recently compared based on application to analysis of six chlorocarbons in water (91). The outcomes of this study indicated that the DAI technique could be the best choice for relatively clean water samples that do not contain nonvolatile organic compounds or inorganic salts, like the swimming pool or drinking water. LLE might be successfully applied for lakes, rivers, and waste water samples, while for really dirty ones, the best solution could be the P&T method.

A report concerning rapid screening of several halogenated volatile compounds in water samples indicated application of SPME (92). It took 5 minutes for both extraction and detection. The short, uncoated fused silica tubing, instead of the capillary column in a GC mode, and an atomic emission spectroscopic detection (AES) were used.

SPME is rather new, rapid, solvent-free and sensitive adsorption and desorption technique, which is increasingly appreciated in application to the analysis of halogenated organic compounds in different types of environmental matrices. This method is based on sorption of analytes which are present in the liquid phase or more frequently in headspace gas phase. The process is carried out on a microfiber covered by a stationary phase and closed in a microsyringe. The fiber coating removes the compounds from the sample by both absorption in the case of liquid coatings and adsorption in the case of a solid. Then, the SPME fiber is inserted directly into the gas chromatograph for thermal desorption and analysis (93). Hence, headspace SPME, which the fiber is exposed to the sample headspace to extract target analytes partitioned between the gaseous and aqueous phase, can be used in any matrix and is especially suitable to the analysis of volatile and semivolatile organic compounds. Simultaneously, it results in high relative recoveries, which can be exemplified by the analysis of ten chlorinated benzenes in environmental water samples (94). Headspace solid phase microextraction was also optimized for determination of CVOCs in drinking water and its chlorinated effluents in Greece, at ng/L levels, in less than 70 minutes. Four types of fibers were tested within this study and the best extraction efficiency was achieved with the 85-μm carboxen/polydimethylsiloxane (CAR/PDMS) fiber (51). Recently, novel activated carbon fiber (ACF) experimentally checked to possess better resistance to organic solvents, longer lifetime, and higher sensitivity than commercially available fibers was found out to be a promising alternative for analysis of chlorinated hydrocarbons in water (95). Several papers reveal optimizing of SPME conditions for the determination of dichloromethane, trichloroethylene, and perchloroethylene in human urine samples, obtained from occupationally exposed workers, with 75-μm carboxen/polydimethylsiloxane fiber (96). Application of CAR/PDMS SPME fiber for static and dynamic sampling of 11 different VOCs with dichloromethane and dichloroethane in air has resulted in short sampling times and limits of detection at the level around μg/m^3 (97). Some reports concern application of a “cold” SPME method for determination of extremely volatile halocarbons present in the atmosphere down to a few ppt levels using 50/30-μm DVB-CAR-PDMS fiber (20). This method makes use of sub-ambient temperature in order to enhance retention capability of the fiber coating.

Reviewed in 2002 (98), SPME applications for sampling and sample preparation has shown its usefulness in the analysis of toxic compounds in indoor air of organic or technological laboratories, bedrooms, swimming pools, or industrial areas with the measured concentration levels and detection limits calculated in ng, ng/L, and ppb units.

Compared to previously described techniques, SPME also has some limitations, firstly exemplified by the extraction fiber properties. Commercially available fibers are expensive and fragile and what is more, they have a limited lifetime (71).

Jo Dewulf and col. (6) have presented a review concentrated on analysis of HVOCs in the time interval from 1999 to 2004. They have confirmed a growing tendency for SPME-based preconcentration methods, except for the use of different types of new solid adsorbents, such as purified multi-walled carbon nanotube (PMWCNT) (99). However, a combination of sorbent cartridges (such as Tenax TA) and SPME, used for determination of chlorobenzenes in air as an alternative for thermal desorption, was found by them in Barro and co-workers paper (37).

In order to minimize the use of solvent in the preconcentration step, the proper choice can be LPME. This technique combines extraction, preconcentration, and sample introduction into one step. The Headspace (HS)-LPME has been successfully applied to preconcentration of four halocarbons ($CHCl_3$, CCl_4, C_2HCl_3, C_2Cl_4) in drinking water samples (100). Another method that requires only nano or micro liters of solvent volume and a standard GC syringe to isolate trace compounds from an aqueous sample is single drop extraction (SDE). The drop of solvent that hangs from the tip of syringe needle is exposed to the sample, allowing analytes to be transferred by diffusion to the solvent drop and further inserted into hot injector of GC. In combination with GC equipped with electron capture detection, SDE was successfully applied to isolation of trihalomethanes from tap water samples. Based on linearity and repeatability of the method resulting from the study, it was found out to be a good alternative to SPME for such types of analysis (101).

