

1 **Methods of assaying volatile oxygenated organic compounds in effluent samples** 2 **by gas chromatography – a review**

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

23
24 **Keywords:** derivatization, effluents, extraction, gas chromatography, sample preparation, volatile
25 organic compounds.

26
27 **Abbreviations:** ACN – acetone, AcCN – acetonitrile, [C₈MIM][PF₆] - 1-octyl-3-methylimidazolium
28 hexafluorophosphate, CAR – Carboxen, CTC – carbon tetrachloride, CW - Carbowax, DAI - Direct Injection
29 Analysis, DCM – Dichloromethane, DHS – Dynamic Headspace, DVB – Divinylbenzene, ECD - Electron
30 Capture Detector, EI - Electron Ionization, FID - Flame Ionization Detector, FPD -Flame Photometric
31 Detector, GC - Gas Chromatography, HF-LPME - Hollow Fiber-Protected Liquid Phase Microextraction,
32 HMDS – Hexamethyldisilazane, HS-K-HFME - Headspace Knotted Hollow Fiber Microextraction, HS-SDME

33 - *Headspace Single-Drop Microextraction, HS-SPME - Headspace Solid-Phase Microextraction, LLE -*
34 *Liquid-Liquid Extraction, LOD - Limit of Detection, LPME - Liquid Phase Microextraction, MS - Mass*
35 *Spectrometry, MSPE - Magnetic Solid Phase Extraction, MTBE - Methyl Tert-Butyl Ether, MTBSTFA - N-*
36 *methyl-N-(tert-butyldimethylsilyl)trifluoroacetamide, NPD – Nitrogen-Phosphorus Detector, O-FID –*
37 *Oxygen-Selective Flame Ionization Detection, O-VOC - Oxygenated Volatile Organic Compounds, PA –*
38 *Polyaniline, PEG - Polyethylene Glycol, PFBBr - Pentafluorobenzyl Bromide, PFBHA - O-(2,3,4,5,6-*
39 *pentafluorophenyl)methylhydroxylamine Hydrochloride, PID -Photoionization Detector, RT – Room*
40 *Temperature, SBSE - Stir Bar Sorptive Extraction, SDME - Single-Drop Microextraction, S-DVB -*
41 *Styrene/Divinylbenzene co-polymer, SHS - Static Headspace, SPE - Solid Phase Extraction, SPME - Solid-*
42 *Phase Microextraction, TBA-Br - Tetrabutylammonium Bromide, TBA-Cl - Tetrabutylammonium Chloride,*
43 *TBA-HSO₄ - Tetrabutylammonium hydrogensulfate, TD - Thermal Desorption, TFA - Trifluoroacetic Acid,*
44 *TMCS - Trimethylsilyl Chloride, TMSA - N,O-bis(trimethylsilyl) Acetamide, TMSDMC - Trimethylsilyl-N,N-*
45 *dimethylcarbamate, TMSIM - N-trimethylsilylimidazole, TOF-MS - Time-Of-Flight Mass Spectrometry, VFA*
46 *- Volatile Fatty Acids, VUV –Vacuum Ultraviolet Absorption.*

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85 1. Introduction

86 Volatile and semivolatile oxygenated organic compounds, which include the organic compounds
87 containing at least one oxygen atom, such as aldehydes, alcohols, phenols, esters, ethers, carboxylic
88 acids and their derivatives are characterized by high toxicity, carcinogenic and mutagenic properties and
89 malodorous character [1-5]. Oxygenated organic compounds commonly occur in municipal wastewater
90 [6-7] as well as in various kinds of industrial effluents, including refinery [8-14], textile [15], coke [16],
91 chemical [17] and food [18] industries. All types of effluents have a very complex matrix, which hinders
92 the determination of individual O-VOCs, whose concentrations can vary from high to trace. Moreover,
93 most O-VOCs are hydrophobic, highly reactive and low-molecular-weight compounds are highly volatile
94 [19].

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

102 Due to their negative impact on the environment, oxygenated organic compounds have recently
103 been an object of considerable interest among the scientists developing new methods of degradation of
104 O-VOCs in effluents and analytical procedures allowing their identification and determination at low
105 concentration levels which is illustrated by the number of relevant papers published between 2004 and
106 2019 (Figure 1). The importance of phenols in effluents is reflected by the number of papers on the
107 presence of O-VOCs in effluents, over 50% of which deals with phenolic compounds (Figure 2).

108 In order to assay the remaining groups of O-VOCs, the methods based on sensitive and selective
109 techniques are needed, including gas chromatography, high-performance liquid chromatography [15-
110 16,25-26], ion chromatography [27] or capillary electrophoresis [28]. Owing to physicochemical
111 properties of O-VOCs, gas chromatography is the preferred technique due to its lower cost of a single
112 analysis, very high resolution and the possibility of fine-tuning selectivity of a procedure through the
113 choice of a wealth of stationary phases as well as the availability of both universal and selective
114 detection methods. However, in order to ensure sufficient sensitivity of a procedure, a sample
115 preparation step providing isolation and enrichment of analytes is usually required.



116 The paper provides a review of the procedures for the determination of content of volatile and
117 semivolatile oxygenated organic compounds in samples of domestic, industrial and municipal
118 wastewater by means of gas chromatography. The available techniques at each step of the analytical
119 procedure are discussed along with the outlook and general problems resulting from the use of various
120 sample preparation and final determination methods. Applications of the discussed procedures to the
121 analysis of real effluents are also included.
122

123 2. Sample preparation methods

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

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

149 2.1 Gas extraction

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

152 2.1.1 Static headspace

153 The procedure of headspace analysis involves placing a sample in a vial which is then tightly
154 closed with a crimp or screw cap equipped with a septum. In addition to the sample, the vial must also
155 contain some headspace. The sample is then thermostatted at a specific temperature until
156 thermodynamic equilibrium between the sample and the headspace is reached. Next, the headspace is
157 sampled using a gas-tight syringe (which is also thermostatted) and injected the GC injection port. The
158 time and temperature of equilibration depend on the rate of diffusion of volatile sample components. As
159 a rule, these parameters are determined experimentally during the development of the procedure. Fully
160 automated autosamplers for SHS are commercially available. A schematic diagram of the SHS procedure
161 is shown in [Figure S1](#). The use of static headspace analysis for the determination of O-VOC content has a



162 number of advantages, including universal applicability, simplicity and the possibility of automation,
163 which is important in the case of a large number of samples. Moreover, in comparison with conventional
164 extraction techniques, SHS does not cause losses of the most volatile organic compounds which are
165 responsible for malodorous properties of wastewater due to their low odor threshold of O-VOCs [33-36].
166 On the other hand, a serious disadvantage of SHS is its insufficient sensitivity for compounds with higher
167 boiling points and the problems related to variable composition of matrices of wastewaters [37-38]. As a
168 result of low sensitivity of SHS for higher boiling O-VOCs, which are commonly present in various kinds of
169 wastewater, the technique is rarely used in the analytics of effluents [37].

