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1	Methods of assaying volatile oxygenated organic compounds in effluent samples
2	by gas chromatography – a review
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14 15 16 17 18 19 20 21 22 22 23	<b>Abstract:</b> 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.
24 25 26	<b>Keywords:</b> derivatization, effluents, extraction, gas chromatography, sample preparation, volatile organic compounds.
27 28 29	<b>Abbreviations:</b> ACN – acetone, AcCN – acetonitrile, [C <sub>8</sub> MIM][PF <sub>6</sub> ] - 1-octyl-3-methylimidazolium hexafluorophosphate, CAR – Carboxen, CTC –carbon tetrachloride, CW - Carbowax, DAI - Direct Injection 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

- Headspace Single-Drop Microextraction, HS-SPME - Headspace Solid-Phase Microextraction, LLE -33 Liquid-Liquid Extraction, LOD - Limit of Detection, LPME - Liquid Phase Microextraction, MS - Mass 34 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-HSO<sub>4</sub> - 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-trimetylosilylimidazole, TOF-MS - Time-Of-Flight Mass Spectrometry, VFA 46 - Volatile Fatty Acids, VUV – Vacuum Ultraviolet Absorption. 47

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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].

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 (Figure 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 (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 detection methods. However, in order to ensure sufficient sensitivity of a procedure, a sample 114 115 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.

#### 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 very low sensitivity can be observed in the determination of acetic acid, which is a very important O-137 138 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.

#### 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 Figure S1. The use of static headspace analysis for the determination of O-VOC content has a

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number of advantages, including universal applicability, simplicity and the possibility of automation, 162 163 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].

### 2.1.2 Dynamic Headspace

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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 with boiling points up to about 150 °C can be extracted [40]. Another limitation of DHS involves the 192 193 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.

# 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 ( $300 - 1000 \text{ m}^2/\text{g}$ ) [43], a porous polymer Tenax TA based on2,6-diphenyl-p-phenylene oxide(specific surface area 18 m<sup>2</sup>/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.

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.

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.

#### 2.2 Liquid extraction

#### 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 of the analytes from the aqueous phase to the organic phase. The procedure is depicted in Figure S3. LLE 239 240 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

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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 so effective as it can be expected. Sometimes, the solubility is even increasing or minor changes are reported after the salt addition.

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# 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  $\mu$ g/L for carboxylic acids [56].

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# 2.2.2.1 Single-Drop Microextraction

One mode of solvent microextraction is single-drop microextraction (SDME), which requires only 0.3-3  $\mu$ L 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 Figure 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 (Figure 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

282 liquid phase microextraction, HF-LPME). Selectivity of the extraction is achieved by selecting the 283 appropriate solvent and the fiber material. The pores in the fiber preclude extraction of large molecules 284 which in the case of wastewater facilitates subsequent GC analysis. An interesting approach is headspace 285 knotted hollow fiber microextraction (HS-K-HFME), in which the knot-shaped commercially available Q 286 3/2 Accurel polypropylene hollow fiber is filled with 25  $\mu$ L of the extraction solvent (1-octanol). The 287 excess solvent forms a large droplet (13 μL) which is held in the center of the knot (Figure S3). The knot-288 shaped fiber has a larger contact area which increases the rate of mass transfer between the headspace 289 and extraction solvent. This technique provided low LOD values for diethyl ether and ethyl acetate equal 290 to 10 µg/L [62].

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#### 2.2.2.2 Dispersive Liquid-Liquid Microextraction

292 A relatively new mode of solvent microextraction is dispersive liquid-liquid microextraction 293 (DLLME) [63]. In this technique, an aqueous sample is placed in a conical centrifuge tube and a mixture 294 of disperser and extraction solvent is added. Then the mixture is agitated and centrifuged. Next, the 295 sedimented organic phase is collected from the bottom of the tube (in some applications the extract is 296 lighter than water and is collected from the top) and injected into the GC (Figure S3). Owing to its 297 simplicity, a very short extraction time (several seconds) and often almost 100% analyte recovery DLLME 298 has become one of the most common modes of liquid-liquid extraction [57]. DLLME was used, among 299 others, in the determination of carboxylic acids [64-65] and 43 volatile oxygenated organic compounds in 300 effluents from the production of petroleum bitumens, including alcohols, esters, ethers, ketones, 301 aldehydes and phenols. Low LOD values ranging from 0.07 to 0.82  $\mu$ g/mL were obtained for all the 302 analytes except for acetaldehyde for which LOD was 2.06 µg/mL [11]. One of the drawbacks of DLLME is 303 the possibility of losses of the most volatile analytes during extraction; therefore, it is recommended for 304 the extraction of compounds with higher boiling points, such as phenols [66-67] or acrylates [68]. Until 305 recently, a serious limitation of DLLME was the inability to automate it. However, some recent papers 306 describe automated DLLME, which makes this sample preparation technique more efficient [69-75]. A 307 comparison of parameters of various liquid-liquid extraction procedures is presented in Table 2.