Thus far, the most common method of separation still remains GC. Different column types like bare graphite for separation of halocarbons and halobenzenes, explored by Butt and col. (102), or columns packed with purified multi-walled carbon nanotubes for VOCs analysis (103) have been verified. In current GC analysis of volatile compounds, the biggest challenge still remains reduction of analysis time, maximizing information that one can get out of sample and the quality assessment (104). The newest development that has appeared in the last few years is a comprehensive two-dimensional GC, which was also successfully applied to CVOCs separation in atmospheric complex samples (6).

Detection of CVOCs

In many cases, halogenated compounds are detected in complex samples, and in spite of the resolving power of both GC and LC, some type of selective detection is required in order to obtain chromatographic peaks free of interferences from underlying components (105). Recently, mass spectrometric (MS) detection is becoming the most popular technique and provides excellent selectivity based on molecular masses. Thus, halogenated compounds may be detected selectively as long as their molecular masses are known in a complicated matrix of other components. In some cases, however, a halogen-selective detector may be an advantage, responding selectively to compounds containing the halogens, and differentiating between them (105). In this context, the most important detector of chlorinated compounds is still the electron capture detector (ECD), which can be supported by various application examples (7, 26, 106, 107). ECD offers a high sensitivity for halogenated compounds and has low detection limits. Some halocarbons were determined in sea water with P&T GC-ECD and GC-MS with the minimum detectable level ranging from amol/L to fmol/L (19). The combination of a small-dimensioned packed trap and a narrow bore capillary column was a practical solution both for GC-ECD and GC-MS. The dsign of a trap allows cooling by circulating water, which ensures trapping of the compounds in the beginning of the trap and eliminates the need of post-desorption cryofocusing. In order to improve ECD detector sensitivity to ppt levels desired for detection of different CVOCs, trials of doping the carrier or make-up gas with oxygen were adopted (107, 108).

However, except for undeniable efforts of ECD, interferences are frequently observed and therefore we can go back to the statement that the MS detector is becoming even more common in the analysis of halogenated compounds (109).

With reference to the detection systems reviewed by Jo Dewulf and col. (6), those two methods, electron capture detection (ECD) and electron impact mass spectrometry (EI-MS), were also described as the most frequently used. The authors have reported a growing number of applications of GC-combustion(C)-isotope-ratio mass spectrometry (IRMS) (three mentioned literature positions), microwaved plasma atomic emission detection (MIP-AED) (three references), integration of AED in a P&T-GC sequence, direct coupling with SPME desorption through the transfer line (two positions) and combined micro-ECD and micro-plasma AED in parallel (one reference). Two other technologies, supported by examples of their applications to detection of halogenated VOCs and worth mentioning, were also plasma-based MS and IRMS detectors (6).

An overview of halogen-specific detection in GC and LC with a brief theory of the detection method, its advantages, limitations, and some application examples has also been made by C. Brede and S. Pedersen-Bjergaard in 2004 (105). This review covers in detail detection by plasma emission spectroscopy and plasma mass spectrometry as the most frequently used; however, other techniques, e.g., flame photometric detection (FPD) or relatively new, chemical reaction interface mass spectrometry (CRIMS) are also briefly described. The authors have illustrated systems of gas chromatography-atomic emission detection (GC-AED) with a detection limit (LOD) at the picogram per second level, which were higher than those obtained for GC-ECD or GC-MS, however successfully utilized for determination of halogen-containing compounds in very complex and dirty samples. Application examples given in this review are focused on environmental analysis, such as analysis of pesticides in water, soil, vegetables, or other agricultural matrices. However, some other compounds, like polychlorinated biphenyls, chlorobenzenes, VOCs, or brominated flame retardants are also specified. Laniewski with co-workers (110) have undertaken a study on the application of the pyrolysis units coupled to gas chromatographs equipped with atomic emission detection (Py-GC-AED) or mass spectrometric detection (Py-GC-MS) to analyse chloroorganic compounds present in rain and snow and their results let us opine that it is an interesting complement to more analytical procedures.