170 **2.1.2 Dynamic Headspace**

171 The problem of relatively low sensitivity of SHS was partially eliminated by using dynamic
172 headspace analysis (DHS), which is often called purge-and-trap, in which analyte enrichment is achieved
173 by a continuous shift of the equilibrium toward headspace [39]. In this way, the detection limit for the
174 same compounds can be lowered by as much as three orders of magnitude compared to SHS. The DHS
175 procedure involves transfer of analytes from the aqueous phase to the headspace by purging the sample
176 with an inert gas followed by trapping volatile components in a trap (using sorption or cryofocusing). The
177 purge can take place in a tightly closed vial equipped with a stopper with a septum through which a
178 purge gas inlet is introduced. Alternatively, U-tube shaped concentrators equipped with sintered glass
179 (for dispersion of the gas) just below the sample can be used. The purge gas outlet is typically made of a
180 stainless steel or fused silica capillary. The purge gas (usually helium or hydrogen, less often nitrogen)
181 flowing through the sample sweeps out volatile compounds and transfers them to a trap packed with a
182 sorbent. A different approach involves the use of a short length of an empty deactivated capillary
183 column made of fused silica and cooled with vapors of liquid nitrogen. The latter approach eliminates the
184 problem of sorbent bed breakthrough and ensures narrower bands of analytes during the desorption
185 step. The limitations of DHS include more expensive equipment, the use of liquid nitrogen and the need
186 for drying the gas to remove water vapor carried from the sample. Volatile chemical compounds are
187 then released from the trap by thermal desorption and introduced into the GC injection port. A
188 schematic diagram of the procedure is shown in Figure S2. The main shortcomings of DHS other than the
189 ones mentioned above include a relatively long time of extraction (as a rule longer than 10 min) and the
190 possibility of analyte losses due to sorbent breakthrough if the extraction time is too long and/or the
191 flow rate of the purge gas is too high. Additionally, as was the case with SHS, only volatile compounds
192 with boiling points up to about 150 °C can be extracted [40]. Another limitation of DHS involves the
193 problem with extraction of samples containing surfactants which require addition of a defoamer, such as
194 1-tetradecanol [41-42]. An important element of any DHS system is a sorbent trap which allows isolation
195 of analytes from the gaseous phase. This step is necessary since volatile compounds in the gaseous
196 phase occur at high concentrations.

197 **2.1.2.1 Enrichment/trapping of oxygenated volatile organic compounds for dynamic headspace**

198 To extract O-VOCs from wastewater samples commercially available sorbents characterized by a
199 high specific surface area, such as carbon molecular sieves Carbosieve S-III and S-II, Carboxen (300 –
200 1000 m²/g) [43], a porous polymer Tenax TA based on 2,6-diphenyl-p-phenylene oxide (specific surface
201 area 18 m²/g [12,44-45] or a composite material containing 70% Tenax TA and 30% graphite carbon

202 (Tenax GR), are predominantly used. Carbosieve S-II is recommended only for the sorption of most
203 volatile compounds whereas the most universal sorbent which has found wide applicability in the
204 analysis of wastewater is Tenax TA [12,44-45]. Another approach which is commercially available is the
205 use of multibed sorbent traps in which the weakest sorbent retaining only heavier O-VOCs is the first in
206 series followed by other sorbents ordered by increasing sorbent strength. Good results of extraction of
207 O-VOCs can also be obtained by using other sorbents, such as a granular activated carbon obtained from
208 macadamia nutshells [46]. However, the alternative sorbents were only tested with standard mixtures.
209 The extraction is also affected by the time and temperature of purge and desorption of analytes.
210 Extraction conditions should be selected depending on the kind and properties of analytes. Elution of
211 analytes from sorbent traps should be carried out countercurrently to the extraction step.

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

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

232 2.2 Liquid extraction

233 2.2.1 "Conventional" Liquid-Liquid Extraction

234 Classical liquid-liquid extraction (LLE) is still very much in use in analytical procedures for the
235 analysis of water and wastewater due to its simplicity and lack of complex equipment. The extraction
236 procedure involves placing a sample in a separatory funnel to which an extraction solvent immiscible
237 with water is then added. Next, the separatory funnel is shaken and left in a stand for the phase
238 separation to take place. The extraction is usually performed repeatedly to transfer a maximum amount
239 of the analytes from the aqueous phase to the organic phase. The procedure is depicted in Figure S3. LLE
240 is time-consuming and labor-intensive which limits its widespread use. Other limitations include the
241 possibility of emulsion formation and large volumes of very pure organic solvents used. Furthermore, the



242 enrichment factor for O-VOC analytes when using LLE is considerably smaller compared with other
243 sample preparation techniques available [47]. The most important factor affecting the extraction yield is
244 the selection of an appropriate solvent. The solvents used most commonly for the extraction of O-VOCs
245 are volatile so that they are eluted before analytes, *i.e.*, diethyl ether [48], dichloromethane (DCM) [49]
246 or methyl *tert*-butyl ether (MTBE) [49-52]. Several papers mention problems with quantitative extraction
247 of acetic and propionic acid by diethyl ether [48] whereas good results were obtained with MTBE for
248 which the extraction yield was about five times higher than for DCM [49]. Bisphenol A and B were best
249 extracted with chloroform [53]. Extracting solvents with high boiling points could co-elute with analytes
250 which is particularly troublesome when universal GC detectors, such as FID, are used. The extraction
251 efficiency can be improved by decreasing the solubility of O-VOCs in water by using the salting out effect
252 (sometimes also used in SHS and DHS) [53] and/or by changing the pH of samples. However, despite such
253 approaches, the detection limits of O-VOCs are often still too high. In addition, salting-out effect might
254 not be so effective as it can be expected. Sometimes, the solubility is even increasing or minor changes
255 are reported after the salt addition.