#### 2.3 Sorbent extraction

#### 2.3.1 Solid-Phase Extraction

310 In order to isolate and enrich of oxygenated organic compounds from wastewater, liquid-solid 311 extraction is commonly used, including solid-phase extraction (SPE). The first step in any SPE procedure 312 involves conditioning of the sorbent bed using a solvent appropriate for a particular sorbent. This step 313 aims at solvation of the sorbent to increase its sorption capacity. Next, a sample of wastewater is loaded 314 onto the SPE column and the analytes are adsorbed onto the sorbent bed. The SPE cartridge is then 315 washed with an aqueous solution to remove impurities, followed by elution of the adsorbed analytes 316 with an appropriate organic solvent. The procedure for SPE extraction is depicted in Figure S4. SPE 317 technique provides high selectivity due to a wide variety of sorbents available and the possibility of 318 fractional elution with a series of solvents. For isolation of phenols the sorbents used most commonly 319 include silica gel modified with octadecyl groups (C18) [76-80] as well as commercially available 320 polymeric sorbents, such as styrene/divinylbenzene co-polymer (S-DVB) [81] or divinylbenzene/N-

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vinylpyrrolidone (DVB/N-VP) [82-84], which have also been successfully used to isolate fatty, benzoic and 321 322 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 an appropriate organic solvent. The extract is then analyzed by GC. The MSPE procedure is depicted in 333 334 Figure S4. Just 40 mg of Fe<sub>3</sub>O<sub>4</sub>@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 335 336 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 disgualify 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 (Figure 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 the less volatile O-VOCs in wastewaters 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

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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), Polydimethylsiloxane/Carboxen/Divinylbenzene (PDMS-CAR-DVB) and Polydimethylsiloxane-Carboxen 364 365 (PDMS–CAR), only PDMS-CAR sorbent provided satisfactory extraction of C<sub>2</sub> and C<sub>3</sub>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  $(C_2 - C_7)$  [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.

# 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

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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 Derivatization 3.

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.

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 -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*-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 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 hours, which limits the use of these reagents in routine determinations of a large number of samples [51].

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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 converted into alkyl (often butyl) esters. The most common ion pairing reagents include 446 447 tetrabutylammonium hydrogensulfate (TBA-HSO<sub>4</sub>) [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**

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. This 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

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477 Some carboxylic acids  $(C_2 - C_3)$  are sufficiently volatile and thermally stable to be determined by GC without derivatization. However, their high polarity and ability to form hydrogen bonds precludes 478 479 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°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].

#### 4.3Ionic 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(2,3dimethylimidazolium)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  $C_{s}$  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].

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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].

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### 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.

#### 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  $\pm$  0.2 % t<sub>R</sub> [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 to 30 %. Such an approach constitutes a sufficient confirmation of peak identification while allowing the determination of analytes at suitably low 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, El and positive Cl 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  $CH_4$ ) and negative (reaction gas  $NH_3$ ) chemical ionization in the determination of volatile fatty acids demonstrated lower detection limits when negative chemical 565 566 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].

#### 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 absorption spectra in the 125 to 240 nm range [144-145]. All compounds absorption in this region have 580 581 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.

#### 5.2 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.

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Theoretically, other selective detectors, such as a nitrogen-phosphorus detector (NPD), chemiluminescence detector (CLD), flame photometric detector (FPD) or apulsed 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].

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Thelist 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 real samples with other methods. In such a case the results obtained by the standard addition methodare accepted as the expected value.

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### 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  $\mu$ g/mL [11,12,68] or  $\mu$ 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  $\mu$ g/L and 95.8  $\mu$ 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  $\mu$ g/L and 0.58  $\mu$ 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  $\mu$ 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  $433 \mu g/mL$  and carboxylic acids at concentrations up to 275 666  $\mu$ g/mL [43,49,90,98]. In addition, municipal wastewater also contained MTBE at 25  $\mu$ g/mL [158] and 667 acetone at 0.62 µg/mL [43].

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

The majority of procedures described in this review pertains 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

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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

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 asproduction 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.

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

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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.

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.

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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# 747 References

- E. Gallego, F.J. Roca, J.F. Perales, G. Sánchez, P. Esplugas, Characterization and determination of the odorous charge in the indoor air of a waste treatment facility through the evaluation of volatile organic compounds (VOCs) using TD–GC/MS, Waste Manage. 32 (2012) 2469-2481.
  - 2. B. Nijssen, T. Kamperman, J. Jetten, Acetaldehyde in mineral water stored in polyethylene terephtalate (PET) bottles: odour threshold and quantification, Packag. Technol. Sci. 9 (1996) 175–185.