Plasma MS instruments have usually been associated with lower detection limits, which is not necessarily in case of halogen selective detection; there are relatively few papers describing such application of GC-ICP-MS. One of the examples shown by Brede and Pedersen-Bjergaard (105) indicated an excellent halogen selective detectability for biogenic halogenated VOCs in aquatic and air samples by GC coupled with combined detection of ECD and ICP-MS, with a sampling technique called stir bar sorption extraction (SBSE) and thermal desorption for introduction of the sample to the system (105). The authors

TABLE 2
Exemplary data of different HVOCs' analysis by GC, depending on the matrix with specified methods of sampling/sample preparation, detection methods, and limits of detection and quantification. (Abbreviations: ns-unspecified)

Analyzed compounds	Matrix	Sample preparation method(s)	Detection	LOD	LOQ	Ref.
14 HVOCs	Air	HS-SPME	ECD	0.3–23.8 ng/L	0.25–79.3 ng/L	53
THMs	Water	P&T	MS	20–120 ppt	ns	54
HVOCs with THMs	Water/ snow	modified P&T	MS	at the ng/L level	ns	88
DCHM, TCE, PCE	Urine	HS-SPME	MS	0.005 μg/L	ns	96
CBs	Air	SPE&SPME	MS ECD	0.004–0.108 ng/m3	0.011–0.238 ng/m^3	37
CBs	Water	HS-SPME	MS	0.003–0.006 μg/L	ns	94
Halocarbons	Water	P&T	ECD MS	0.2–2 fmol/l 100–500 fmol/L	ns	19
Halocarbons, $CHCl_3$, CCl_4, C_2HCl_3, C_2Cl_4	Water	HS-LPME	μECD	0.003–0.146 μg/L	ns	100
THMs	Urine	Headspace extraction technique	MS	3–10 ng/L	ns	59
THMs	Water	LLE DAI P&T	ECD	0.02–0.07μg/L 0.3–0.8 μg/L 0.6–1.5 μg/L	ns	91
Multicomponent VOCs (with CVOCs)	Water	P&T	MS	0.002–0.1 μg/L	ns	87
THMs	Water	On-line P&T	DELCD	<1.0 μg/L	ns	89
HVOCs (e.g., THMs)	Air	Multibed sorption traps, followed by TD	MS	0.01–1.11 μg/m^3	0.02–1.67 μg/m^3	81
TCHM, DCHM, CCl_4, TCE, tetrachloroethylene penta-, heksa chlorobenzene, octachlorostyrene, and other organochlorine compounds	Water	P&T	FID and ECD in parallel	0.02–0.2 μg/L	ns	32
DCHM, TCHM, CCl_4, and other organochlorine compounds	Air	SPE	FID ECD	3.4–15.1 μg/m^3 1.7–4240 ng/m^3	ns	83
Chlorinated hydrocarbons with, e.g., DCHM, TCHM, CCl_4	Water	HS-SPME	MS	106–195 ng/L	ns	95

of review concluded that halogen selective detection is still far from realizing its full potential in many areas, which is related to limited detectability and lack of commercial instrumentation.

A portable GC equipped with unique detectors in—series photoionization (PID), flame ionization (FID), and dry electrolytic conductivity (DELCD)—provided almost real time analysis for volatile compounds including chloroform and trichloroethene during indoor air quality surveys (111). In this case, however, DELCD was more sensitive to halogenated VOCs in the standard mixtures and method detection limits for this detector were equal to 100 ppt for trichloroethene.

It should be also emphasized that the developed analytical procedure has to be assessed on the basis of a number of parameters, such as limits of detection (LOD) and quantification (LOQ), accuracy, specificity, repeatability, or reproducibility. We can underline after Dewulf and Langenhove (104) that in the literature of volatile compounds the validation parameters are usually not presented. Several collected values of LOD and LOQ found in the review of analysis of exemplary CVOCs are given in Table 2. They are expressed in different concentration units; in some cases, however, even if the values are not given, the authors show all the details of LOD and LOQ calculations. LOD, in most cases is calculated as LOD = 3 * S.D./M (106), where S.D. signifies the standard deviation of noise peaks and M is the slope of calibration curves, while LOQ = 3 LOD (97).

Conclusions and Final Remarks

CVOCs are the subject absorbing a big part of research studies and causing unabated interest. Within this group of compounds, not all of them have been studied in detail nor have all of their properties been discovered. Numerous reviews described in this paper concern such issues as methods of their determination, analytical aspects including isolation, preconcentration and detection techniques, and overview of their environmental hazards. Although much data exists on the subject of CVOCs, there still remains a vast field for further studies.

Due to their persistence in the environment and the toxic properties of CVOCs, research in the area of their influence on human health, both in working and living environment, will be certainly continued.