256

257 2.2.2 Liquid-Liquid Microextraction techniques

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

266 2.2.2.1 Single-Drop Microextraction

267 One mode of solvent microextraction is single-drop microextraction (SDME), which requires only
268 0.3-3 μL of the extractant. The sample is placed in a tightly closed vial with a cap equipped with a
269 septum. The extractant is drawn into a GC microsyringe, and the tip of the needle of the microsyringe is
270 placed either inside the sample. The extractant is then extruded from the microsyringe forming a drop at
271 the tip of the needle. The extraction is typically performed for 5 – 30 min. Following extraction, the drop
272 is withdrawn into the microsyringe and the extract is injected into the GC [57]. A schematic diagram of
273 the procedure is shown in Figure S3. Advantages of SDME include a high enrichment factor (mostly due
274 to the phase ratio), simplicity and the possibility of automation [58]. The technique was successfully used
275 in the determination of phenols in municipal wastewater with low detection limits (0.45 – 1.5 ng/mL)
276 and a good reproducibility of results [59]. However, a significant problem in SDME is drop instability and
277 a limited drop volume as well as the problem of solvent volatility. The problem of drop instability in
278 SDME was partially solved by placing the drop in the headspace above the sample (Figure S3) (headspace
279 single-drop microextraction, HS-SDME) [60] and the use of mixtures of solvents with different densities,
280 such as chloroform and 1-octanol (1:1 v/v), which improved the stability of the hanging drop [61] and, to
281 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 (Figure 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 $\mu\text{g/L}$ [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 (Figure 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 $\mu\text{g/mL}$ were obtained for all the analytes except for acetaldehyde for which LOD was 2.06 $\mu\text{g/mL}$ [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 Figure 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-



321 vinylpyrrolidone (DVB/N-VP) [82-84], which have also been successfully used to isolate fatty, benzoic and
322 dicarboxylic acids [84]. For isolation of carboxylic, benzoic and hydroxybenzoic acids, a mixture of
323 commercial SPE sorbents containing C18 and ethyl vinyl benzene-divinyl benzene polymer was used
324 (EVB-DVB/C18) (1:1) [85]. Compared to classical LLE extraction, SPE provides greater enrichment factors;
325 however, its main disadvantages are the need for large sample volumes (100 – 500 mL) [76-77,82] and,
326 sometimes, the use of toxic organic solvents as well as a long extraction time which can exceed 2 h [82].
327 In standard SPE assemblies, the eluent flow is driven by reduced pressure, which entails the risk of losses
328 of most volatile analytes. In order to shorten the extraction time to 20 min and reduce sample volume to
329 10 mL, magnetic solid phase extraction (MSPE) can be used. In this technique, either the sorbents have
330 magnetic properties or they are immobilized on magnetic cores. Sorbent particles are added to a
331 wastewater sample and left in it until the analytes are adsorbed. Next, the sorbent particles are
332 attracted by a magnet while the sample matrix is decanted. This is followed by analyte desorption using
333 an appropriate organic solvent. The extract is then analyzed by GC. The MSPE procedure is depicted in
334 Figure S4. Just 40 mg of Fe₃O₄@C@polyaniline magnetic microspheres were needed to obtain high
335 recoveries (85.3–110.6%) and low LOD values (0.89 – 7.58 ng/mL) for phenols extracted from 10 mL of
336 wastewater samples [86].

337 2.3.2 Stir Bar Sorptive Extraction

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

347 2.3.3 Solid Phase Microextraction

348 Solid phase microextraction (SPME) is a miniaturized version of SPE. In this technique, analytes
349 are sorbed onto a layer of extracting phase coated onto a fused silica fiber which is placed inside a
350 needle held in a holder. After introduction of the needle into a sample the fiber is exposed to the
351 sample. Next, the fiber is retracted into the needle which is then inserted into the GC injection port for
352 thermal desorption of analytes. SPME can be performed in the direct immersion mode (DI-SPME) in
353 which the fiber is immersed directly into an aqueous sample or in the headspace mode (HS-SPME) where
354 in the fiber is placed in the headspace above the sample (Figure S6). The latter mode is more favorable
355 for analysis of wastewater as it protects the fiber from mechanical damage by solids present in the
356 sample and prevents extraction of analytes of low volatility or nonvolatile which could contaminate both
357 the fiber and the chromatographic system [88]. However, DI mode allows the determination of the less
358 volatile O-VOCs in wastewaters samples, which cannot be determined using the HS mode. Regardless of
359 SPME mode, the key role in extraction is played by the kind of sorbent and shape of the fiber [89]. A