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751

- 753 3. P.H. Dalton, D.D. Dilks, M.I. Banton, Evaluation of odor and sensory irritation thresholds for methyl isobutyl
  754 ketone in humans, AIHAJ, 61 (2000) 340-350.
- Regulation of the Minister of Health of 28 September 2005 on the list of dangerous substances and their
   classification and labeling (Dz. U. 2005 nr 201, poz. 1674).
- 757 5. R.M. Thomas, The rising incidence of asthma, Asthma Mag. 4 (1999) 6-8.
- M. A. Ullah, K-H. Kim, J.E. Szulejko, J. Cho, The gas chromatographic determination of volatile fatty acids in wastewater samples: Evaluation of experimental biases in direct injection method against thermal desorption method, Anal. Chim. Acta 820 (2014) 159–167.
- 761 7. A. Talaiekhozani, M. Bagheri, A. Goli, M.R.T. Khoozani, An overview of principles of odor production, emission,
   762 and control methods in wastewater collection and treatment systems, J. Environ. Manage. 170 (2016) 186 763 206.
- 8. G. Boczkaj, A. Przyjazny, M. Kamiński, Characteristics of volatile organic compounds emission profiles from hot
   road bitumens, Chemosphere 104 (2014) 23-30.
- 9. G. Boczkaj, M. Kamiński, A. Przyjazny, Process control and investigation of oxidation kinetics of postoxidative
  effluents using gas chromatography with pulsed flame photometric detector (GC-PFPD), Ind. Eng.Chem. Res.
  49 (2010) 12654-12662.
- 769 10. E. Cetin, M. Odabasi, R. Seyfioglu, Ambient volatile organic compound (VOC) concentrations around a
   770 petrochemical complex and a petroleum refinery, Sci. Total Environ. 312 (2003) 103–112.
- 11. G. Boczkaj, P. Makoś, A. Przyjazny, Application of dispersive liquid liquid microextraction and gas
   chromatography-mass spectrometry for the determination of oxygenated volatile organic compounds in
   effluents from the production of petroleum bitumen, J. Sep. Sci. 39 (2016) 2604 2615.
- G. Boczkaj, P. Makoś, A. Przyjazny, Application of dynamic headspace and gas chromatography coupled to
   mass spectrometry (DHS-GC-MS) for the determination of oxygenated volatile organic compounds in refinery
   effluents, Anal. Methods 8 (2016) 3570 3577.
  - A. Fernandes, P. Makoś, G. Boczkaj, Treatment of bitumen post oxidative effluents by sulfate radicals based advanced oxidation processes (S-AOPs) under alkaline pH conditions, J. Clean. Prod. (2018) DOI: 10.1016/j.jclepro.2018.05.207.
- M. Gągol, A. Przyjazny, G. Boczkaj, Effective method of treatment of industrial effluents under basic pH
   conditions using acoustic cavitation A comprehensive comparison with hydrodynamic cavitation processes.
   Chem. Eng. Process. 128 (2018) 103 113.
  - 15. L. Ciofia, C. Ancillotti, U. Chiuminatto, D. Fibbi, L. Checchini, S. Orlandini, M. Del Bubba, Liquid chromatographic-tandem mass spectrometric method for the simultaneous determination of alkylphenols polyethoxylates, alkylphenoxy carboxylates and alkylphenols in wastewater and surface-water, J. Chromatogr. A 1362 (2014) 75–88.
  - 16. L. Martínkova, M. Chmatal, The integration of cyanide hydratase and tyrosinase catalysts enables effective degradation of cyanide and phenol in coking wastewaters, Water Res. 102 (2016) 90-95.
  - 17. B. Yu, Y. Song, L. Han, H. Yu, Y. Liu, H. Liu, Optimizations of packed sorbent and inlet temperature for large volume-direct aqueous injection-gas chromatography to determine high boiling volatile organic compounds in water, J. Chromatogr. A, 1356 (2014) 221–229.
  - 18. P. Vergine, F. Sousa, M. Lopes, F. Silva, T. Gameiro, H. Nadais, I. Capela, Synthetic soft drink wastewater suitability for the production of volatile fatty acids, Process Biochem.50 (2015) 1308–1312.
  - R. Beale, P.S. Liss, J.L. Dixon, P.D. Nightingale, Quantification of oxygenated volatile organic compounds in seawater by membrane inlet-proton transfer reaction/mass spectrometry. Anal. Chim. Acta706 (2011) 128-134.