Concerning analytical aspects, analysts must face a problem of choosing an appropriate technique for isolation, separation, and detection of HVOCs, taking into account their characteristics, concentration levels, and the sample matrix. The matrix itself can cause troubles (61, 65), so the decisions of analysts regarding the proper choice of analytical method require not only good theoretical knowledge but also experience in the analytical field.

Still critical, but less recognized aspects are such stages as sampling, transport, storage, and samples preparation before the proper chromatographic analysis. Methods of storage and transporting sample to the laboratory are usually omitted in the literature. The greatest improvement over the current practice would consist in sample preparation and analysis in the field where the sample was collected, which could possibly reduce errors associated with handling and storing steps (93).

Sampling techniques, such as, e.g., canister sampling, useful for very volatile and reactive compounds, are not sufficient alone since they are not preconcentration techniques (68) and require additional steps. The reason for that is that concentrations found in air are usually too low for analytical instrumentation. Although numerous preconcentration procedures exist, the problem lack of one versatile, ideal technique of isolation and preconcentration appears. As it has been mentioned before, it comes to mind the conclusion that so far, the most common preconcentration techniques were sorbent trapping, HS, P&T, and SPME. SPME, practically from its beginning, found a good position in HVOCs analyses, regardless of the fact that it still can not be treated as a quantitative method. In this range, however, commonly used adsorbents could be a good solution.

Some drawbacks can be overcome by application of another technique. It does not mean, however, that the new one will not bring any new disadvantages. Therefore, the most commonly used sorbent trapping is influenced by artifacts formation and water interferences, although still less than in cryogenic sampling. Various solutions for existing gaps in the sorbent area were given by Harper (78), and included placing a few sorbents in one tube or application of novel adsorbents. He also stressed the need for good communication between the analytical laboratory and field personnel when selecting an air sampling method. MS and ECD are still the most frequently applied detection methods; however, single examples of other detectors were also found.

Several modifications of the technical solutions were elaborated in order to achieve better detection limits. A wide spectrum of innovations of the existing methods, as well as new exciting applications, such as, e.g., human breath, may be also find in the latest literature sources (38, 41, 112).

Finally, it should be emphasized that more attention should also be paid to the analytical quality assurance in a systematic way (68). We have found very few references with the given values of validation parameters.

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ABBREVIATIONS

HVOCs	halogenated volatile organic compounds
CVOCs	chlorinated volatile organic compounds
VOCs	volatile organic compounds
THMs	trihalomethanes
CFCs	chlorofluorocarbons
HFCs	hydrofluorocarbons
CBs	chlorobenzenes
DCHM	dichloromethane

TCHM	trichloromethane
TCE	trichloroethylene
PCE	perchloroethylene
SUMMA canister	canisters with chemically inert internal surface passivated using process combining electro-polishing step with chemical deactivation
FSL canisters	canisters with thin fused-silica layer chemically bonded to the metal interior surface
PTFE	polytetrafluoroethylene
LLE	liquid-liquid extraction
SPE	solid phase extraction
SPME	solid phase microextraction
HS	headspace
HS-SPME	headspace solid phase microextraction
DAI	direct aqueous injection
SDME	single drop microextraction
SDE	single drop extraction
LPME	liquid phase microextraction
DLLME	dispersive liquid-liquid microextraction
P&T	purge and trap
SBSE	stir bar sorption extraction
CAR/PDMS	carboxen/polydimethylsiloxane fiber
ACF	activated carbon fiber
DVB-CAR-PDMS	divinylbenzene/carboxen/ polydimethylsiloxane fiber
PMWCNT	purified multi-walled carbon nanotube
GC	gas chromatography
LC	liquid chromatography
ECD	electron capture detector
MS	mass spectrometry
EI-MS	electron impact mass spectrometry
IRMS	isotope-ratio mass spectrometry
CRIMS	chemical reaction interface mass spectrometry
FPD	flame photometric detection
PID	photo ionization detector
FID	flame ionization detector
DELCD	dry electrolytic conductivity detectors
MIP-AED	microwaved plasma atomic emission detection
ICP-MS	inductively coupled plasma mass spectrometry
AES	atomic emission spectroscopic detection
Py-GC-AED	pyrolysis unit coupled to gas chromatograph equipped with atomic emission detection
Py-GC-MS	pyrolysis unit coupled to gas chromatograph equipped with mass spectrometric detection
P&T-GC-C-irMS	purge and trap injection system coupled to gas chromatography combustion isotope ratio mass spectrometry
PTI-GC-MS	purge and trap injection system coupled to gas chromatography with mass spectrometric detection
LOD	limit of detection
LOQ	limit of quantification;

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