360 number of fibers of varying polarities are now available commercially for extraction of various groups of
361 chemical compounds. In the determination of volatile fatty acids numerous problems are posed by short-
362 chain acids, *i.e.*, acetic and propionic acid [90-92]. Among five fibers, including polyacrylate,
363 Carbowax/Divinylbenzene (CAR-DVB), Polydimethylsiloxane/Divinylbenzene(PDMS-DVB),
364 Polydimethylsiloxane/Carboxen/Divinylbenzene (PDMS-CAR-DVB) and Polydimethylsiloxane-Carboxen
365 (PDMS-CAR), only PDMS-CAR sorbent provided satisfactory extraction of C₂ and C₃ acids [93]. The same
366 sorbent was highly effective in the extraction of phenols [94]. In the determination of bisphenol A (BPA),
367 *tert*-nonylphenol and formaldehyde in samples of wastewater the highest extraction efficiency was
368 achieved using PDMS/DVB; however, the use of such a fiber can introduce errors due to the presence of
369 BPA in epoxy resin that is used to attach the fiber to the holder. A decrease in the amount of released
370 BPA is observed after multiple extractions which results in the aging of the fiber and deterioration of
371 extraction efficiency. The fiber coated with PDMS/DVB is highly effective for about 100 extractions.
372 Consequently, fibers coated with polyacrylate are recommended for extraction of BPA from wastewater
373 [95-96]. For carboxylic acids with a longer chain and for aldehydes and volatile phenols the best results
374 were obtained when using PDMS-CAR-DVB [90,97]. Other investigations demonstrated improved
375 extraction efficiency for polyethylene glycol as a fiber coating. Selectivity of sorption of individual
376 analytes present in the headspace, in addition to elimination of analytical signal of undetermined VOCs
377 in the chromatogram, also affects the sorption capacity of the fiber, since only the analytes of interest
378 will be accumulated. Compared to the fiber coated with PDMS-CAR, extraction using PEG provided lower
379 detection limits for the majority of carboxylic acids (C₂ -C₇) [98] while LOD values for the same analytes
380 extracted with CAR-DVB were lower by a factor of 300 compared with direct aqueous injection. Only
381 extraction of formic acid yielded a twofold increase in sensitivity compared to DAI [99]. Similar results
382 were obtained in other investigations [88]. The use of fibers coated with polymeric materials has a
383 number of disadvantages, including relatively low maximum desorption temperatures, which generally
384 ranges from 240 to 280°C, instability and too low polarity which limits their usefulness for some
385 compounds. High thermal stability is required for the thermal desorption step. Insufficient desorption
386 temperature will cause peak broadening and tailing as well as discrimination of higher boiling analytes.

387 **2.3.3.1 Developments in Solid-Phase Microextraction for oxygenated volatile organic** 388 **compounds analytics**

389 Therefore, a number of novel fiber coatings have recently appeared, such as carbon nanotubes,
390 including multiwalled carbon nanotubes [100-102], ionic liquids [103] or based on calixarenes, *i.e.* amide
391 bridged-C[4]/OH-TSO(25,27-dihydroxy-26,28-oxy(2',7'-dioxo-3',6'-diazaoctyl)oxy-*p-tert*-
392 butylcalix[4]arene/hydroxy-terminated silicone oil) [104], which eliminate the problems mentioned
393 above and can be successfully used for the determination of O-VOCs in wastewater samples. An increase
394 in volume of the extracting phase in SPME results in lowering detection limits and extending a linear
395 range; however, until now the increase in the amount of sorbent required modification not only of the
396 SPME apparatus but also of the thermal desorption module. The problem has recently been eliminated
397 by the introduction of the PAL SPME Arrow system, which contains a stainless steel wire coated with a
398 greater amount of a sorbent compared to a typical SPME fiber and ending with the arrow-shaped tip.
399 This arrangement ensures compatibility with the commercially available thermal desorbers and liners. In



400 addition, the presence of a steel wire provides a much improved fiber stability [105-106]. The SPME
401 Arrow system has not yet been used for extraction of O-VOCs from wastewater samples. Another
402 important parameter is extraction temperature. An increase in extraction temperature can accelerate
403 adsorption of analytes on the fiber but too high a temperature can result in desorption and losses of the
404 most volatile sample components. Consequently, the procedures for the determination of volatile fatty
405 acids made use of mostly room temperature and time ranging from 15 to 60 min [88-90,93,98-99]
406 whereas extraction of phenols and aldehydes was carried out at substantially higher temperatures (from
407 50 to 100°C) [94-97,102,104]. SPME technique requires splitless injection using narrow glass liners in
408 order to create high carrier gas velocity around the fiber which allows rapid removal of desorbed
409 analytes from the injection port [107]. However, some papers report successful use of the split injection
410 [104]. So far, no formation of O-VOCs artifacts on the SPME fibers have been reported in the literature
411 although such problems are known for other groups of volatile organic compounds, *i.e.*, organosulfur
412 compounds. This phenomenon should be taken into consideration in the investigations of more reactive
413 O-VOCs.

414 A compilation of solid-phase extraction procedures used for the determination of O-VOCs is
415 shown in Table3.

416 3. Derivatization

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

428 Derivatization methods have been described in a number of papers [47,110-114]. The most common
429 reagents used for derivatization of O-VOCs, which block polar groups being proton donors (*i.e.*, -OH and
430 -COOH), include alkylsilanes, such as N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) [51-52,79,83,85-
431 86] N-trimethylsilylimidazole (TMSIM), trimethylchlorosilane (TMCS) [51-52], N,O-bis(trimethylsilyl)
432 acetamide (TMSA) [53], hexamethyldisilazane (HMDS) [84] and N-methyl-N-(*tert*-
433 butyldimethylsilyl)trifluoroacetamide (MTBSTFA) [76-77,87]. They allow introduction of the trimethylsilyl
434 group (TMS) to analyte molecules thus increasing volatility of the analytes, improving separation of
435 isomers and enhancing sensitivity of detection when using a mass spectrometer operated in the positive
436 chemical ionization mode. However, despite numerous advantages, silyl derivatives are very unstable
437 and the analysis must be carried out within 12-24 hours, which limits the use of these reagents in routine
438 determinations of a large number of samples [51].



439 Carboxylic acids can undergo direct 100% reaction yield in 2-3 min is diazomethane; however, it is
440 not recommended due to its irritating, carcinogenic and explosive properties [47,113]. Consequently,
441 diazomethane is often replaced with less hazardous reagents, such as pentafluorobenzyl bromide
442 (PFBBr), which provides much lower yields and the reaction takes several hours [113,115]. The method
443 of derivatization of carboxylic acids that is not time consuming and enables automation is the formation
444 of ion pairs through the reaction of carboxyl or hydroxyl groups with tetraalkylammonium salts in the
445 sample solution. The ion pairs formed after being injected into the hot (>280°C) GC injection port are
446 converted into alkyl (often butyl) esters. The most common ion pairing reagents include
447 tetrabutylammonium hydrogensulfate (TBA-HSO₄) [56,64], tetrabutylammonium chloride (TBA-Cl) and
448 tetrabutylammonium bromide (TBA-Br) [56,59,61]. The butyl esters formed have greater mass-to-charge
449 (m/z) ratio compared to methyl esters which improves selectivity in GC-MS analysis [56,68,116]. Another
450 interesting approach is the procedure based on the use of inexpensive and simple to synthesize deep
451 eutectic solvent composed of choline chloride and 4-methyl phenol in 1:2 molar ratio (ChCh:4MPh1:2)
452 for both the extraction of the analytes and their ion pair derivatization [65]. Another class of reagents
453 allowing derivatization of carboxylic acids to alkyl esters in aqueous are alkyl chloroformates. The alkyl
454 esters formed can be readily extracted into nontoxic organic solvents [117].