778

779

783

784

785

786

787

788

789

790

791

792

793

794

795

- 797 20. Regulation of the Minister of the Environment of 24 July 2006 on the conditions to be met for the introduction
  798 of sewage into waters or to land and on substances particularly harmful to the aquatic environment (Dz. U. z
  799 dnia 31 lipca 2006 r.) http://brasil.cel.agh.edu.pl/~09skmolfa/file/Dz.U.2006.137.984.R4.pdf (accessed on
  800 13.10.2016).
- 801 21. Environmental Control Rules and Requirements, Fourth Edition, Group Environment, Health & Safety
   802 Department, Ports, Customs & Free Zone Corporation, Dubai, UAE. 2005.
- 80322.PollutionControlActs,Rules,andNotifications804issued thereunder.http://admin.indiaenvironmentportal.org.in/files/file/PollutionControlLaw.pdf(accessed805on 30.05.2018)
- 806 23. Estonian Governmental Regulation no. 269 from the 21st of July 2001. Effluent guidelines for wastewater807 discharges to reservoirs and surface waters.
- Regulation of the Minister of Construction of 14 July 2006 on how to fulfill the obligation of industrial
  wastewater providers and the conditions for introducing sewage into sewerage equipment (Dz. U. z dnia 28
  lipca 2006 r.) http://www.abc.com.pl/du-akt/-/akt/dz-u-2006-136-964 (accessed on 13.10.2016).
- 811 25. F.P. Bigley, R.L. Grob, Determination of phenols in water and wastewater by post-column reaction detection
  812 high-performance liquid chromatography, J. Chromatogr. A 350 (1985) 407-416.
- 813 26. R. Wissiack, E. Rosenberg, Universal screening method for the determination of US21 Environmental
  814 Protection Agency phenols at the lower ng level in water samples by on-line solid-phase extraction-high
  815 performance liquid chromatography-atmospheric pressure chemical ionization mass spectrometry within a
  816 single run, J. Chromatogr. A 963 (2002) 149–157.
- 817 27. S. Wu, B. Yang, L. Xi, Y. Zhu, Determination of phenols with ion chromatography-online electrochemical
  818 derivatization based on porous electrode–fluorescence detection, J. Chromatogr. A 1229 (2012) 288–292.
- 819 28. S. Morales, R. Cela, Highly selective and efficient determination of US Environmental Protection Agency
   820 priority phenols employing solid-phase extraction and non-aqueous capillary electrophoresis, J. Chromatogr. A
   821 896 (2000) 95-104.
- W. Ziemer, M. Wortberg, C. Eichberger, J. Gerstel, W. Kerl, Direct aqueous injection with backflush thermal
   desorption for wastewater monitoring by online GC-MS, Anal Bioanal Chem 397 (2010) 1315–1324.
- 824 30. F. Raposo, R. Borja, J.A. Cacho, J. Mumme, K. Orupõld, S. Esteves, J. Noguerol-Arias, S. Picard , A. Nielfa, P.
  825 Scherer, I. Wierinck, E. Aymerich, C. Cavinato, D.C. Rodriguez, N. García-Mancha, P.N.T. Lens, V. Fernández826 Cegrí, First international comparative study of volatile fatty acids in aqueous samples by chromatographic
  827 techniques: Evaluating sources of error, TrAC 51 (2013) 127–143.
  - 31. S. Armenta, S. Garrigues, M.de la Guardia, The role of green extraction techniques in Green Analytical Chemistry, TrAC 71 (2015) 2–8.
  - 32. A. Gałuszka, Z. Migaszewski, J. Namieśnik, The 12 principles of green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices, TrAC 50 (2013) 78–84.
  - P. Lewkowska, B. Cieślik, T. Dymerski, P. Konieczka, J. Namieśnik, Characteristics of odors emitted from municipal wastewater treatment plant and methods for their identification and deodorization techniques, Environ. Res. 151 (2016) 573–586.
  - 34. J.-J. Fang, N. Yang, D.-Y. Cen, L.-M. Shao, P.-J. He, Odor compounds from different sources of landfill: Characterization and source identification, Waste Manage. 32 (2012) 1401–1410.
  - C. Rodríguez-Navas, R. Forteza, V. Cerdà, Use of thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS) on identification of odorant emission focus by volatile organic compounds characterisation, Chemosphere 89 (2012) 1426–1436.
  - 36. E. Davoli, M.L. Gangai, L. Morselli, D. Tonelli, Characterisation of odorants emissions from landfills by SPME and GC/MS, Chemosphere 51 (2003) 357–368.

