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Methods of assaying volatile oxygenated organic compounds in effluent samples by gas chromatography—A review

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ABSTRACT

The paper is a review of the procedures for the determination of volatile and semivolatile oxygenated organic compounds (O-VOCs) in effluent samples by gas chromatography. Current trends and outlook for individual steps of the procedure for the determination of O-VOCs in effluents are discussed. The available sample preparation techniques and their limitations are described along with GC capillary columns used for O-VOCs separation and selective and universal detectors used for their determination. The results of determination of O-VOC content in various types of real effluents are presented. The lack of legal regulations regarding the presence of the majority of O-VOCs is pointed out as well as the availability of just a few procedures allowing a comprehensive evaluation of the O-VOC content in effluents.

1. Introduction

Volatile and semivolatile oxygenated organic compounds, which include the organic compounds containing at least one oxygen atom, such as aldehydes, alcohols, phenols, esters, ethers, carboxylic acids and their derivatives are characterized by high toxicity, carcinogenic and mutagenic properties and malodorous character [1–5]. Oxygenated organic compounds commonly occur in municipal wastewater [6,7] as well as in various kinds of industrial effluents, including refinery [8–14], textile [15], coke [16], chemical [17] and food [18] industries. All types of effluents have a very complex matrix, which hinders the determination of individual O-VOCs, whose concentrations can vary from high to trace. Moreover, most O-VOCs are hydrophobic, highly reactive and low-molecular-weight compounds are highly volatile [19].

Despite their noxiousness, the content of the majority of O-VOCs in effluents is not regulated. The maximum allowed concentrations in industrial and municipal effluents involve primarily organochlorine compounds, hydrocarbons, heavy metals as well as total parameters, *i.e.*, chemical oxygen demand, biochemical oxygen demand or total organic carbon. Among a wide variety of O-VOCs, currently, the only regulation of many countries concerns volatile phenols determined as the phenol index whose allowed values are from 0.1 to 15 mg/L and from 5 to15 to mg/L for industrial effluents discharged to environmental waters or soil and sewage systems, respectively [20–24].

Due to their negative impact on the environment, oxygenated organic compounds have recently been an object of considerable interest among the scientists developing new methods of degradation of O-VOCs in effluents and analytical procedures allowing their identification and determination at low concentration levels which is illustrated by the number of relevant papers published between 2004 and 2019 (Fig. 1). The importance of phenols in effluents is reflected by the number of papers on the presence of O-VOCs in effluents, over 50% of which deals with phenolic compounds (Fig. 2).

In order to assay the remaining groups of O-VOCs, the methods based on sensitive and selective techniques are needed, including gas chromatography, high-performance liquid chromatography [15,16,25,26], ion chromatography [27] or capillary electrophoresis [28]. Owing to physicochemical properties of O-VOCs, gas chromatography is the preferred technique due to its lower cost of a single analysis, very high resolution and the possibility of fine-tuning selectivity of a procedure through the choice of a wealth of stationary phases as well as the availability of both universal and selective detection methods. However, in order to ensure sufficient

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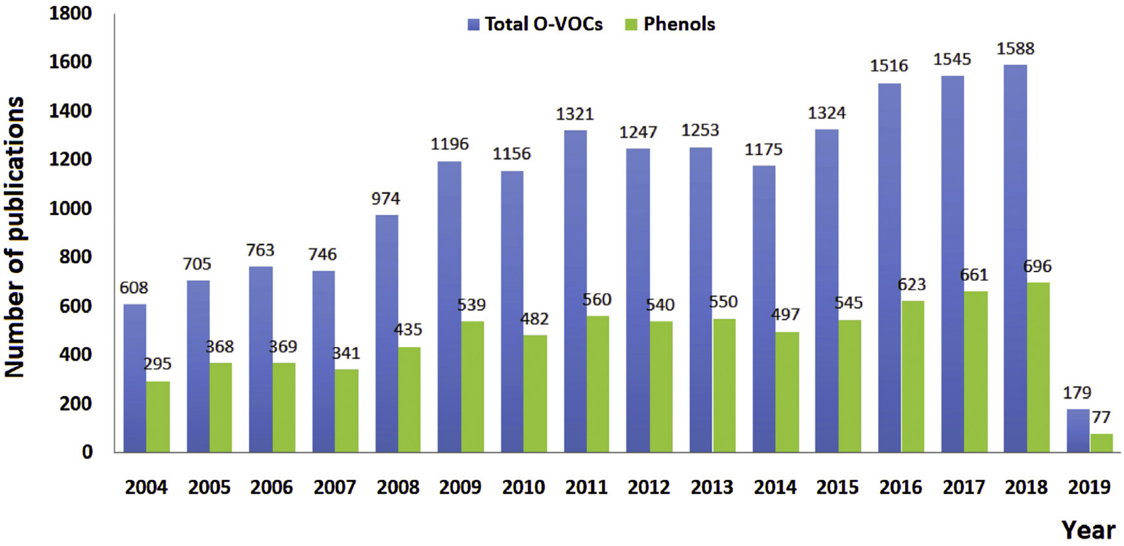


Fig. 1. Number of papers published during 2004–2019 on the presence of oxygenated organic compoundsin effluents - based on Scopus database(searched keywords: aldehydes, ketones, ethers, esters, alcohols, phenols, carboxylic acids, wastewater or effluent; accessed on 04.01.2019).

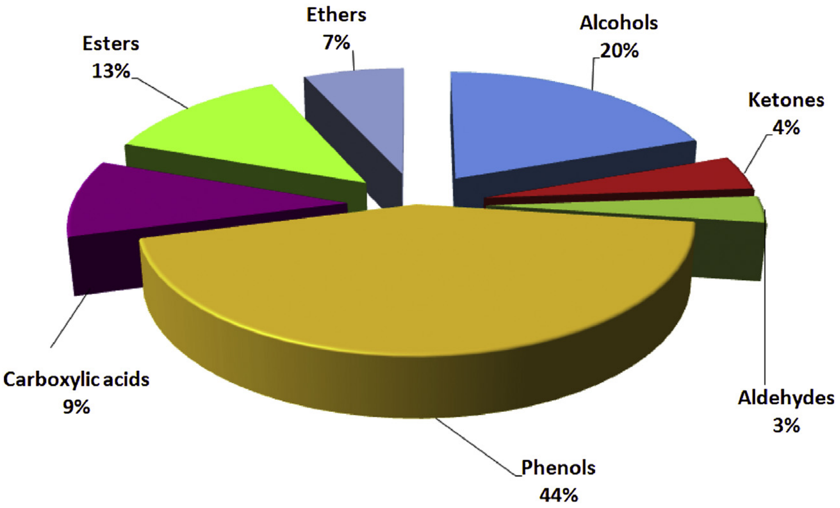


Fig. 2. Percent of papers published during 2004–2019 dealing with the presence of oxygenated organic compounds in effluents - based on Scopus database (searched keywords: aldehydes, ketones, ethers, esters, alcohols, phenols, carboxylic acids, wastewater or effluent; accessed on 04.01.2019).

sensitivity of a procedure, a sample preparation step providing isolation and enrichment of analytes is usually required.

The paper provides a review of the procedures for the determination of content of volatile and semivolatile oxygenated organic compounds in samples of domestic, industrial and municipal wastewater by means of gas chromatography. The available techniques at each step of the analytical procedure are discussed along with the outlook and general problems resulting from the use of various sample preparation and final determination methods. Applications of the discussed procedures to the analysis of real effluents are also included.

2. Sample preparation methods

Among the available methods of introduction of liquid samples with aqueous matrices into the GC injection port, a direct aqueous injection (DAI) technique has gained some popularity. In this approach, on-column injection is typically used, recently along with programmed temperature vaporization (PTV). The syringe needle is introduced directly on-column (or into a deactivated pre-column such as an empty capillary column). Water is retained in the initial segment of the column and the analytes, released by the flowing carrier gas, are retained as a narrow band further down the column. This is a simple technique which does not require any special sample preparation. Thus, DAI can significantly reduce the time of analysis and decrease the loss of volatile analytes which can take place during sample preparation. However, DAI is not recommended for samples of wastewater since it precludes determination of compounds present at low concentrations and can cause contamination of a GC column with contaminants and inorganic salts thus shortening the column lifespan. There are just a few reports on the application of DAI in the analysis of wastewater but they only confirm the problems with peak tailing, the appearance of ghost peaks, shifts of retention times, *etc.* [6,29]. Special problems due to very low sensitivity can be observed in the determination of acetic acid, which is a very important O-VOC, during monitoring wastewater treatment in anaerobic reactors [30]. A somewhat better approach to the determination of carboxylic acids in wastewater is thermal desorption (TD) due to an improved reproducibility of the results and minimization of the problem of retention time

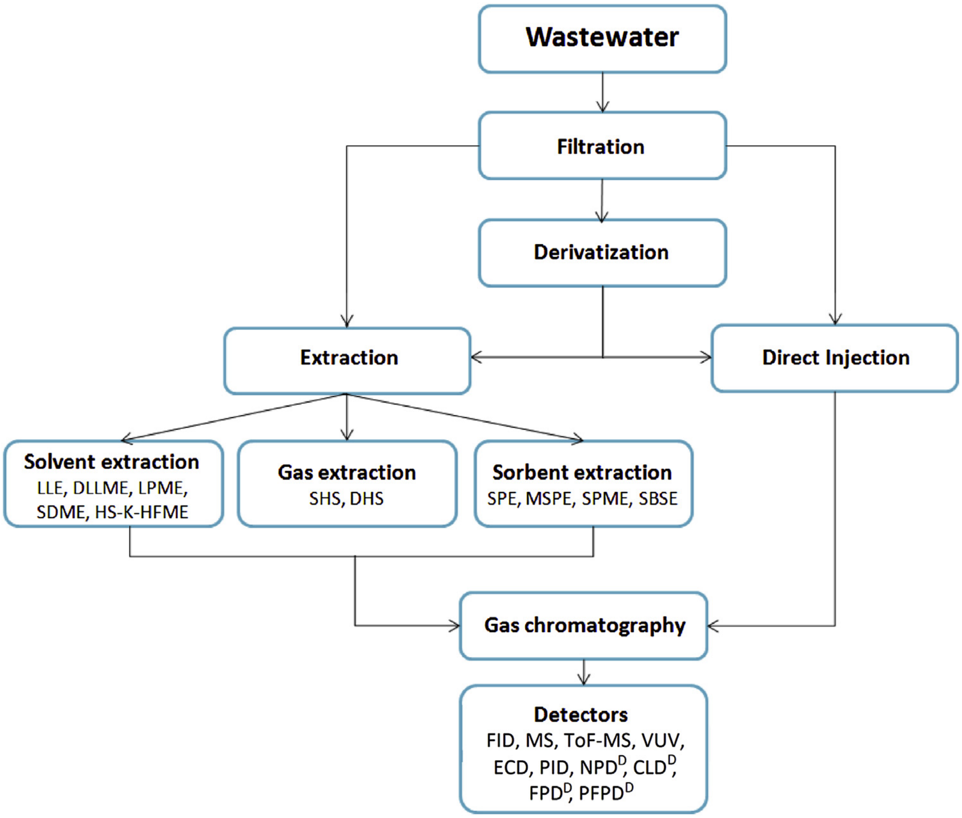


Fig. 3. Schematic diagram of the procedure for the determination of volatile oxygenated organic compounds in wastewater samples using gas chromatography (^{D} – detectors used for the determination of O-VOCs after derivatization).

shifts. Nevertheless, similarly to DAI, also thermal desorption does not allow the determination of volatile fatty acids at sufficiently low concentrations [6].