455 **4. Separation proces - Stationary phases**

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

462

463 **4.1 Polydimethylsiloxane based stationary phases**

464 For direct injection of aqueous solutions without prior removal of the water matrix, a polar
465 stationary phase, such as a wax-based sol-gel phase [118] or, alternatively, a stationary phase of low
466 polarity, *i.e.*, polydimethylsiloxane or 5% phenyl 95% polydimethylsiloxane should be used. This
467 stationary phase practically do not interact with water so they are not damaged by aqueous samples
468 [119]. Another option is to use apolar-deactivated guard column, which enables complete evaporation of
469 water prior to introduction of analytes onto the column [119-120].

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

475

476 **4.2 Polyethylene glycol based stationary phases**

477 Some carboxylic acids ($C_2 - C_8$) are sufficiently volatile and thermally stable to be determined by GC
478 without derivatization. However, their high polarity and ability to form hydrogen bonds precludes
479 obtaining symmetrical peaks with most popular stationary phases of low and medium polarity.
480 Consequently, polar stationary phases based on polyethylene glycol (PEG) are recommended for the
481 separation of volatile fatty acids [120-124]. Alkane monocarboxylic acids tend to adsorb in the injection
482 port or on the column, therefore, many reports recommend the use of PEG modified with 2-
483 nitroterephthalic acid (called free fatty acid phase – FFAP), which deactivates its basic sites [43,49,88-
484 90,93,98-99,103,125]. FFAP was also successfully used for the separation of phenols [60]. Another
485 interesting approach is to connect several capillary columns in series, including a column with a polar
486 stationary phase connected to a short deactivated column, followed by a PDMS column and another
487 deactivated column. The use of such a sequence allows complete separation of carboxylic acids $C_2- C_8$.
488 Furthermore, using a polar stationary phase in the first column resulted in obtaining narrow and
489 symmetrical peaks [126]. A significant disadvantage of polar stationary phases is their relatively low
490 maximum operating temperature ($<260^\circ\text{C}$) which makes them unsuitable for the analysis of higher
491 boiling compounds, such as long-chain carboxylic acids or dicarboxylic acids [127].

492 The most recent (and most expensive) approach is the coupling of time-of-flight mass
493 spectrometer (TOF-MS) with comprehensive two-dimensional gas chromatography (GCxGC). Two-
494 dimensional GC separation of analytes greatly improves peak capacity and enables a very effective
495 separation. Typically, analytes are separated on a column with the stationary phase of a low polarity in
496 the first dimension, followed by the separation of each fraction on a more polar stationary phase in the
497 second dimension. However, a reverse order of polarity of the stationary phases is sometimes used. The
498 technique GC x GC-ToF-MS was used to determine isomers of nonylphenol. This approach allowed to
499 minimize co-elution of analytes and to identify a larger number of isomers which could not be separated
500 in the SIM mode by GC-MS [128-129].

501

502 **4.3 Ionic liquids**

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

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



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

520 **5. Detection**

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

525

526 **5.1 Oxygenate selective Flame Ionization Detector**

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

538

539 **5.2 Mass Spectrometry**

540 At present, a mass spectrometer is the detector most commonly used in the determination of
541 volatile oxygenated organic compounds in wastewater. When using selected ion monitoring (SIM) mode,
542 the MS can selectively detect analytes in the presence of co-eluting matrix components. Moreover, when
543 used with an analyte isolation and enrichment procedure, GC-MS allows determination of analytes at a
544 $\mu\text{g/L}$ or even ng/L level [51-53,56,62,85]. A major advantage of a mass spectrometer over the other GC
545 detectors is its ability to identify unknown compounds in the SCAN mode based on comparison of the
546 obtained spectra with vast mass spectral libraries when the electron ionization (EI) is used. On the other
547 hand, in the SIM mode identification of analytes is carried out by comparison of their retention times
548 with those of standards, taking a confidence interval of $\pm 0.2\%$ t_R [min], as well as on the basis of
549 selected characteristic values of mass-to-charge ratios and comparison of their intensities. As a rule,
550 several characteristic ions are selected for each compound in a given interval of retention time. It should
551 be noted, however, that the detector sensitivity decreases with an increase in number of monitored
552 ions. Therefore, a reasonable approach is to select two characteristic mass-to-charge values, of which
553 one is used for integration of the peak while the other is used to confirm the peak identity based on the
554 ratio of intensities with an assumed confidence interval of 15 to 30 %. Such an approach constitutes a
555 sufficient confirmation of peak identification while allowing the determination of analytes at suitably low
556 concentration levels [11-12].



557 The second type of ionization commonly used in a mass spectrometer is positive or negative
558 chemical ionization (CI), which does not ensure such a high reproducibility of ionization as was the case
559 with EI, which results in the absence of commercially available mass spectral libraries and identification
560 is carried out on the basis of an intense molecular ion which is possible due to soft ionization. The
561 studies in which two modes of ionization, EI and positive CI in which ammonia was used as a reagent gas,
562 were compared revealed only slight differences in reproducibility of the results obtained in the SIM
563 mode for 22 carboxylic acids, LOD values lower by a factor of *ca.* 25 and a wider linear range for EI-MS
564 [85]. A comparison of positive (reaction gas CH₄) and negative (reaction gas NH₃) chemical ionization in
565 the determination of volatile fatty acids demonstrated lower detection limits when negative chemical
566 ionization was used [93].

567 A complex matrix composition of wastewater sample often precludes direct identification due to
568 co-elution of many analytes. To accomplish peak resolution and obtain pure spectra, chemometric
569 models such as Parallel Factorial Analysis (PARAFAC) [140] or Multivariate Curve Resolution Alternating
570 Least Squares (MCR-ALS) [141-142] can be used. A different approach involves the use of a time-of-flight
571 mass spectrometer which offers a much improved resolution and the determination of *m/z* with an
572 accuracy of 0.1 mDa [143].