829

830

831

832

833

834

835

836

837

838

839

840 841

- 37. J.A. Cruwys, R.M. Dinsdale, F.R. Hawkes, D.L. Hawkes, Development of a static headspace gas
  chromatographic procedure for the routine analysis of volatile fatty acids in wastewaters, J. Chromatogr. A
  945 (2002) 195–209.
- 845 38. B. Kolb, L.S. Ettre, Static Headspace-Gas Chromatography: Theory and Practice, 2nd Edition, Wiley, 2006.
- A. Kremser, M.A. Jochmann, T. C. Schmidt, Systematic comparison of static and dynamic headspace sampling
   techniques for gas chromatography. Anal. Bioanal. Chem. 408 (2016) 6567-6579.
- 848 40. P.L. Wylie, Comparing headspace with purge and trap for analysis of volatile priority pollutants, J. Am. Water
  849 Works Assoc. 80 (1988) 65–72.
- 850 41. C. Soria, I. Martínez-Castro, J. Sanz, Study of the precision in the purge-and-trap–gas chromatography–mass
   851 spectrometry analysis of volatile compounds in honey, J. Chromatogr. A 1216 (2009) 3300–3304.
- 42. A.C. Soria, M.J. García-Sarrió, M.L. Sanz, Volatile sampling by headspace techniques, TrAC 71 (2015) 85–99.
- 43. H.-W. Liu, Y.-T. Liu, B.-Z. Wu, H.-C. Nian, H.-J. Chen, K.-H. Chiu, J.-G. Lo, Process sampling module coupled with
  purge and trap–GC–FID for in situ auto-monitoring of volatile organic compounds in wastewater, Talanta 80
  (2009) 903–908.
- 44. A. Tanabe, Y. Tsuchida, T. Ibaraki, K. Kawata, A. Yasuhara, T. Shibamoto, Investigation of methyl tert-butyl
  ether levels in river-, ground-, and sewage-waters analyzed using a purge-and-trap interfaced to a gas
  chromatograph–mass spectrometer. J. Chromatogr. A, 1066 (2005) 159–164.
- 45. C. Wu, Y. Zhou, Q. Sun, L. Fu, H. Xi, Y. Yua, R. Yu, Appling hydrolysis acidification-anoxic-oxic process in the
  treatment of petrochemical wastewater: From bench scale reactor to full scale wastewater treatment plant, J.
  Hazard. Mater. 309 (2016) 185–191.
- 46. L.H. Wartelle, W.E. Marshall , C.A. Toles , M.M. Johns, Comparison of nutshell granular activated carbons to
  commercial adsorbents for the purge-and-trap gas chromatographic analysis of volatile organic compounds. J.
  Chromatogr. A, 879 (2000) 169–175.
- 47. M. A. Farajzadeh, N. Nouri, P. Khorram, Derivatization and microextraction methods for determination of
   organic compounds by gas chromatography, TrAC 55 (2014) 14–23.
- 48. G. Manni, F. Caron, Calibration and determination of volatile fatty acids in waste leachates by gas
  chromatography, J. Chromatogr. A 690 (1995) 237-242.
- 869 49. N.T. Mkhize, T.A.M. Msagati, B.B. Mamba, M. Momba, Determination of volatile fatty acids in wastewater by
   870 solvent extraction and gas chromatography, Phys Chem Earth 67–69 (2014) 86–92.
  - A. Banel, B.Zygmunt, Application of gas chromatography-mass spectrometry preceded by solvent extraction to determine volatile fatty acids in wastewater of municipal, animal farm and landfill origin, Water Sci. Technol. 63 (2011) 590-597.
  - 51. A. Latorre, A. Rigol, S. Lacorte, D. Barcelo, Comparison of gas chromatography–mass spectrometry and liquid chromatography–mass spectrometry for the determination of fatty and resin acids in paper mill process waters. J. Chromatogr. A 991 (2003) 205–215.
  - 52. A. Rigol, A. Latorre, S. Lacorte, D. Barceló, Determination of toxic compounds in paper-recycling process waters by gas chromatography–mass spectrometry and liquid chromatography–mass spectrometry, J. Chromatogr. A 963 (2002) 265–275.
  - J.L. VIIchez, A. Zafra, A. González-Casado, E. Hontoria, M. del Olmo. Determination of trace amounts of bisphenol F, bisphenol A and their diglycidyl ethers in wastewater by gas chromatography–mass spectrometry, Anal. Chim. Acta 431 (2001) 31–40.
  - 54. E. Carasek, L. Morés, J. Merib, Basic principles, recent trends and future directions of microextraction techniques for the analysis of aqueous environmental samples. Trends Environ. Anal. Chem. 19 (2018) 1-18.
  - 55. T. Zhang, X. Chen, P. Liang, C. Liu, Determination of Phenolic Compounds in Wastewater by Liquid-Phase Microextraction Coupled with Gas Chromatography, J. Chromatogr. Sci. 44 (2006) 619 624.