Consequently, isolation and enrichment of analytes from wastewater samples is the required step in a procedure. Owing to environmental concerns and according to green chemistry principles, sample preparation techniques should meet a number of requirements, including possibility of automation, small sample volumes and being so-called solventless sample preparation techniques, *i.e.*, the techniques that either do not use organic solvents at all or use only small volumes of them [31,32]. A standard procedure for the determination of O-VOCs in wastewater samples is shown in Fig. 3.

2.1. *Gas extraction*

One of the sample preparation techniques meeting all the requirements of green chemistry is headspace analysis, which can be carried out either in static or dynamic mode.

2.1.1. *Static headspace*

The procedure of headspace analysis involves placing a sample in a vial which is then tightly closed with a crimp or screw cap equipped with a septum. In addition to the sample, the vial must also contain some headspace. The sample is then thermostatted at a specific temperature until thermodynamic equilibrium between the sample and the headspace is reached. Next, the headspace is sampled using a gas-tight syringe (which is also thermostatted) and injected the GC injection port. The time and temperature of equilibration depend on the rate of diffusion of volatile sample components. As a rule, these parameters are determined experimentally during the development of the procedure. Fully automated autosamplers for SHS are commercially available. A schematic diagram of the SHS procedure is shown in Fig. S1. The use of static headspace analysis for the determination of O-VOC content has a number of advantages, including universal applicability, simplicity and the possibility of automation, which is important in the case of a large number of samples. Moreover, in comparison with conventional extraction techniques, SHS does not cause losses of the most volatile organic compounds which are responsible for malodorous properties of wastewater due to their low odor threshold of O-VOCs [33–36]. On the other hand, a serious disadvantage of SHS is its insufficient sensitivity for compounds with higher boiling points and the problems related to variable composition of matrices of wastewaters [37,38]. As a result of low sensitivity of SHS for higher boiling O-VOCs, which are commonly present in various kinds of wastewater, the technique is rarely used in the analytics of effluents [37].

2.1.2. *Dynamic headspace*

The problem of relatively low sensitivity of SHS was partially eliminated by using dynamic headspace analysis (DHS), which is often called purge-and-trap, in which analyte enrichment is achieved by a continuous shift of the equilibrium toward headspace [39]. In this way, the detection limit for the same compounds can be lowered by as much as three orders of magnitude compared to SHS. The DHS procedure involves transfer of analytes from the aqueous phase to the headspace by purging the sample with an inert gas followed by trapping volatile components in a trap (using sorption or cryofocusing). The purge can take place in a tightly closed vial equipped with a stopper with a septum through which a purge gas inlet is introduced. Alternatively, U-tube shaped concentrators equipped with sintered glass (for dispersion of the gas) just below the sample can be used. The purge gas outlet is typically

Table 1
Compilation of conditions for DHS extraction.

Analytes	Purge time [min]	Gas flow rate [ml/min]	Purge temperature [°C]	Desorption time [min]	Desorption temperature [°C]	Sorbent	LOD	RSD [%]	R [%]	Ref.
Alcohols, phenols, ketones, aldehydes, esters, ethers (36 O-VOCs)	5	20 (H_2)	20	4	250	Tenax TA	0.005–20 mg/L	<5.0	–	[12]
MTBE	10	–	40	10	220	Tenax TA	2.9 ng/L	–	99.1	[44]
Alcohols, phenols, ketones, aldehydes (28 O-VOCs)	10	100 (N_2)	–	10	220	Tenax TA	–	–	–	[45]
Acetone	12	–	60	4	260	Carbopack B/Carbosieve III	0.32–2.39 µg/L	< 13.4	–	[43]

made of a stainless steel or fused silica capillary. The purge gas (usually helium or hydrogen, less often nitrogen) flowing through the sample sweeps out volatile compounds and transfers them to a trap packed with a sorbent. A different approach involves the use of a short length of an empty deactivated capillary column made of fused silica and cooled with vapors of liquid nitrogen. The latter approach eliminates the problem of sorbent bed breakthrough and ensures narrower bands of analytes during the desorption step. The limitations of DHS include more expensive equipment, the use of liquid nitrogen and the need for drying the gas to remove water vapor carried from the sample. Volatile chemical compounds are then released from the trap by thermal desorption and introduced into the GC injection port. A schematic diagram of the procedure is shown in Fig. S2. The main shortcomings of DHS other than the ones mentioned above include a relatively long time of extraction (as a rule longer than 10 min) and the possibility of analyte losses due to sorbent breakthrough if the extraction time is too long and/or the flow rate of the purge gas is too high. Additionally, as was the case with SHS, only volatile compounds with boiling points up to about 150 °C can be extracted [40]. Another limitation of DHS involves the problem with extraction of samples containing surfactants which require addition of a defoamer, such as 1-tetradecanol [41,42]. An important element of any DHS system is a sorbent trap which allows isolation of analytes from the gaseous phase. This step is necessary since volatile compounds in the gaseous phase occur at high concentrations.

2.1.2.1. Enrichment/trapping of oxygenated volatile organic compounds for dynamic headspace. To extract O-VOCs from wastewater samples commercially available sorbents characterized by a high specific surface area, such as carbon molecular sieves Carbosieve S-III and S-II, Carboxen (300–1000 m^2/g) [43], a porous polymer Tenax TA based on2,6-diphenyl-p-phenylene oxide(specific surface area 18 m^2/g [12,44,45] or a composite material containing 70% Tenax TA and 30% graphite carbon (Tenax GR), are predominantly used. Carbosieve S-II is recommended only for the sorption of most volatile compounds whereas the most universal sorbent which has found wide applicability in the analysis of wastewater is Tenax TA [12,44,45]. Another approach which is commercially available is the use of multibed sorbent traps in which the weakest sorbent retaining only heavier O-VOCs is the first in series followed by other sorbents ordered by increasing sorbent strength. Good results of extraction of O-VOCs can also be obtained by using other sorbents, such as a granular activated carbon obtained from macadamia nutshells [46]. However, the alternative sorbents were only tested with standard mixtures. The extraction is also affected by the time and temperature of purge and desorption of analytes. Extraction conditions should be selected depending on the kind and properties of analytes. Elution of analytes from sorbent traps should be carried out countercurrently to the extraction step.

An essential criterion for the selection of a sorbent is its water sorption capacity and the effect of water on the trapping efficiency of individual O-VOCs. Lowering the amount water vapor introduced onto the sorbent can be accomplished by using either micro condensers installed in the DHS-trap line or membrane dryers (usually Nafion). In order to avoid introducing water collected in the trap into the chromatographic system, an additional step, so-called dry purge is added, during which water vapor having low retention on the sorbent bed is removed from the bed by purging with a dry gas in the same direction as that during the extraction step.

Some examples of extraction conditions for extraction of O-VOCs are listed in Table 1. It is also possible to combine DHS-GC with an automated sampling device which allows performing wastewater sample analysis *in situ*. Such an approach eliminates the possibility of analyte losses during transport of samples to the laboratory and reduces the time of analysis [43]. The DHS technique coupled with gas chromatography allows the determination of a wide variety of O-VOCs, including alcohols, aldehydes, phenols, ketones, esters and ethers present at low concentrations in samples having a complex matrix, *i.e.*, effluents from the production of petroleum bitumens [12], petrochemical effluents [45] or municipal effluents [43]. The detection limit values are typically in the order of single ppb. However, due to the problem with the determination of compounds having medium or low volatility in order to ensure comprehensive analysis of organic compounds occurring in wastewater, other types of extraction should also be considered. The dynamic headspace technique generally offers good reproducibility with RSDs varying from 2 to 10% evaluated in one batch, and from 3 to 15% related to batch-to-batch variation. Usually, the linearity for quantitative analysis is over two orders of magnitude.

2.2. Liquid extraction

2.2.1. "Conventional" liquid-liquid extraction

Classical liquid-liquid extraction (LLE) is still very much in use in analytical procedures for the analysis of water and wastewater due to its simplicity and lack of complex equipment. The extraction procedure involves placing a sample in a separatory funnel to which an extraction solvent immiscible with water is then added. Next, the separatory funnel is shaken and left in a stand for the phase separation to take place. The extraction is usually performed repeatedly to transfer a maximum amount of the analytes from the aqueous phase to the organic phase. The procedure is depicted in Fig. S3. LLE is time-consuming and labor-intensive which limits its widespread use. Other limitations include the possibility of emulsion formation and large volumes of very pure organic solvents used. Furthermore, the enrichment factor for O-VOC analytes when using LLE is considerably smaller compared with other sample preparation techniques available [47]. The most important factor affecting the extraction yield is the selection of an appropriate solvent. The solvents used most commonly for the extraction of O-VOCs are volatile so that they are eluted before analytes, *i.e.,* diethyl ether [48], dichloromethane (DCM) [49] or methyl *tert*-butyl ether (MTBE) [49–52]. Several papers mention problems with quantitative extraction of acetic and propionic acid by diethyl ether [48] whereas good results were obtained with MTBE for which the extraction yield was about five times higher than for DCM [49]. Bisphenol A and B were best extracted with chloroform [53]. Extracting solvents with high boiling points could co-elute with analytes which is particularly troublesome when universal GC detectors, such as FID, are used. The extraction efficiency can be improved by decreasing the solubility of O-VOCs in water by using the salting out effect (sometimes also used in SHS and DHS) [53] and/or by changing the pH of samples. However, despite such approaches, the detection limits of O-VOCs are often still too high. In addition, salting-out effect might not be as effective as it can be expected. Sometimes, the solubility is even increasing or minor changes are reported after the salt addition.