573

574 **5.3 Detectors based on ultraviolet light**

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

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

589

590 **5.2 Other detectors**

591 Electron capture detector (ECD), which is based on absorption of electrons by electrophilic
592 molecules, is highly selective toward compounds having a high electron affinity, such as organochlorine
593 compounds for which ECD is specific. ECD is selective to O-VOCs; however, this selectivity is insufficient
594 for analysis of samples having a very complex matrix. The presence of water in extracts, even at trace
595 levels, is also a problem due to a large ECD response to water. Therefore, analytes should be converted
596 into derivatives containing atoms of chlorine, bromine [152] or fluorine [153] to obtain high sensitivity of
597 detection. However, this approach has not found a widespread use in the analysis of wastewater.



598 Theoretically, other selective detectors, such as a nitrogen-phosphorus detector (NPD),
599 chemiluminescence detector (CLD), flame photometric detector (FPD) or apulsed flame photometric
600 detector (PFPD) and sulfur chemiluminescence detector (SCD), could be used for the determination of O-
601 VOCs in wastewater samples after conversion of analytes into suitable derivatives. Nonetheless, despite
602 their high sensitivity these detectors have not found use in routine analyses of wastewater samples.

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

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

609 **6. Quantitative analysis**

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



637 real samples with other methods. In such a case the results obtained by the standard addition method
638 are accepted as the expected value.

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

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

658 Strongly contaminated industrial effluents have to undergo preliminary treatment before being
659 sent to municipal or industrial wastewater treatment plants (WWTP) in order to meet the required
660 specifications. The limits set pertain mostly to total parameters and not individual compounds; thus, the
661 concentrations of particular analytes are relatively high. In WWTP industrial wastewater is combined
662 with domestic wastewater, rain water and snowmelt, forming so-called municipal wastewater, wherein
663 both typical compounds found in domestic wastewater and compounds originating from industrial
664 wastewater can be identified. Common components of municipal and sanitary wastewater are phenols,
665 whose concentrations can be as high as 433 $\mu\text{g/mL}$ and carboxylic acids at concentrations up to 275
666 $\mu\text{g/mL}$ [43,49,90,98]. In addition, municipal wastewater also contained MTBE at 25 $\mu\text{g/mL}$ [158] and
667 acetone at 0.62 $\mu\text{g/mL}$ [43].

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

670 The majority of procedures described in this review pertains to the determination of carboxylic acids
671 and phenols in wastewater. There are just a few reports dealing with the presence and concentrations of
672 other O-VOC compounds in various types of wastewater. There exist no procedures that would allow a
673 comprehensive evaluation of content of various kinds of O-VOCs in wastewater samples. The conclusions
674 from reviews discussing investigations of advanced oxidation processes [159-160] used for chemical



675 degradation of organic pollutants in industrial effluents reveal that due to the lack of recent procedures
676 for detailed characterization of the effluents, the research is often based solely on changes in total
677 parameters, *i.e.*, biochemical oxygen demand and chemical oxygen demand or total organic carbon.
678 Dissemination of chromatographic procedures based on gas chromatographs commonly available in the
679 laboratories of industrial facilities and sample preparation techniques not requiring special equipment
680 should result in an increase in the scope and degree of detail of the results of analyses.

681 The described analytical methods can also be used for the determination of O-VOCs in other
682 aqueous samples which have a very complex matrix. One of the examples is leachates from landfills which
683 contains large amounts of toxic organic compounds including phenols [129,161-162], dioxanes [163] and
684 carboxylic acids [164]. The methods could also be used for the determination of contaminations in
685 different types of environmental samples, *i.e.* airport runoff water containing glycols [165], groundwater
686 [166], rivers [167] and lakes located near factories [168] as well as for the determination of O-VOCs in
687 process water for evaluating and controlling the process such as production of biogas [169].

688 8. Summary and outlook

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

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

712 In general, derivatization is not recommended in the analysis of wastewater due to complex sample
713 matrix and a likelihood of unwanted chemical reactions. Furthermore, in most cases the derivatization



714 procedure is complex and time-consuming. Nevertheless, the determination of some compounds, such
715 as carboxylic acids with more than 9 carbon atoms or dicarboxylic acids at low concentrations in
716 wastewater samples is very difficult. Therefore, in such cases a good approach is to use
717 tetrabutylammonium reagents which results in formation of derivatives in the GC injection port. This
718 approach is not labor-intensive and be automated which limits the activity of the analyst during the
719 sample preparation step thus eliminating a number of errors and improving repeatability of results.

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

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

742

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1163 **Tables**

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1165 **Table1** 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]

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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 / 4 µL	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 ₈ MIM][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 / chlorobenz en 2:1 v/v (ACN - disperser)	-	5 mL / 15 µL	2 min	MS	-	< 9.1	68 - 104	[67]
	Acrylates	Chlorobenz en (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 mL / 300 µL	60 s	MS	6.9-1120 µg/L	< 6.4	69 - 126	[64]
	Carboxylic acids	ChCl:4MPH (1:2 molar)	ChCl:4MPH (1:2 molar ratio)	9 mL / 500 µL	10 min	MS	1.7–8.3 µg/L	< 6.7	82 - 106	[65]

		ratio (MeOH- disperser)								
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1170 **Table 3** Compilation of various types of solid-phase extraction procedures in the determination of O-VOCs in wastewater
1171 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]
	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]
HS-SPME	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	270°C / -	-	MS	0.001 –	< 16.2	-	[94]

				min				0.04 µg/L			
	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]

1172 a) Solvent used for elution of fraction of interest,

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1188 **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
Intermediate polarity	5% Phenyl 95% dimethylpolysiloxane	phenols, aldehydes, ketones, alcohols
	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

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1190 **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], <i>n</i> -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]