872

873

874

875

876

877

878

879

880

881

882

883

884

885

- 56. J. Wu, H. K. Lee, Ion-pair dynamic liquid-phase microextraction combined with injection-port derivatization for
   the determination of long-chain fatty acids in water samples, J. Chromatogr. A 1133 (2006) 13–20.
- 889 57. J.M. Kokosa, Advances in solvent microextraction techniques, TrAC 43 (2013) 2-13.
- 58. J. Lee, H.K. Lee, Fully Automated Dynamic In-Syringe Liquid-Phase Microextraction and On-Column
   Derivatization of Carbamate Pesticides with Gas Chromatography/Mass Spectrometric Analysis, Anal. Chem.
   83 (2011) 6856–6861.
- 893 59. Y. C. Fiamegos, A.-P. Kefala, C.D. Stalikas, Ion-pair single-drop microextraction versus phase-transfer catalytic
  894 extraction for the gas chromatographic determination of phenols as tosylated derivatives, J. Chromatogr. A
  895 1190 (2008) 44–51.
- F.-Q. Zhao, J. Li, B.-Z. Zeng, Coupling of ionic liquid-based headspace single-drop microextraction with GC for
   sensitive detection of phenols, J. Sep. Sci. 31 (2008) 3045 3049.
- 898 61. Y.C. Fiamegos, C. D. Stalikas, In-drop derivatisation liquid-phase microextraction assisted by ion-pairing
   899 transfer for the gas chromatographic determination of phenolic endocrine disruptors, Anal. Chim. Acta 597
   900 (2007) 32–40.
- 901 62. P.-S. Chena, Y.-H. Tseng, Y.-L. Chuang, J.-H. Chen, Determination of volatile organic compounds in water using
   902 headspace knotted hollow fiber microextraction, J. Chromatogr. A 1395 (2015) 41–47.
- 903 63. M. Rezaee, Y. Assadi, M.R.M. Hosseini, E. Aghaee, F. Ahmadi, S. Berijani, Determination of organic compounds
   904 in water using dispersive liquid–liquid microextraction. J. Chromatogr. A 1116 (2006) 1 9.
- 905 64. P. Makoś, A. Fernandes, G. Boczkaj, Method for the determination of carboxylic acids in industrial effluents
   906 using dispersive liquid-liquid microextraction with injection port derivatization gas chromatography–mass
   907 spectrometry, J. Chromatogr. A 1517 (2017) 26–34.
- 908 65. P. Makoś, A. Fernandes, A. Przyjazny, G. Boczkaj, Sample preparation procedure using extraction and
   909 derivatization ofcarboxylic acids from aqueous samples by means of deep eutectic solvents for gas
   910 chromatographic-mass spectrometric analysis, J. Chromatogr. A1555 (2018) 10–19.
- 911 66. J. Sun, H. Tao, Determination of Phenols in Wastewater by Dispersive Liquid-Liquid Microextraction Coupled
   912 to Capillary Gas Chromatography, International Conference on Chemical, Material and Food Engineering
   913 (CMFE-2015).DOI: 10.2991/cmfe-15.2015.87.
  - 67. G. Song, C. Zhu, Y. Hu, J. Chen, H. Cheng, Determination of organic pollutants in coking wastewater by dispersive liquid–liquid microextraction/GC/MS, J. Sep. Sci. 36 (2013) 1644–1651.
  - 68. J. Sun, F. Zeng, X. Liu, Determination of Acrylates in Wastewater by Dispersive Liquid-liquid Microextraction Coupled to Capillary Gas Chromatography, Adv. Mat. Res. 881-883 (2014) 627-630.
  - 69. A. González, J. Avivar, V. Cerdà, Estrogens determination in wastewater samples by automatic in-syringe dispersive liquid–liquid microextraction prior to silylation and gas chromatography. J. Chromatogr. A 1413 (2015) 1–8.
  - 70. Y.-M. Liua, F.-P. Zhanga, B.-Y. Jiaoa, J.-Y. Raoa, G. Leng, Automated dispersive liquid-liquid microextraction coupled to high performance liquid chromatography cold vapour atomic fluorescence spectroscopy for the determination of mercury species in natural water samples, J. Chromatogr. A 1493 (2017) 1–9.
  - M. Alexovič, M. Wieczorek, J. Kozak, P. Kościelniak, I.S. Balogh, V. Andruch, An automatic, vigorous-injection assisted dispersive liquid–liquid microextraction technique for stopped-flow spectrophotometric detection of boron, Talanta 133 (2015) 127–133.
  - 72. B. Horstkottea, K. Fikarová, D. J. Cocovi-Solberg , H. Sklenářová, P. Solicha , M. Miró, Online coupling of fully automatic in-syringe dispersive liquid-liquid microextraction with oxidative back-extraction to inductively coupled plasma spectrometry for sample clean-up in elemental analysis: A proof of concept, Talanta 173 (2017) 79–87.