2.2.2. *Liquid-liquid microextraction techniques*

Due to disadvantages of LLE and general trends in sample preparation techniques, methods minimizing the volume of organic solvents used are becoming increasingly popular. Such techniques are generally called either liquid phase microextraction (LPME) or solvent microextraction (SME) [54]. The difference between LPME and classical LLE involves much smaller volumes of both samples and extracting solvents. In the determination of phenols and carboxylic acids, 3 μL of organic solvents were sufficient to obtain a high extraction yield of the analytes with a good reproducibility of results. The procedures also offered low LOD values when using the FID detector, ranging from 0.94 to 1.97 μg/L for phenols [55] and 0.0093 to 0.015 μg/L for carboxylic acids [56].

2.2.2.1. Single-drop microextraction. One mode of solvent microextraction is single-drop microextraction (SDME), which requires only 0.3–3 μL of the extractant. The sample is placed in a tightly closed vial with a cap equipped with a septum. The extractant is drawn into a GC microsyringe, and the tip of the needle of the microsyringe is placed either inside the sample. The extractant is then extruded from the microsyringe forming a drop at the tip of the needle. The extraction is typically performed for 5–30 min. Following extraction, the drop is withdrawn into the microsyringe and the extract is injected into the GC [57]. A schematic diagram of the procedure is shown in Fig. S3. Advantages of SDME include a high enrichment factor (mostly due to the phase ratio), simplicity and the possibility of automation [58]. The technique was successfully used in the determination of phenols in municipal wastewater with low detection limits (0.45 – 1.5 ng/mL) and a good reproducibility of results [59]. However, a significant problem in SDME is drop instability and a limited drop volume as well as the problem of solvent volatility. The problem of drop instability in SDME was partially solved by placing the drop in the headspace above the sample (Fig. S3) (headspace single-drop microextraction, HS-SDME) [60] and the use of mixtures of solvents with different densities, such as chloroform and 1-octanol (1:1 v/v), which improved the stability of the hanging drop [61] and, to a greater extent, by placing the solvent in the lumen of a porous hollow fiber (hollow fiber-protected liquid phase microextraction, HF-LPME). Selectivity of the extraction is achieved by selecting the appropriate solvent and the fiber material. The pores in the fiber preclude extraction of large molecules which in the case of wastewater facilitates subsequent GC analysis. An interesting approach is headspace knotted hollow fiber microextraction (HS-K-HFME), in which the knot-shaped commercially available Q 3/2 Accurel polypropylene hollow fiber is filled with 25 μL of the extraction solvent (1-octanol). The excess solvent forms a large droplet (13 μL) which is held in the center of the knot (Fig. S3). The knot-shaped fiber has a larger contact area which increases the rate of mass transfer between the headspace and extraction solvent. This technique provided low LOD values for diethyl ether and ethyl acetate equal to 10 μg/L [62].

2.2.2.2. Dispersive liquid-liquid microextraction. A relatively new mode of solvent microextraction is dispersive liquid-liquid microextraction (DLLME) [63]. In this technique, an aqueous sample is placed in a conical centrifuge tube and a mixture of disperser and extraction solvent is added. Then the mixture is agitated and centrifuged. Next, the sedimented organic phase is collected from the bottom of the tube (in some applications the extract is lighter than water and is collected from the top) and injected into the GC (Fig. S3). Owing to its simplicity, a very short extraction time (several seconds) and often almost 100% analyte recovery DLLME has become one of the most common modes of liquid-liquid extraction [57]. DLLME was used, among others, in the determination of carboxylic acids [64,65] and 43 volatile oxygenated organic compounds in effluents from the production of petroleum bitumens, including alcohols, esters, ethers, ketones, aldehydes and phenols. Low LOD values ranging from 0.07 to 0.82 μg/mL were obtained for all the analytes except for acetaldehyde for which LOD was 2.06 μg/mL [11]. One of the drawbacks of DLLME is the possibility of losses of the most volatile analytes during extraction; therefore, it is recommended for the extraction of compounds with higher boiling points, such as phenols [66,67] or acrylates [68]. Until recently, a serious limitation of DLLME was the inability to automate it. However, some recent papers describe automated DLLME, which makes this sample preparation technique more efficient [69–75]. A comparison of parameters of various liquid-liquid extraction procedures is presented in Table 2.

2.3. *Sorbent extraction*

2.3.1. *Solid-phase extraction*

In order to isolate and enrich of oxygenated organic compounds from wastewater, liquid-solid extraction is commonly used, including solid-phase extraction (SPE). The first step in any SPE procedure involves conditioning of the sorbent bed using a solvent appropriate for a particular sorbent. This step aims at solvation of the sorbent to increase its sorption capacity. Next, a sample of wastewater is loaded onto the SPE column and the analytes are adsorbed onto the sorbent bed. The SPE cartridge is then washed with an aqueous solution to remove impurities, followed by elution of the adsorbed analytes with an appropriate organic solvent. The procedure for SPE extraction is depicted in Fig. S4. SPE technique provides high selectivity due to a wide variety of sorbents available and the possibility of fractional elution with a series of solvents. For isolation of phenols the sorbents used most commonly include silica gel modified with octadecyl groups (C18) [76–80] as well as commercially available polymeric sorbents, such as styrene/divinylbenzene co-polymer (S-DVB) [81] or divinylbenzene/N-vinylpyrrolidone (DVB/N-VP) [82–84], which have also been successfully used to isolate fatty, benzoic and dicarboxylic acids [84]. For isolation of carboxylic, benzoic and hydroxybenzoic acids, a mixture of commercial SPE sorbents containing C18 and ethyl vinyl benzene-divinyl benzene polymer was used (EVB-DVB/C18) (1:1) [85]. Compared to classical LLE extraction, SPE provides greater enrichment factors; however, its main disadvantages are the need for large sample volumes (100–500 mL) [76,77,82] and, sometimes, the use of toxic organic solvents as well as a long extraction time which can exceed 2 h [82]. In standard SPE assemblies, the eluent flow is driven by reduced pressure, which entails the risk of losses of most volatile analytes. In order to shorten the extraction time to 20 min and reduce sample volume to 10 mL, magnetic solid phase extraction (MSPE) can be used. In this technique, either the sorbents have magnetic properties or they are immobilized on magnetic cores.

Table 2
Compilation of parameters of liquid-liquid extraction.

Extraction technique	Analytes	Extractant	Derivatization	Sample volume/ extractant volume	Extraction time	Detector	LOD	RSD [%]	R [%]	Ref.
LLE	Carboxylic acids	Diethyl ether	–	1 mL/1 mL	30 s	FID	–	<2.7	–	[48]
	Carboxylic acids	MTBE/DCM	–	10 mL/10 mL	10 min	MS	–	–	–	[49]
	Carboxylic acids	MTBE	–	4 mL/2 mL	–	MS	0.1–0.5 mg/L	<1.3	–	[50]
	Carboxylic acids	MTBE	BSTFA, TMCS	4 mL/2 mL	2 min	MS	0.03–0.2 μg/L	<2.1	92–106	[51]
	Carboxylic acids	MTBE	BSTFA, TMCS	4 mL/4 mL	2 min	MS	0.8–4.2 μg/L	<9	61–79	[52]
	BPA, BPF	$CHCl_3$	TMSA	500 mL/5 mL	1 min	MS	0.006–0.02 μg/L	<5.6	–	[53]
HF-LPME	Carboxylic acids	1-Octanol	TBA-HSO_4	3 mL/4μL	10 min	MS	0.0093–0.015 μg/L	<11.5	–	[56]
DI-SDME	Phenols	Chloroform	TBA-Br	5 mL/3 μL	20 min	MS	–	<7.5	96–121	[59]
	Phenols	Chloroform:1-octanol (1:1)	TBA-Br	3 mL/3 μL	12 min	FID, MS	0.2–0.7 μg/L (MS); 12–17.3 μg/L (FID)	<5.4 (GC-MS), <7.1 (GC-FID)	–	[61]
HS-SDME	Phenols	$[C_8MIM][PF_6]$	–	10 mL/1 μL	25 min	FID	0.1–0.4 μg/L	<9.5	81–111	[60]
HS-K-HFME	Diethyl ether, ethyl acetate	1-Octanol	–	4 mL/25 μL	20 min	MS	10 μg/L	<11.6	96–104	[62]
DLLME	Phenols, aldehydes, ketones, alcohols, esters, ethers	DCM, (ACN-disperser)	–	10 mL/0.5 mL	60 s	MS	0.07–0.82 mg/L	<5	71–119	[11]
	Phenols	DCM, (IPA –disperser)	–	5 mL/0.2 mL	–	FID	0.32–0.34 μg/L	<3.2	85–96	[66]
	Phenols	CTC/chlorobenzen 2:1 v/v (ACN - disperser)	–	5 mL/15 μL	2 min	MS	–	<9.1	68–104	[67]
	Acrylates	Chlorobenzen (AcCN-disperser)	–	5 mL/20 μL	5 min	FID	0.071–0.13 μg/L	<9.1	81–109	[68]
	Carboxylic acids	Chloroform (IPA- disperser)	TBA-HSO_4	9 m L/300 μL	60 s	MS	6.9–1120 μg/L	<6.4	69–126	[64]
	Carboxylic acids	ChCl:4MPh (1:2 molar ratio) (MeOH-disperser)	ChCl:4MPh (1:2 molar ratio)	9 m L/500 μL	10 min	MS	1.7–8.3 μg/L	<6.7	82–106	[65]

Sorbent particles are added to a wastewater sample and left in it until the analytes are adsorbed. Next, the sorbent particles are attracted by a magnet while the sample matrix is decanted. This is followed by analyte desorption using an appropriate organic solvent. The extract is then analyzed by GC. The MSPE procedure is depicted in Fig. S4. Just 40 mg of Fe_3O_4@C@polyaniline magnetic microspheres were needed to obtain high recoveries (85.3–110.6%) and low LOD values (0.89–7.58 ng/mL) for phenols extracted from 10 mL of wastewater samples [86].