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1193 **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	<i>o</i> -ethylphenol (2750 µg/mL), 2,3-dimethylphenol (3480 µg/mL)	[88]
	phenols	SPME-GC-FID	1240 – 22900 µg/mL	<i>o</i> -ethylphenol (1240 µg/mL), <i>p</i> -ethylphenol (22900 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]
Municipal wastewater	MTBE	DHS-GC-MS	3 – 25 µg/mL	methyl <i>tert</i> -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	820-12950 µg/mL	4- <i>tert</i> -octylphenol (10780 µg/mL), 4- <i>tert</i> -nonylphenol (12950 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]
	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- <i>sec</i> -butylphenol (348 µg/L), phenol (34.6 µg/L), <i>m</i> -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), <i>m</i> -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)	45-19611 µg/L	acetic acid (19611 µg/L), propionic acid (7812 µg/L), butyric acid (1338 µg/L)	[90]
	phenols	HS-SPME-GC-MS	0.073-2.1 ng/mL	<i>p</i> -cresol (2.1 ng/mL), 3,4-dimethylphenol (2.1 ng/mL)	[94]
	phenols	DI-SDME-GC-MS	-	<i>o</i> -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- <i>tert</i> -octylphenol (0.16 µg/L), 4- <i>n</i> -nonylphenol (0.08 µg/L), 2,4-dimethylphenol (0.06 µg/L)	[82]
MTBE	SPE-GC-MS	25 -300 ng/L	methyl <i>tert</i> -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- <i>tert</i> -butyl-4- ethylphenol (1.23 µg/L) butyltetramethylphenol (0.34 µg/L)	[156]
Tannery effluent	phenols, carboxylic acids	SPE-GC-MS	-	<i>p</i> -cresol, 4-methylbenzoic acid	[157]
	phenols,	HT-GC-MS	0.01 – 0.03 µg/L	2,6-di- <i>tert</i> -butyl-4- methoxymethylphenol	[156]

	carboxylic acids, alcohols, ketones			(0.03 µg/L), tetra-ethoxynonylphenol (0.03 µg/L)	
Coking plant wastewater	phenols	HS-SPME-GC-FID	4.4 – 131.8 µg/mL	phenol (131.8 µg/mL), <i>p</i> -cresol (51.2 µg/mL)	[104]
	phenols	LPME-GC-FID	1.51-213.23 mg/L	phenol (213.23 mg/L), <i>o</i> -cresol (23.05 mg/L), <i>m</i> -cresol (59.11 mg/L)	[55]
	phenols	DLLME-GC-MS	0.4 – 13.4 µg/mL	phenol (13.4 µg/mL), <i>m</i> -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), <i>m</i> -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 to 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 <i>tert</i> -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]

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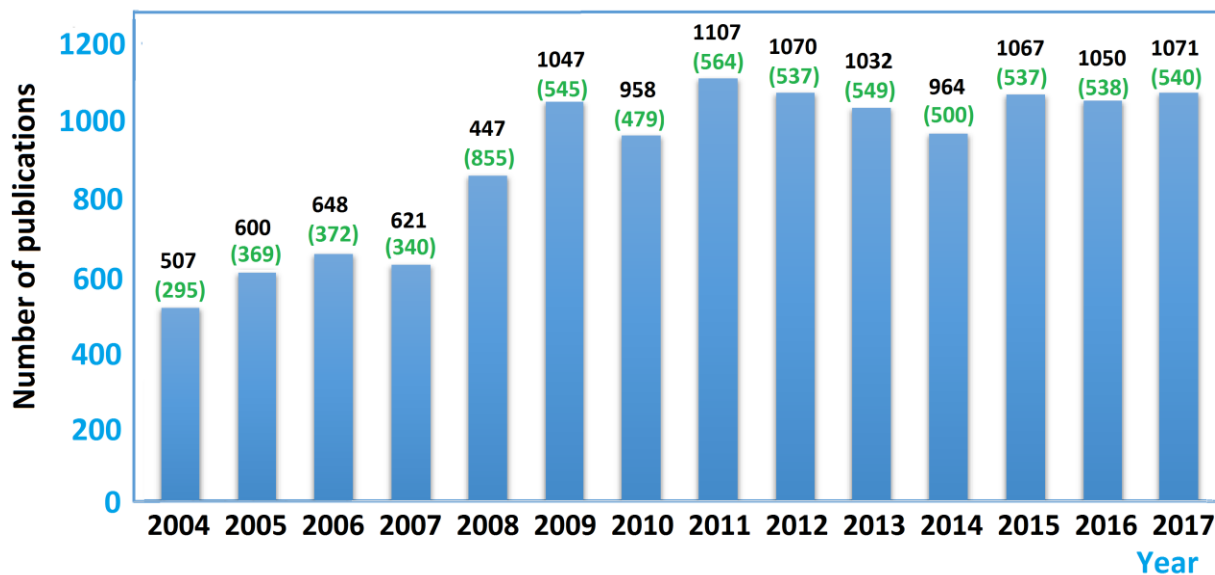
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1203 Figures