915

916

917

918

919

920

921

922

923

924

925

926

927

928

929

- 931 73. F. Maya, B. Horstkotte, J. M. Estela, V. Cerdà, Automated in-syringe dispersive liquid-liquid microextraction,
   932 TrAC 59 (2014) 1–8.
- 933 74. L. Guo, S. Tana, X. Li, H.K. Lee, Fast automated dual-syringe based dispersive liquid–liquid microextraction
  934 coupled with gas chromatography–mass spectrometry for the determination of polycyclic aromatic
  935 hydrocarbons in environmental water samples, J. Chromatogr. A 1438 (2016) 1–9.
- 936 75. S. Li, L. Hu, K. Chen, H. Gao, Extensible automated dispersive liquid–liquid microextraction, Anal. Chim. Acta
  937 872 (2015) 46–54.
- 938 76. O.O. Olujimi, O.S. Fatoki, J.P. Odendaal, A.P. Daso, Chemical monitoring and temporal variation in levels of
   939 endocrine disrupting chemicals (priority phenols and phthalate esters) from selected wastewater treatment
   940 plant and freshwater systems in Republic of South Africa, Microchem. J. 101 (2012) 11–23.
- 941 77. O.O. Olujimi, O.S. Fatoki, J.P. Odendaal, Method development for simultaneous determination of phthalate
  942 and eleven priority phenols as tert-butyldimethylsilyl derivatives in grab samples from wastewater treatment
  943 plants using GC-MS in Cape Town, South Africa, Fresen. Environ. Bull. 20 (2011) 69-77.
- 944 78. Q. Yang, P. Xiong, P. Ding, L. Chu, J. Wang, Treatment of petrochemical wastewater by microaerobic hydrolysis
  945 and anoxic/oxic processes and analysis of bacterial diversity, Bioresour. Technol. 196 (2015) 169–175.
- 946 79. G. Gatidou, N. S. Thomaidis, A.S. Stasinakis, T.D. Lekkas, Simultaneous determination of the endocrine
  947 disrupting compounds nonylphenol, nonylphenol ethoxylates, triclosan and bisphenol A in wastewater and
  948 sewage sludge by gas chromatography–mass spectrometry, J. Chromatogr. A 1138 (2007) 32–41.
- 80. N. Nakada, H. Nyunoya, M. Nakamura, A. Hara, T. Iguchi, H. Takada, Identification of estrogenic compounds in
  wastewater effluent, Environ. Toxicol. Chem. 23 (2004) 2807–2815.
- 81. A. Kovacs, A. Kende, M. Mortl, G. Volk, T. Rikker, K. Torkos, Determination of phenols and chlorophenols as
  trimethylsilyl derivatives using gas chromatography–mass spectrometry, J. Chromatogr. A 1194 (2008) 139–
  142.
- 954 82. J.A. Padilla-Sánchez, P. Plaza-Bolanos, R. Romero-González, N. Barco-Bonilla, J.L. Martínez-Vidal, A. Garrido 955 Frenich, Simultaneous analysis of chlorophenols, alkylphenols, nitrophenols and cresols in wastewater
   956 effluents, using solid phase extraction and further determination by gas chromatography-tandem mass
   957 spectrometry, Talanta 85 (2011) 2397–2404.
- 958 83. W.J. Zhong, D.H. Wang, X.W. Xu, B.Y. Wang, Q. Luo, S.S. Kumaran, Z.J. Wang, A gas chromatography/mass
  959 spectrometry method for the simultaneous analysis of 50 phenols in wastewater using deconvolution
  960 technology, Chinese Sci. Bull. 56 (2011) 275–284.
  - Á. Sebok, A. Vasanits-Zsigrai, A. Helenkár, G. Záray, I. Molnár-Perl, Multiresidue analysis of pollutants as their trimethylsilyl derivatives, by gas chromatography–mass spectrometry, J. Chromatogr. A 1216 (2009) 2288– 2301.
  - B. Jurado-Sánchez, E. Ballesteros, M. Gallego, Determination of carboxylic acids in water by gas chromatography–mass spectrometry after continuous extraction and derivatisation, Talanta 93 (2012) 224– 232.
  - 86. J. Meng, C. Shi, B. Wei, W. Yub, C. Deng, X. Zhang, Preparation of Fe3O4@C@PANI magnetic microspheres for the extraction and analysis of phenolic compounds in water samples by gas chromatography–mass spectrometry. J. Chromatogr. A 1218 (2011) 2841–2847.
  - 87. J.B. Quintana, R. Rodil, S. Muniategui-Lorenzo, P. Lopez-Mahia, D. Prada-Rodriguez, Multiresidue analysis of acidic and polar organic contaminants in water samples by stir-bar sorptive extraction—liquid desorption—gas chromatography—mass spectrometry, J. Chromatogr. A 1174 (2007) 27–39.
  - 88. L. Feng, Y. Huang, H. Wang, Solid-phase microextraction in combination with GC-FID for quantification of the volatile free fatty acids in wastewater from constructed wetlands, J. Chromatogr. Sci. 46 (2008) 577-584.