2.3.2. Stir bar sorptive extraction

Another extraction technique that can be used for the determination of phenols and carboxylic acids is stir bar sorptive extraction (SBSE). SBSE procedure calls for transfer of analytes from the aqueous phase to a sorbent layer (usually PDMS) coated onto a magnetic stir bar. During extraction wastewater samples are stirred magnetically using the stir bar. Next, the adsorbed analytes are recovered from the stir bar using either thermal desorption or extraction with an appropriate organic solvent (Fig. S5). In SBSE the sorbent (PDMS) volume is 50 to 250 times greater than that in SPME, which results in higher recoveries and enrichment factors for the majority of O-VOCs. However, because of long extraction times (as much as 240 min) and relatively low extraction efficiency (for example, 1% for salicylic acid) disqualify SBSE as a sample preparation method for routine analyses of wastewater [87].

2.3.3. Solid phase microextraction

Solid phase microextraction (SPME) is a miniaturized version of SPE. In this technique, analytes are sorbed onto a layer of extracting phase coated onto a fused silica fiber which is placed inside a needle held in a holder. After introduction of the needle into a sample the fiber is exposed to the sample. Next, the fiber is retracted into the needle which is then inserted into the GC injection port for thermal desorption of analytes. SPME can be performed in the direct immersion mode (DI-SPME) in which the fiber is immersed directly into an aqueous sample or in the headspace mode (HS-SPME) where in the fiber is placed in the headspace above the sample (Fig. S6). The latter mode is more favorable for analysis of wastewater as it protects the fiber from mechanical damage by solids present in the sample and prevents extraction of analytes of low volatility or nonvolatile which could contaminate both the fiber and the chromatographic system [88]. However, DI mode allows the determination of less volatile O-VOCs in wastewater samples, which cannot be determined using the HS mode. Regardless of SPME mode, the key role in extraction is played by the kind of sorbent and shape of the fiber [89]. A number of fibers of varying polarities are now available commercially for extraction of various groups of chemical compounds. In the determination of volatile fatty acids numerous problems are posed by short-chain acids, *i.e.*, acetic and propionic acid [90–92]. Among five fibers, including polyacrylate, Carbowax/Divinylbenzene (CAR-DVB), Polydimethylsiloxane/Divinylbenzene(PDMS–DVB), Polydimethylsiloxane/Carboxen/Divinylbenzene (PDMS–CAR–DVB) and Polydimethylsiloxane–Carboxen (PDMS–CAR), only PDMS-CAR sorbent provided satisfactory extraction of C_2 and C_3acids [93]. The same sorbent was highly effective in the extraction of phenols [94]. In the determination of bisphenol A (BPA), *tert*-nonylphenol and formaldehyde in samples of wastewater the highest extraction efficiency was achieved using PDMS/DVB; however, the use of such a fiber can introduce errors due to the presence of BPA in epoxy resin that is used to attach the fiber to the holder. A decrease in the amount of released BPA is observed after multiple extractions which results in the aging of the fiber and deterioration of extraction efficiency. The fiber coated with PDMS/DVB is highly effective for about 100 extractions. Consequently, fibers coated with polyacrylate are recommended for extraction of BPA from wastewater [95,96]. For carboxylic acids with a longer chain and for aldehydes and volatile phenols the best results were obtained when using PDMS-CAR-DVB [90,97]. Other investigations demonstrated improved extraction efficiency for polyethylene glycol as a fiber coating. Selectivity of sorption of individual analytes present in the headspace, in addition to elimination of analytical signal of undetermined VOCs in the chromatogram, also affects the sorption capacity of the fiber, since only the analytes of interest will be accumulated. Compared to the fiber coated with PDMS-CAR, extraction using PEG provided lower detection limits for the majority of carboxylic acids (C_2 –C_7) [98] while LOD values for the same analytes extracted with CAR-DVB were lower by a factor of 300 compared with direct aqueous injection. Only extraction of formic acid yielded a twofold increase in sensitivity compared to DAI [99]. Similar results were obtained in other investigations [88]. The use of fibers coated with polymeric materials has a number of disadvantages, including relatively low maximum desorption temperatures, which generally ranges from 240 to 280 °C, instability and too low polarity which limits their usefulness for some compounds. High thermal stability is required for the thermal desorption step. Insufficient desorption temperature will cause peak broadening and tailing as well as discrimination of higher boiling analytes.

2.3.3.1. Developments in solid-phase microextraction for oxygenated volatile organic compounds analytics.

Therefore, a number of novel fiber coatings have recently appeared, such as carbon nanotubes, including multiwalled carbon nanotubes [100–102], ionic liquids [103] or based on calixarenes, *i.e.* amide bridged-C[4]/OH-TSO(25,27-dihydroxy-26,28-oxy(2′,7′-dioxo-3′,6′-diazaoctyl)oxy-p-tert-butylcalix[4]arene/hydroxy-terminated silicone oil) [104], which eliminate the problems mentioned above and can be successfully used for the determination of O-VOCs in wastewater samples. An increase in volume of the extracting phase in SPME results in lowering detection limits and extending a linear range; however, until now the increase in the amount of sorbent required modification not only of the SPME apparatus but also of the thermal desorption module. The problem has recently been eliminated by the introduction of the PAL SPME Arrow system, which contains a stainless steel wire coated with a greater amount of a sorbent compared to a typical SPME fiber and ending with the arrow-shaped tip. This arrangement ensures compatibility with the commercially available thermal desorbers and liners. In addition, the presence of a steel wire provides a much improved fiber stability [105,106]. The SPME Arrow system has not yet been used for extraction of O-VOCs from wastewater samples. Another important parameter is extraction temperature. An increase in extraction temperature can accelerate adsorption of analytes on the fiber but too high a temperature can result in desorption and losses of the most volatile sample components. Consequently, the procedures for the determination of volatile fatty acids made use of mostly room temperature and time ranging from 15 to 60 min [88–90,93,98,99] whereas extraction of phenols and aldehydes was carried out at substantially higher temperatures (from 50 to 100 °C) [94–97,102,104]. SPME technique requires splitless injection using narrow glass liners in order to create high carrier gas velocity around the fiber which allows rapid removal of desorbed analytes from the injection port [107]. However, some papers report successful use of the split injection [104]. So far, no formation of O-VOCs artifacts on the SPME fibers have been reported in the literature although such problems are known for other groups of volatile organic compounds, *i.e.*, organosulfur compounds. This phenomenon should be taken into consideration in the investigations of more reactive O-VOCs.

Table 3
Compilation of various types of solid-phase extraction procedures in the determination of O-VOCs in wastewater samples.

Extraction technique	Analytes	Sorbent	Derivatization	Extraction temp./time	Thermal desorption temperature/time	Elution eluent/time	Detector	LOD	RSD [%]	R [%]	Ref.
SPE	phenols	C18	MTBSTFA	RT	–	MeOH (5 mL), hexane:ACN (50:50, v/v)(3.5 mL)/–	MS	0.6–3.16 μg/L	–	93	[77,78]
	phenols	C18	BSTFA/pyridine	RT/80 min	–	DCM (4 mL), hexane (2 mL)	MS	0.03– 0.41 μg/L	<13.9	>60	[79]
	phenols	DVB/N-VP	AAA	RT/over 2 h	–	ACN (3 mL) and DCM (2 mL)	MS/MS	0.03–2.5 μg/L	<30	60–135	[82]
	phenols	C18 - DVB/N-VP	BSTFA/TMCS	RT	–	DCM	MS	3.64–97.64 ng/L	<13.6	–	[83]
	esters, carboxylic acids, phenols	DSC-18	HMDS/TFA	RT	–	Hexane (5mL), ethyl acetate (5 mL), MeOH 14mL)	MS	0.92–600 ng/L	<10	94	[84]
	carboxylic acids	EVB-DVB/C18	BSTFA/TMCS	RT	–	MeOH (200 μL)	MS	0.6–15 ng/L	<4.6	93–101	[85]
MSPE	phenols	Fe3O4@C@PANI microspheres	BSTFA/TMCS	RT/20 min	–	Ethyl acetate/5min	MS	0.89–7.58 μg/L	<13.1	85–111	[86]
SBSE	Phenols and carboxylic acids	PDMS	MTBSTFA	RT/240 min	–	Ethyl acetate (0.2 mL)/30 min	MS	1–800 ng/L	<20	70 – 130	[87]
SPME	formaldehyde	PDMS-DVB	PFBHA	50 °C/40 min	250 °C/7 min	–	MS	10 mg/L	<23	–	[96]
	carboxylic acids	CAR-DVB	–	25 °C/20 min	250 °C/3 min	–	MS	11.5 mM/L	<16.7	77–114	[99]
	carboxylic acids	Ionic liquid: Poly (1-Vinyl-3-Hexylimidazolium) Chloride	–	35 °C/10 min	170 °C/4 min	–	MS	–	–	–	[103]
HS-SPME	phenols	MWCNTs	–	70 °C/50 min	280 °C/5 min	–	FID	5–50 μg/L	<6.5	88–112	[100,102]
	phenols	Polyamide	–	30 °C/60 min	280 °C/3 min	–	MS	0.04–1 μg/L	<10	–	[95]
	phenols	MWCNTs	–	50 °C/40 min	250 °C/3 min	–	FID	1.89–65.9 ng/L	<12.4	88–112	[101]
	phenols	PDMS–CAR	AAA	100 °C/30 min	270 °C/–	–	MS	0.001–0.04 μg/L	<16.2	–	[94]
	phenols	Amide bridged-C[4]/OH-TSO	–	50 °C/15 min	260 °C/3 min	–	FID	0.47–9.01 μg/L	<9.1	90–103	[104]
	phenols, aldehydes	PDMS-CAR-DVB	–	70 °C/30 min	250 °C/1 min	–	MS	0.003–0.6 μg/L	<16	>70	[97]
	carboxylic acids	CAR-DVB	–	25 °C/20 min	250 °C/3 min	–	FID	3–467 μg/L	<10	85–117	[88]
	carboxylic acids	PEG	–	25 °C/40 min	230 °C/3 min	–	MS	0.017–0.064 mg/L	–	–	[98]
	carboxylic acids	PDMS-CAR	–	25 °C/20 min	300 °C/5 min	–	FID	6–675 μg/L	<13.3	–	[90]
	carboxylic acids	PDMS-CAR	–	25 °C/–	300 °C/5 min	–	FID, NCI-MS (NH$_3$), PCI-MS (CH$_4$)	6–675 μg/L (FID), 2–6 μg/L (NCI-MS), 10–115 μg/L (PCI- MS)	<16	–	[93]

Solvent used for elution of fraction of interest.