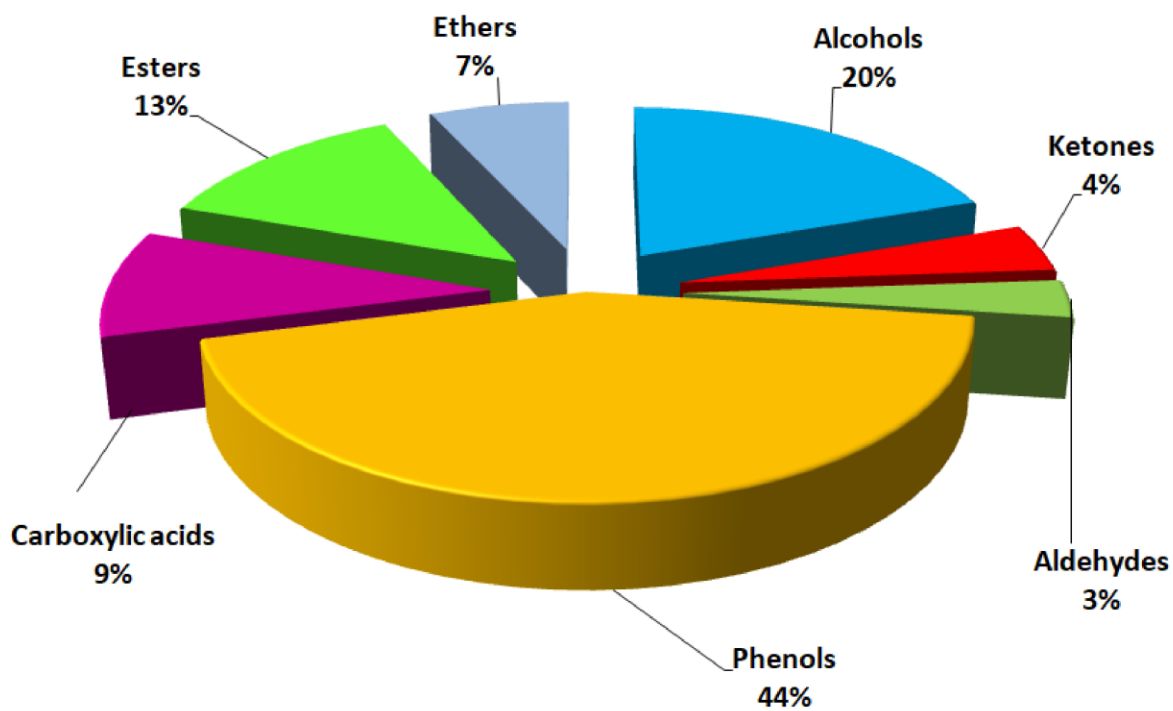
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1205 **Figure 1** Number of papers published during 2004-2019 on the presence of oxygenated organic
1206 compounds in effluents - based on Scopus database (searched keywords: aldehydes, ketones, ethers,
1207 esters, alcohols, phenols, carboxylic acids, wastewater or effluent; accessed on 04.01.2019).

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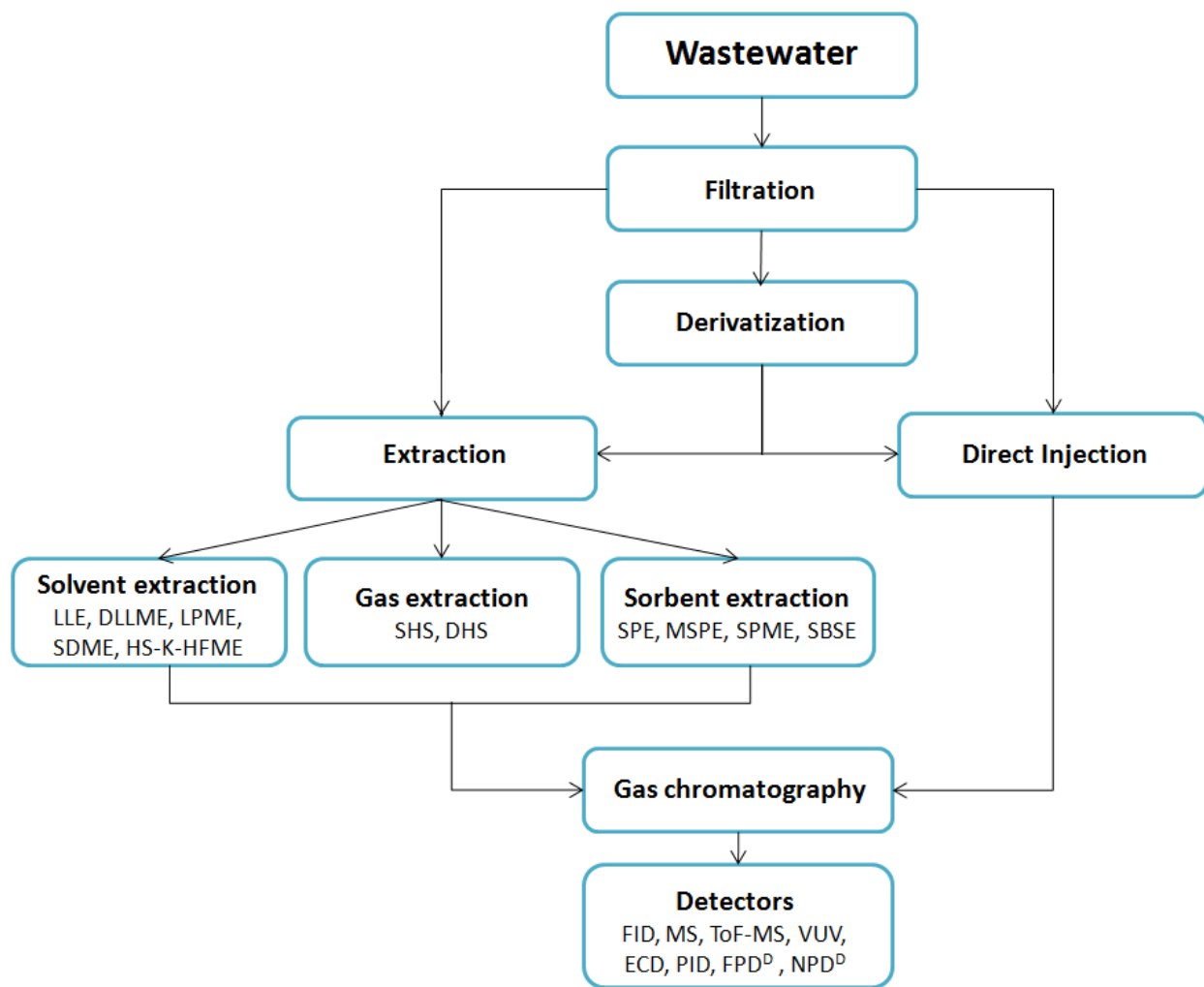
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1212 **Figure 2** Number of papers published during 2004 – 2017 dealing with the presence of oxygenated
 1213 organic compounds in effluents - based on Scopus database (searched keywords: aldehydes, ketones,
 1214 ethers, esters, alcohols, phenols, carboxylic acids, wastewater or effluent; accessed on 04.01.2019).



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1216 **Figure 3** Schematic diagram of the procedure for the determination of volatile oxygenated organic
 1217 compounds in wastewater samples using gas chromatography (^D – detectors used for the determination
 1218 of O-VOCs after derivatization).

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		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	

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