A compilation of solid-phase extraction procedures used for the determination of O-VOCs is shown in Table 3.

3. Derivatization

Derivatization is carried out in order to improve physicochemical properties of analytes, including change in polarity, lowering of boiling point and improvement of thermal stability. Furthermore, by introducing a functional group containing for example a halogen, the sensitivity of the determination can be improved by using the selective electron capture detector (ECD) [108,109]. On the other hand, derivatization of wastewater samples having a very complex matrix can result in unwanted chemical reactions in the sample. In addition, introduction of a derivatizing agent can contaminate a sample and extend the time of sample preparation. Consequently, derivatization of analytes should be considered as a last resort used only for the analytes for which direct determination at low concentrations is very difficult or impossible, including compounds containing carboxyl or hydroxyl groups. Depending on the group of analytes investigated, various types of derivatization reactions are carried out, including silylation, esterification, alkylation or acylation.

Derivatization methods have been described in a number of papers [47,110–114]. The most common reagents used for derivatization of O-VOCs, which block polar groups being proton donors (*i.e.,* –OH and –COOH), include alkylsilanes, such as N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) [51,52,79,83,85,86] N-trimethylsilylimidazole (TMSIM), trimethylchlorosilane (TMCS) [51,52], N,O-bis(trimethylsilyl) acetamide (TMSA) [53], hexamethyldisilazane (HMDS) [84] and N-methyl-N-(*tert*-butyldimethylsilyl)trifluoroacetamide (MTBSTFA) [76,77,87]. They allow introduction of the trimethylsilyl group (TMS) to analyte molecules thus increasing volatility of the analytes, improving separation of isomers and enhancing sensitivity of detection when using a mass spectrometer operated in the positive chemical ionization mode. However, despite numerous advantages, silyl derivatives are very unstable and the analysis must be carried out within 12–24 h, which limits the use of these reagents in routine determinations of a large number of samples [51].

Carboxylic acids can undergo direct 100% reaction yield in 2–3 min is diazomethane; however, it is not recommended due to its irritating, carcinogenic and explosive properties [47,113]. Consequently, diazomethane is often replaced with less hazardous reagents, such as pentafluorobenzyl bromide (PFBBr), which provides much lower yields and the reaction takes several hours [113,115]. The method of derivatization of carboxylic acids that is not time consuming and enables automation is the formation of ion pairs through the reaction of carboxyl or hydroxyl groups with tetraalkylammonium salts in the sample solution. The ion pairs formed after being injected into the hot (>280 °C) GC injection port are converted into alkyl (often butyl) esters. The most common ion pairing reagents include tetrabutylammonium hydrogensulfate (TBA-HSO_4) [56,64], tetrabutylammonium chloride (TBA-Cl) and tetrabutylammonium bromide (TBA-Br) [56,59,61]. The butyl esters formed have greater mass-to-charge (*m/z*) ratio compared to methyl esters which improves selectivity in GC—MS analysis [56,68,116]. Another interesting approach is the procedure based on the use of inexpensive and simple to synthesize deep eutectic solvent composed of choline chloride and 4-methyl phenol in 1:2 M ratio (ChCh:4MPh1:2) for both the extraction of the analytes and their ion pair derivatization [65].Another class of reagents allowing derivatization of carboxylic acids to alkyl esters in aqueous are alkyl chloroformates. The alkyl esters formed can be readily extracted into nontoxic organic solvents [117].

4. Separation proces - stationary phases

The selection of a proper chromatographic column has a decisive effect on the results of both qualitative and quantitative analysis. Efficient separation of analytes is required for correct identification, accurate determination and thus applicability of an analytical procedure. A number of commercial capillary columns with various types of stationary phases are now available, which are recommended for the analysis of individual groups of chemical compounds in order to ensure the best selectivity and resolution.

4.1. Polydimethylsiloxane based stationary phases

For direct injection of aqueous solutions without prior removal of the water matrix, a polar stationary phase, such as a wax-based sol-gel phase [118] or, alternatively, a stationary phase of low polarity, *i.e.,* polydimethylsiloxane or 5% phenyl 95% polydimethylsiloxane should be used. These stationary phase practically do not interact with water so they are not damaged by aqueous samples [119]. Another option is to use apolar-deactivated guard column, which enables complete evaporation of water prior to introduction of analytes onto the column [119,120].

The use of PDMS as a stationary phase is recommended for the separation of phenols due to strong dispersive forces which leads to elution of the majority of analytes according to their boiling point, thus facilitating identification [100,109]. The most common stationary phases used for the separation of volatile oxygenated organic compounds, except for carboxylic acids, from wastewater samples are 5% phenyl 95% dimethylpolysiloxane and 5% phenyl 95% dimethylarylenesiloxane, which have low polarity.

4.2. Polyethylene glycol based stationary phases

Some carboxylic acids (C_2 – C_8) are sufficiently volatile and thermally stable to be determined by GC without derivatization. However, their high polarity and ability to form hydrogen bonds precludes obtaining symmetrical peaks with most popular stationary phases of low and medium polarity. Consequently, polar stationary phases based on polyethylene glycol (PEG) are recommended for the separation of volatile fatty acids [120–124]. Alkane monocarboxylic acids tend to adsorb in the injection port or on the column, therefore, many reports recommend the use of PEG modified with 2-nitroterephthalic acid (called free fatty acid phase – FFAP), which deactivates its basic sites [43,49,88–90,93,98,99,103,125]. FFAP was also successfully used for the separation of phenols [60]. Another interesting approach is to connect several capillary columns in series, including a column with a polar stationary phase connected to a short deactivated column, followed by a PDMS column and another deactivated column. The use of such a sequence allows complete separation of carboxylic acids C_2- C_8. Furthermore, using a polar stationary phase in the first column resulted in obtaining narrow and symmetrical peaks [126]. A significant disadvantage of polar stationary phases is their relatively low maximum operating temperature (<260 °C) which makes them unsuitable for the analysis of higher boiling compounds, such as long-chain carboxylic acids or dicarboxylic acids [127].

The most recent (and most expensive) approach is the coupling of time-of-flight mass spectrometer (TOF-MS) with comprehensive two-dimensional gas chromatography (GCxGC). Two-dimensional GC separation of analytes greatly improves peak capacity and enables a very effective separation. Typically, analytes are separated on a column with the stationary phase of a low polarity in the first dimension, followed by the separation of each fraction on a more polar stationary phase in the second dimension. However, a reverse order of polarity of the stationary phases is sometimes used. The technique GC x GC-ToF-MS was used to determine isomers of

Table 4
A list of the most popular commercially available stationary phases for the separation of selected groups of O-VOCs.

Polarity	Stationary phase	Analytes
Non-polar	Dimethylpolysiloxane	phenols, aldehydes, ketones, alcohols, esters, ethers
	5% Phenyl 95% dimethylpolysiloxane	phenols, aldehydes, ketones, alcohols
Intermediate polarity	5% Phenyl 95% dimethyl arylene siloxane	phenols, aldehydes
	6% Cyanopropyl-phenyl, 94% dimethyl polysiloxane	phenols, aldehydes, ketones, alcohols, esters, ethers
Polar	Polyethylene glycol	carboxylic acids
	Polyethylene glycol modified with 2-nitroterephthalic acid	carboxylic acids, phenols
Highly polar	(1,5-di(2,3-dimethylimidazolium)pentane bis(tri fluoromethylsulfonyl)imide)	phenols, aldehydes, ketones, alcohols, esters, ethers

nonylphenol. This approach allowed to minimize co-elution of analytes and to identify a larger number of isomers which could not be separated in the SIM mode by GC—MS [128,129].

4.3. Ionic liquids

An alternative to stationary phases based on polyethylene glycol are novel stationary phases based on ionic liquids which, due to unique properties of ionic liquids, are polar or extremely polar. At the same time, columns with ionic liquids as the stationary phase can operate at higher temperatures compared to conventional polar columns [130–132]. When separating a model mixture containing 36 O-VOC compounds, the highest selectivity was obtained with an ionic liquid (1,5-di(2,3-dimethylimidazolium)pentane bis(trifluoromethylsulfonyl)imide) as the stationary phase compared to traditional stationary phases of low and medium polarity. Co-elution was observed only for several compounds with substantially different mass spectra due to occurrence of specific fragment ions, which did not interfere with quantitative analysis. Moreover, the use of the column with the ionic liquid resulted in elution of $C_5$to $C_8$$n$-alkanes in dead time which reduced matrix interference since these alkanes are commonly present in petroleum refinery effluents [9,11,12,133].

Oxygenated organic compounds are also separated on stationary phases based on carbon nanotubes whose properties can be modified by binding various functional groups improving their selectivity toward alcohols and esters and reducing the time of analysis. However, most of the papers published report the use of such stationary phases for the separation of model mixtures [134–136].

A list of the most popular commercially available stationary phases for separating selected groups of O-VOC is compiled in Table 4.

5. Detection

A popular detector used in the analyses of wastewater is the universal flame ionization detector (FID) [55,60,61,66,68,85,93]. However, due to its lack of selectivity toward oxygenated organic compounds and a considerably lower sensitivity, it is not recommended for the determination of O-VOCs in samples with very complex matrices, such as wastewater [85,93].

5.1. Oxygenate selective flame ionization detector

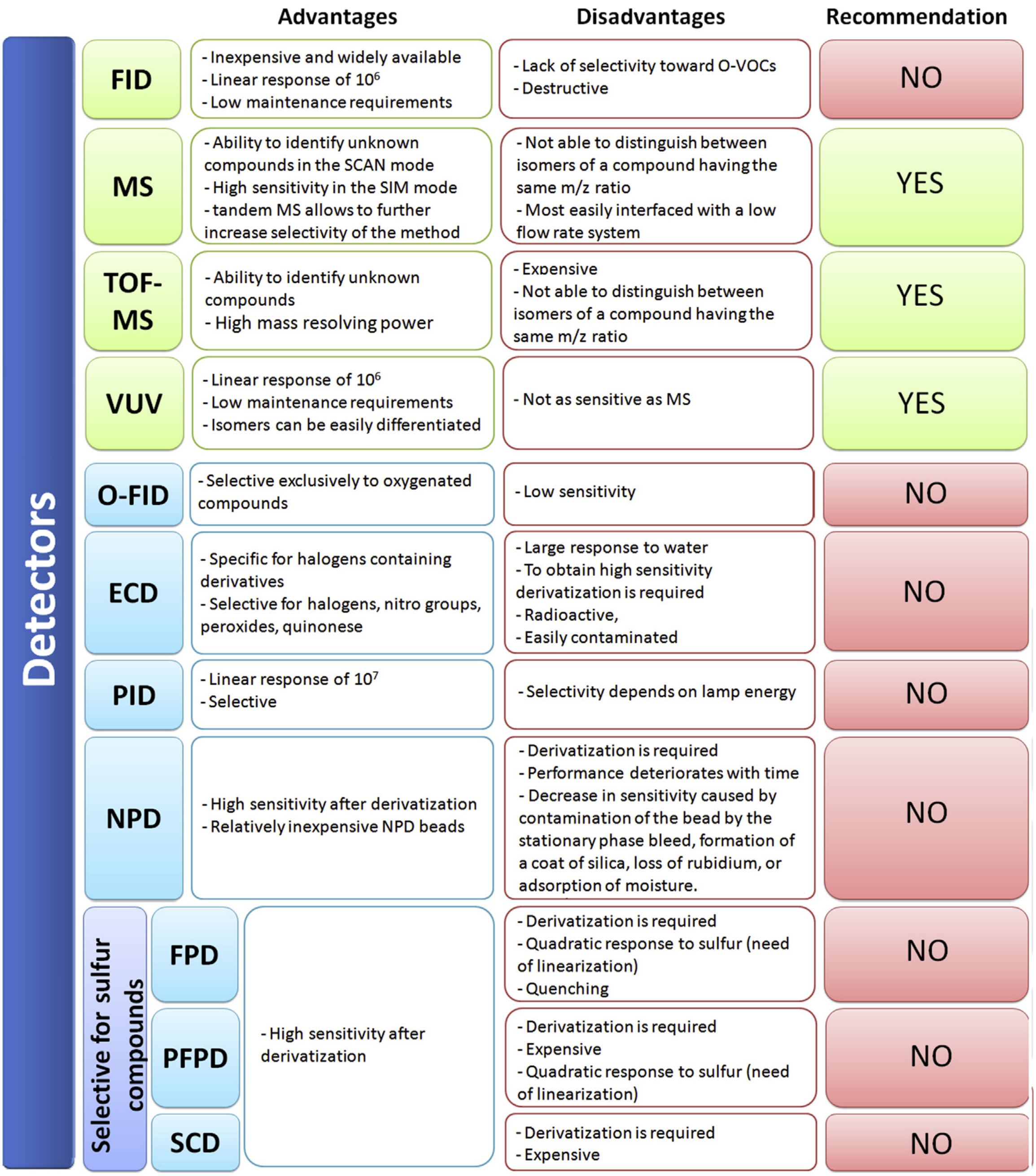
The only GC detector selective exclusively to oxygenated compounds is oxygenate selective flame ionization detector (O-FID) [137]. The detector includes a cracking reactor which converts any oxygenated compounds to carbon monoxide and a special FID with a microreactor for the catalytic hydrogenation of CO and detection of methane Hydrocarbons give no signal. Peaks in the chromatogram represent solely oxygenated organic compounds and the peak areas depend upon the analyte content and the number of oxygen atoms in a molecule [137,138]. GC-O-FID enables the determination of O-VOCs at concentration levels 0.17–15% (m/m) [139]. Such high LOD values disqualify this detector for determination of volatile oxygenates in wastewater samples, in which the analytes occur at concentrations in the order of ppb and ppm. Thus far, no procedures for the determination of O-VOCs in wastewater making use of analyte enrichment and derivatization combined with GC-O-FID have been reported.

5.2. Mass spectrometry

At present, a mass spectrometer is the detector most commonly used in the determination of volatile oxygenated organic compounds in wastewater. When using selected ion monitoring (SIM) mode, the MS can selectively detect analytes in the presence of co-eluting matrix components. Moreover, when used with an analyte isolation and enrichment procedure, GC–MS allows determination of analytes at a μg/L or even ng/L level [51–53,56,62,85]. A major advantage of a mass spectrometer over the other GC detectors is its ability to identify unknown compounds in the SCAN mode based on comparison of the obtained spectra with vast mass spectral libraries when the electron ionization (EI) is used. On the other hand, in the SIM mode identification of analytes is carried out by comparison of their retention times with those of standards, taking a confidence interval of ± 0.2% t_R [min], as well as on the basis of selected characteristic values of mass-to-charge ratios and comparison of their intensities. As a rule, several characteristic ions are selected for each compound in a given interval of retention time. It should be noted, however, that the detector sensitivity decreases with an increase in number of monitored ions. Therefore, a reasonable approach is to select two characteristic mass-to-charge values, of which one is used for integration of the peak while the other is used to confirm the peak identity based on the ratio of intensities with an assumed confidence interval of 15–30 %. Such an approach constitutes a sufficient confirmation of peak identification while allowing the determination of analytes at suitably low concentration levels [11,12].

The second type of ionization commonly used in a mass spectrometer is positive or negative chemical ionization (CI), which does not ensure such a high reproducibility of ionization as was the case with EI, which results in the absence of commercially available mass spectral libraries and identification is carried out on the basis of an intense molecular ion which is possible due to soft ionization. The studies in which two modes of ionization, EI and positive CI in which ammonia was used as a reagent gas, were compared revealed only slight differences in reproducibility of the results obtained in the SIM mode for 22 carboxylic acids, LOD values lower by a factor of *ca.* 25 and a wider linear range for EI-MS [85]. A comparison of positive(reaction gas CH_4) and negative (reaction gas NH_3) chemical ionization in the determination of volatile fatty acids demonstrated lower detection limits when negative chemical ionization was used [93].

A complex matrix composition of wastewater sample often precludes direct identification due to co-elution of many analytes. To accomplish peak resolution and obtain pure spectra, chemometric models such as Parallel Factorial Analysis (PARAFAC) [140] or Multivariate Curve Resolution Alternating Least Squares (MCR-



Detectors	Selective for sulfur compounds	Detector	Advantages	Disadvantages	Recommendation
Detectors		FID	- Inexpensive and widely available - Linear response of 10^6 - Low maintenance requirements	- Lack of selectivity toward O-VOCs - Destructive	NO
		MS	- Ability to identify unknown compounds in the SCAN mode - High sensitivity in the SIM mode - tandem MS allows to further increase selectivity of the method	- Not able to distinguish between isomers of a compound having the same m/z ratio - Most easily interfaced with a low flow rate system	YES
		TOF-MS	- Ability to identify unknown compounds - High mass resolving power	- Expensive - Not able to distinguish between isomers of a compound having the same m/z ratio	YES
		VUV	- Linear response of 10^6 - Low maintenance requirements - Isomers can be easily differentiated	- Not as sensitive as MS	YES
		O-FID	- Selective exclusively to oxygenated compounds	- Low sensitivity	NO
		ECD	- Specific for halogens containing derivatives - Selective for halogens, nitro groups, peroxides, quinonese	- Large response to water - To obtain high sensitivity derivatization is required - Radioactive, - Easily contaminated	NO
		PID	- Linear response of 10^7 - Selective	- Selectivity depends on lamp energy	NO
		NPD	- High sensitivity after derivatization - Relatively inexpensive NPD beads	- Derivatization is required - Performance deteriorates with time - Decrease in sensitivity caused by contamination of the bead by the stationary phase bleed, formation of a coat of silica, loss of rubidium, or adsorption of moisture.	NO
	Selective for sulfur compounds	FPD	- High sensitivity after derivatization	- Derivatization is required - Quadratic response to sulfur (need of linearization) - Quenching	NO
		PFPD		- Derivatization is required - Expensive - Quadratic response to sulfur (need of linearization)	NO
		SCD		- Derivatization is required - Expensive	NO

Fig. 4. The advantages and disadvantages of universal and selective detectors for the determination of O-VOCs in wastewater samples.

ALS) [141,142] can be used. A different approach involves the use of a time-of-flight mass spectrometer which offers a much improved resolution and the determination of *m/z* with an accuracy of 0.1 m Da [143].

5.3. Detectors based on ultraviolet light

Theoretically, oxygenated organic compounds could also be determined without derivatization by a photoionization detector (PID). However, this method has not found a wide use in process analysis of wastewater.

Another universal detector allowing both qualitative and quantitative determinations is a vacuum ultraviolet detector (VUV) introduced in 2014. Detector VUV allows the measurement of absorption spectra in the 125–240 nm range [144,145]. All compounds absorption in this region have unique absorption spectra, especially low-molar-mass oxygenates, including esters, aldehydes, ketones and short-chain volatile fatty acids. So far, this technique was applied to study the compounds exhaled with human breath [146]. Additionally, GC-VUV has found use in the analysis of fatty acid methyl esters in edible oils [147], hydrocarbons in diesel fuels [148], pesticides [149], polychlorinated biphenyls [150] and investigation of isomers whose separation is difficult by other standard procedures [151]. Thus far, however, GC-VUV has not been used for the determination of O-VOCs in wastewater samples although due to its specific properties and the possibility of determination of oxygenated compounds at low concentrations it could be utilized for routine analyses of O-VOCs in samples of wastewater.

5.4. Other detectors

Electron capture detector (ECD), which is based on absorption of electrons by electrophilic molecules, is highly selective toward compounds having a high electron affinity, such as organochlorine compounds for which ECD is specific. ECD is selective to O-VOCs; however, this selectivity is insufficient for analysis of samples having a very complex matrix. The presence of water in extracts, even at trace levels, is also a problem due to a large ECD response to water. Therefore, analytes should be converted into derivatives containing atoms of chlorine, bromine [152] or fluorine [153] to obtain high sensitivity of detection. However, this approach has not found a widespread use in the analysis of wastewater. Theoretically, other selective detectors, such as a nitrogen-phosphorus detector (NPD), chemiluminescence detector (CLD), flame photometric detector (FPD) or a pulsed flame photometric detector (PFPD) and sulfur chemiluminescence detector (SCD), could be used for the determination of O-VOCs in wastewater samples after conversion of analytes into suitable derivatives. Nonetheless, despite their high sensitivity these detectors have not found use in routine analyses of wastewater samples.

Research is continuing on the development of novel types of GC detectors, such as an amperometric detector based on a silica sol-gel solid electrolyte. This detector is not selective toward hydrocarbons but it enables identification of compounds such as phenol or *p*-cresol at low concentrations. Thus, it could be successfully used for the analysis of O-VOCs in among others, petroleum refinery effluents which have a matrix rich in hydrocarbons [154].

The list of detectors along with their advantages and disadvantages is depicted in Fig. 4.

Table 5
List of internal standards used in quantitative analysis of O-VOCs.

Analytes	Internal standards
Alcohols	4-chloro-2-butanol [11],4-chlorophenol [11],1,1,3,3-tetramethoxypropane [29], N,N-diisopropylformamide [29]
Aldehydes	4-chloro-2-butanol [11], 3-chloro-2-butanone [11], 4-chlorophenol [11],acetone-d_6 [96]
Ketones	3-chloro-2-butanone [11], 4-chlorophenol [11],1,1,3,3-tetramethoxypropane [29], N,N-diisopropylformamide [29]
Esters	4-chloro-2-butanol [11]
Ethers	4-chloro-2-butanol [11], 1,1,3,3-tetramethoxypropane [29], N,N-diisopropylformamide [29], MTBE-d_{16} [44]
Phenols	4-chlorophenol [11], n-pentadecane [59,61], 1,1,3,3-tetramethoxypropane [29], N,N-diisopropylformamide [29], bisphenol-d_{16} [79], [$^{13}C_6$]-pentachlorophenol [82], phenol-d_5 [87], 2-chlorophenol-d_4 [87], 2,4-dimethylphenol-d_3 [87], 4-chloro-3-methylphenol-d_2 [87], 2,4-dichlorophenol-d_3 [87], 2-nitrophenol-d_4 [87], 2,4,6-trichlorophenol-d_2 [87], 4-nitrophenol-d_4 [87], 2,4-dinitrophenol-d_3 [87], pentachlorophenol-$^{13}C_6$ [87], 2-methyl-4,6-dinitrophenol-d_2 [87]
Carboxylic acids	2-ethylbutyric acid [37,90,93], margaric acid [51], heneicosanoic acid [52], anthracene-d_{10} [53], 2-chlorobenzoic acid [64,65], triphenylphosphate [85]

6. Quantitative analysis

Quantitative analysis of O-VOCs in wastewater samples is usually carried out by a calibration curve (external standard) method. However, when using some GC detectors, including mass spectrometer, the detector sensitivity can gradually deteriorate after a dozen or so analyses. Thus, to ensure reliability of the results, calibration should be often repeated which makes application of the developed procedures to routine analyses more challenging. The problem can be minimized by using the internal standard method which allows a much longer stability period of the procedure provided that the detector response changes to the same extent for analytes and the standard. An internal standard is selected on the basis of similarity of its physicochemical properties to those of analytes, such as boiling point, volatility, octanol-water partition coefficient, *etc.* It must also be absent from real samples, be separated on the chromatogram from analytes, be chemically stable and the detector response to the internal standard must be similar to those of analytes. Examples of internal standards selected for the determination of specific groups of compounds are compiled in Table 5. The internal standard method works best for complex, multistep procedures, since it corrects for analyte losses which take place at every step of an analytical procedure and also accounts for variations in sample volume during the injection step. Another approach is to use isotope dilution which is a version of internal standard method wherein the internal standard differs from the analyte solely in its isotope composition (deuterated derivatives of analytes are used most often). Using the internal standard method introduces an additional step to the analytical procedure (addition of an internal standard/standards to the sample) but current commercial automated equipment, such as an P&T extraction module, allow automatic addition of internal standards [106]. However, the internal standard method may not find application in the analyses of wastewater samples making use of universal detectors, such as FID, due to very complex matrix composition and the difficulty of selecting an internal standard which would not co-elute with the matrix components. Another common method of quantitative analysis is the standard addition method which involves addition to a sample known amounts of the analyte, followed by chromatographic analysis. This method has not found widespread use in the quantitative analysis of wastewater since it is tedious and time-consuming but it useful during the development of new analytical procedures because it allows a comparison of the agreement of the results obtained by the procedure being developed for real samples with other methods. In such a case the results obtained by the standard addition method are accepted as the expected value.

7. Oxygenated volatile organic compounds content in various kinds of wastewater

The presence of various groups of O-VOCs and their content is closely related to the kind of wastewater. Chemical plants typically generate high volumes of wastewater containing chemicals being the main products as well byproducts [43]. For example, wastewater from coke manufacturing plants contains considerable amounts of phenol whose concentration can be as high as 213.23 mg/L and large amounts of cresols [55,67,104]. These values significantly exceed the maximum allowed concentrations in industrial effluents discharged to the environment [20–24]. Phenols also commonly occur in the effluents from the petroleum industry, including refineries [68,155], effluents from the production of bitumens [11,12] and petrochemical wastewater [45,78,156]. The content of phenolic compounds is lower compared to coke wastewater but petroleum wastewater also contain other kinds of toxic O-VOCs, including alcohols, benzoic acids, acrylates, aldehydes, ketones and ethers at concentrations in the order of μg/mL [11,12,68] or μg/L in the case of MTBE [155]. On the other hand, wastewater from the paper industry contains mostly palmitic and stearic acids [51,52]. The same compounds are also present in wastewater from the production of antibiotics at concentrations equal to 80 μg/L and 95.8 μg/L for palmitic and stearic acid, respectively [56]. Oxygenated organic compounds, including phenols, benzoic acids, ketones and esters were detected in wastewater from the textile industry, with 2,6-di-*tert*-butyl-4-ethylphenol and butyltetramethylphenol having the highest concentrations (1.23 μg/L and 0.58 μg/L, respectively) [156] whereas the tannery wastewater contained alcohols, phenols, carboxylic acids and ketones at concentrations ranging from 0.01 to 0.03 μg/L [156,157].

Strongly contaminated industrial effluents have to undergo preliminary treatment before being sent to municipal or industrial wastewater treatment plants (WWTP) in order to meet the required specifications. The limits set pertain mostly to total parameters and not individual compounds; thus, the concentrations of particular analytes are relatively high. In WWTP industrial wastewater is combined with domestic wastewater, rain water and snowmelt, forming so-called municipal wastewater, wherein both typical compounds found in domestic wastewater and compounds originating from industrial wastewater can be identified. Common components of municipal and sanitary wastewater are phenols, whose concentrations can be as high as 433 μg/mL and carboxylic acids at concentrations up to 275 μg/mL [43,49,90,98]. In addition, municipal wastewater also contained MTBE at 25 μg/mL [158] and acetone at 0.62 μg/mL [43].

Examples of various kinds of wastewater along with concentrations of main O-VOC components are compiled in Table 6.

The majority of procedures described in this review pertain to the determination of carboxylic acids and phenols in wastewater. There are just a few reports dealing with the presence and concentrations of other O-VOC compounds in various types of wastewater. There exist no procedures that would allow a comprehensive evaluation of content of various kinds of O-VOCs in wastewater samples. The conclusions from reviews discussing investigations of advanced oxidation processes [159,160] used for chemical degradation of organic pollutants in industrial effluents reveal that due to the lack of recent procedures for detailed characterization of the effluents, the research is often based solely on changes in total parameters, *i.e.*, biochemical oxygen demand and chemical oxygen demand or total organic carbon. Dissemination of chromatographic procedures based on gas chromatographs commonly available in the laboratories of industrial facilities and sample preparation techniques not requiring special equipment should result in an increase in the scope and degree of detail of the results of analyses.

The described analytical methods can also be used for the determination of O-VOCs in other aqueous samples which have a very complex matrix. One of the examples are leachates from landfills which contain large amounts of toxic organic compounds including phenols [129,161,162], dioxanes [163] and carboxylic acids [164]. The methods could also be used for the determination of contaminations in different types of environmental samples, *i.e.* airport runoff water containing glycols [165], groundwater [166], rivers [167] and lakes located near factories [168] as well as for the determination of O-VOCs in process water for evaluating and controlling the process such as production of biogas [169].

8. Summary and outlook

Industrial, domestic and municipal wastewater contains a number of toxic volatile and semivolatile oxygenated organic compounds with widely varying concentrations in very complex matrices which makes their determination a serious challenge. Consequently, there is a continuing need to develop novel, effective procedures for the determination of low concentrations of O-VOCs in wastewater samples. A necessary step of each such procedure is extraction of analytes since direct analysis of such complex matrices can contaminate the GC system. Among the existing procedures for isolation of analytes from the aqueous matrix, headspace techniques are not the best choice despite full automation due to discrimination of compounds having a medium or low volatility. Classical LLE, which enables enrichment of both volatile and semivolatile analytes, is being gradually replaced by microextraction techniques as a result of consumption of large volumes of solvents and toxicity of some of them. At present, the technique most often used during the development of new procedures is DLLME due to its simplicity, short time and small volumes of organic solvents used. However, DLLME is difficult to automate which constitutes its main disadvantage. Literature search revealed several attempts at automation of DLLME, however, these designs are still at a development stage aiming at improvements in reproducibility, recovery and an increase in the number of samples processed. Hopefully, new and improved automated DLLME systems will become available in the near future. Other types of solvent microextraction, including SDME, HS-K-HFME, and LPME were also discussed in this review but all these modes are characterized by a long extraction time which is a significant disadvantage if a large number of samples has to be analyzed.

Among liquid-solid extraction techniques, similarly to LLE, the most common solid-phase extraction is being replaced by miniaturized versions which consume less sample and organic solvents. There is considerable interest in new stationary phases for SPME which is likely to be continued, especially in the area of polar sorbents which will have improved selectivity toward, for example, carboxylic acids.

In general, derivatization is not recommended in the analysis of wastewater due to complex sample matrix and a likelihood of unwanted chemical reactions. Furthermore, in most cases the derivatization procedure is complex and time-consuming. Nevertheless, the determination of some compounds, such as carboxylic acids with more than 9 carbon atoms or dicarboxylic acids at low concentrations in wastewater samples is very difficult. Therefore, in such cases a good approach is to use tetrabutylammonium reagents which results in formation of derivatives in the GC injection port. This approach is not labor-intensive and be automated which limits the activity of the analyst during the sample preparation step thus eliminating a number of errors and improving repeatability of results.

The availability of a variety of analytical procedures for the determination of individual groups of O-VOCs in wastewater samples requires performance of a number of time-consuming analyses. Consequently, the approach involving combination of gas chromatography with MS in electron impact ionization mode is becoming increasingly more popular. This approach allows not only quantitative analysis in the SIM mode but also identification of unknown analytes based on matching their mass spectra with those present in comprehensive spectral libraries. However, a complex matrix often precludes correct identification of analytes due to numerous co-elutions. An improved resolution can be obtained by using GC-TOF-MS but the high cost still hinders its widespread use. Therefore, chemometric models combined with GC—MS in the EI mode constitute a viable alternative, which allows obtaining a complete resolution of chromatographic peaks and pure mass spectra. With the comprehensive two-dimensional gas chromatography (GCxGC) instrumentation becoming more available, new procedures for the determination of O-VOCs making use of this technique are likely to appear. Orthogonality of the stationary phases used in the two dimensions should allow a simplification of sample preparation steps. In addition, the VUV detector has found increased use

Table 6
Compilation of O-VOCs occurring in various types of wastewater.

Matrix	Analytes	Method of determination	Concentration range	Compounds occurring at highest concentration	Ref.
Sanitary wastewater	phenols	SPME-GC-FID	1210–3480 μg/mL	*o*-ethylphenol (2750 μg/mL), 2,3-dimethylphenol (3480 μg/mL)	[88]
	phenols	SPME-GC-FID	1240–22,900 μg/mL	*o*-ethylphenol (1240 μg/mL), *p*-ethylphenol (22,900 μg/mL)	[90]
Municipal, animal farm and landfill wastewater	carboxylic acids	LLE-GC-MS	0.18–726 μg/mL	acetic acid (726 μg/mL), propionic acid (58.2 μg/mL)	[50]
	MTBE	DHS-GC-MS	3–25 μg/mL	methyl *tert*-butyl ether (3–25 μg/mL)	[44]
	acetone	DHS-GC-FID	0.25–0.62 μg/mL	acetone (0.25–0.62 μg/mL)	[43]
	phenols	SDE-GCxGC-ToF-MS	820–12,950 μg/mL	4-*tert*-octylphenol (10,780 μg/mL), 4-*tert*-nonylphenol (12,950 μg/mL)	[129]
	phenols	SPE-GC-MS	37.6–555 μg/mL	nonylphenol (555 μg/mL), octylphenol (182 μg/mL), bisphenol A (38.8 μg/mL)	[80]
Municipal wastewater	phenols	SPE-GC-MS	43–433 μg/L	phenol (433 μg/L), 2,4-dimethylphenol (240 μg/L)	[77]
	phenols	SPE-GC-MS	115–235 μg/L	phenol (235 μg/L)	[76]
	phenols	SPE-GC-MS	0.1–348 μg/L	2-*sec*-butylphenol (348 μg/L), phenol (34.6 μg/L), *m*-cresol (31.0 μg/L)	[83]
	phenols	MSPE-GC-MS	7.94–8.15 μg/L	phenol (8.15 μg/L), bisphenol A (7.94 μg/L)	[86]
	phenols, aldehydes	HS-SPME- GC-MS	0.5–151 μg/L	phenol (39.3 μg/L), *m*-cresol (151 μg/L)	[97]
	carboxylic acids	HS-SPME-GC-MS	0.065–102 μg/mL	acetic acid (102 μg/mL), propionic acid (19.6 μg/mL)	[98]
	carboxylic acids	HS-SPME-GC-NCI/MS (NH_3)	45–19,611 μg/L	acetic acid (19,611 μg/L), propionic acid (7812 μg/L), butyric acid (1338 μg/L)	[90]
	phenols	HS-SPME-GC-MS	0.073–2.1 ng/mL	*p*-cresol (2.1 ng/mL), 3,4-dimethylphenol (2.1 ng/mL)	[94]
	phenols	DI-SDME-GC-MS	–	*o*-cresol, 2,3,5-trimethylphenol	[59]
	phenols	LLE-GC-MS	0.046–0.245 μg/L	bisphenol A (0.245 μg/L), bisphenol F (0.057 μg/L)	[53]
	phenols	SPE-GC-MS/MS	0.04–0.16 μg/L	4-*tert*-octylphenol (0.16 μg/L), 4-n-nonylphenol (0.08 μg/L), 2,4-dimethylphenol (0.06 μg/L)	[82]
	MTBE	SPE-GC-MS	25–300 ng/L	methyl *tert*-butyl ether (25 -300 ng/L)	[158]
Paper mill process water	carboxylic acids	LLE-GC-MS	49–275 μg/mL	palmitic acid (49–275 μg/mL)	[51]
Paper-recycling process water	carboxylic acids	LLE-GC-MS	0.8–4.2 μg/mL	palmitic acid (4.2 μg/mL), stearic acid (3.4 μg/mL)	[52]
Wastewater from antibiotics manufacturing factory	carboxylic acids	LPME-GC-MS	35.2–95.8 μg/mL	palmitic acid (80 μg/mL), stearic acid (95.8 μg/mL)	[56]
Effluent from textile industry	phenols, benzoic acids, ketones and esters	HT-GC-MS	0.01–1.23 μg/L	2,6-di-*tert*-butyl-4-ethylphenol (1.23 μg/L) butyltetramethylphenol (0.34 μg/L)	[156]
Tannery effluent	phenols, carboxylic acids	SPE-GC-MS	–	*p*-cresol, 4-methylbenzoic acid	[157]
	phenols, carboxylic acids, alcohols, ketones	HT-GC-MS	0.01–0.03 μg/L	2,6-di-*tert*-butyl-4- methoxymethylphenol (0.03 μg/L), tetra-ethoxynonylphenol (0.03 μg/L)	[156]
Coking plant wastewater	phenols	HS-SPME-GC-FID	4.4–131.8 μg/mL	phenol (131.8 μg/mL), *p*-cresol (51.2 μg/mL)	[104]
	phenols	LPME-GC-FID	1.51–213.23 mg/L	phenol (213.23 mg/L), *o*-cresol (23.05 mg/L), *m*-cresol (59.11 mg/L)	[55]
	phenols	DLLME-GC-MS	0.4–13.4 μg/mL	phenol (13.4 μg/mL), *m*-cresol (9.4 μg/mL)	[67]
Petrochemical wastewater	aldehydes, ketones, alcohols, phenols	DHS-GC-MS	0.5–21.55 μg/mL	2-butenal (21.55 μg/mL), phenol (19.9 μg/mL)	[45]
	alcohols, ketones, phenols	SPE-GC-MS	–	phenol, 2-ethylhexyl alcohol, acetophenone	[78]
	alcohols, ketones, phenols, esters	HT-GC-MS	0.01–0.05 ng/mL	trimethylbenzoic acid (0.05 μg/mL), 2,5-dimethylbenzoic acid (0.03 μg/mL)	[156]
Effluents from production of petroleum bitumens	phenols, ketones, alcohols, aldehydes, esters, ethers	DHS-GC-MS	0.18–39.16 μg/mL	furfural (39.16 μg/mL), cyklohexanol (19.28 μg/mL), 2-pentanone (18.7 μg/mL), 2-butanol (14.75 μg/mL)	[12]
	phenols, ketones, alcohols, aldehydes, esters, ethers	DLLME-GC-MS	0.37–27.43 μg/mL	phenol (27.43 μg/mL), *m*-cresol (13.7 μg/mL), 1-propanol (24.88 μg/mL)	[11]
	carboxylic acids	DLLME-GC-MS	0.13–15.06 μg/mL	heptanoic acid (15.06 μg/mL), benzoic acid (7.52 μg/mL)	[64]
	carboxylic acids	USA-DLLME-GC-MS	0.33–43.3 μg/mL	benzoic acid (43.3μg/mL), octanoic acid (30.1 μg/mL), nonanoic acid (21.9 μg/mL)	[65]
Effluents from crude oil refinery	MTBE	HS-SPME/GC-MS	34.3–1877.5 ng/mL	methyl *tert*-butyl ether (34.3–1877.5 μg/mL)	[155]
	acrylates	DLLME-GC-FID	54.08–68.42 μg/mL	methyl acrylate (68.42 μg/mL), methyl methacrylate (64.72 μg/mL)	[68]

owing to the possibility of both qualitative and quantitative analysis. It is thus anticipated that this detector will also be utilized in the determination of O-VOCs in wastewater samples.

The kind of stationary phase plays a major role primarily in the analyses of carboxylic acids whose GC peaks tend to exhibit tailing; therefore, for this group of analytes it is recommended to a polar stationary phase: PEG modified with 2-nitro-terephthalic acid, which eliminates this problem. The remaining groups of O-VOC analytes can be separated on commercial GC columns with stationary phases of low and medium polarity. Research is continuing on the application of new materials as stationary phases that would provide high resolution of selected groups of chemical compounds [170].

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Appendix A. Supplementary data

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