962

963

964

965

966

967

968

969

970

971

972

973

- 975 89. H. Piri-Moghadam, M.N. Alam, J. Pawliszyn, Review of geometries and coating materials in solid phase 976 microextraction: Opportunities, limitations, and future perspectives, Analytica Chimica Acta (2017), 977 http://dx.doi.org/10.1016/j.aca.2017.05.035.
- 978 90. M. Abalos, J.M. Bayona, J. Pawliszyn, Development of a headspace solid-phase microextraction procedure for 979 the determination of free volatile fatty acids in waste waters, J. Chromatogr. A 873 (2000) 107–115.
- 980 91. L. Pan, M. Adams, J. Pawliszyn, Determination of Fatty Acids Using Solid-Phase Microextraction, Anal. Chem. 981 67 (1995) 4396-4403.
- 982 92. L. Pan, J. Pawliszyn, Derivatization/Solid-Phase Microextraction: New Approach to Polar Analytes, Anal. Chem. 983 69 (1997) 196-205.
- 984 93. M. Ábalos, J.M. Bayona, Application of gas chromatography coupled to chemical ionisation mass spectrometry 985 following headspace solid-phase microextraction for the determination of free volatile fatty acids in aqueous 986 samples, J. Chromatogr. A 891 (2000) 287-294.
- 987 94. M. Llompart, M. Lourido, P. Landın, C. Garcia-Jares, R. Cela, Optimization of a derivatization-solid-phase 988 microextraction method for the analysis of thirty phenolic pollutants in water samples, J. Chromatogr. A 963 989 (2002) 137-148.
- 990 95. P. Braun, M. Moeder, St. Schrader, P. Popp, P. Kuschk, W. Engewald, Trace analysis of technical nonylphenol, 991 bisphenol A and 17alpha-ethinylestradiol in wastewater using solid-phase microextraction and gas 992 chromatography-mass spectrometry, J. Chromatogr. A 988 (2003) 41-51.
- 993 96. R. A. Trenholm, F.L. Rosario-Ortiz, S.A. Snyder, Analysis of formaldehyde formation in wastewater using on-994 fiber derivatization-solid-phase microextraction-gas chromatography-mass spectrometry, J. Chromatogr. A 995 1210 (2008) 25-29.
- 996 97. A. Godayol, M. Alonso, E. Besalú, J.M. Sanchez, E. Anticó, Odour-causing organic compounds in wastewater 997 treatment plants: Evaluation of headspace solid-phase microextraction as a concentration technique, J. 998 Chromatogr. A 1218 (2011) 4863-4868.
- 999 98. A. Banel, M. Wasielewska, B. Zygmunt, Application of headspace solid-phase microextraction followed by gas 1000 chromatography-mass spectrometry to determine short-chain alkane monocarboxylic acids in aqueous 1001 samples, Anal Bioanal. Chem. 399 (2011) 3299-3303.
  - 99. S.-P. Yo, Analysis of volatile fatty acids in wastewater collected from a pig farm by a solid phase microextraction method, Chemosphere 38 (1999) 823-834.
  - 100. H. Liua, L. Ji, J.i Li, S. Liu, X. Liu, S. Jiang, Magnetron sputtering Si interlayer: A protocol to prepare solid phase microextraction coatings on metal-based fiber, J. Chromatogr. A 1218 (2011) 2835–2840.
  - 101. W. Du, F. Zhao, B. Zeng, Novel multiwalled carbon nanotubes-polyaniline composite film coated platinum wire for headspace solid-phase microextraction and gas chromatographic determination of phenolic compounds, J. Chromatogr. A 1216 (2009) 3751-3757.
  - 102. H. Liu, J. Li, X. Liu, S. Jiang, A novel multiwalled carbon nanotubes bonded fused-silica fiber for solid phase microextraction-gas chromatographic analysis of phenols in water samples. Talanta 78 (2009) 929-935.
  - 103. M. Wasielewska, A. Banel, B. Zygmunt, Solid Phase Micro-Extraction, a Versatile and Handy Tool in Environmental Trace Organic Analysis, Gets a New Class of Coatings, Polymeric Ionic Liquids, Int. J. Environ. Sci. Technol. 4 (2013) 221-224.
  - 104. F. Zhou, X. Li, Z. Zeng, Determination of phenolic compounds in wastewater samples using a novel fiber by solid-phase microextraction coupled to gas chromatography, Anal. Chim. Acta 538 (2005) 63–70.
  - 105. K.H. Schueller, C. Schillig, Extraction device, US patent application US20140220701 A1.
  - 106. D.E. Raynie, New Sample Preparation Products and Accessories for 2017. LCGC Europe, 30 (2017)298-305.
  - 107. J. Pawliszyn, Solid-Phase Microextraction: Theory and Practice, Wiley-VCH, New York (1997).

.015

.016

.017

.018

- 1019 108. L.T. McGrath, C.D. Weir, S. Maynard, B.J. Rowlands, Gas-liquid chromatographic analysis of volatile short chain 1020 fatty acids in fecal samples as pentafluorobenzyl esters, Anal. Biochem. 207 (1992) 227-230.
- 1021 109. Methods for organic chemical analysis of municipal and industrial wastewater method 604-phenols 1022 https://www.epa.gov/sites/production/files/2015-08/documents/method 604 1984.pdf (02.11.2016).
- 1023 110. H. Lin, J. Wang, L. Zeng, G. Li, Y. Sha, D. Wu, B. Liu, Development of solvent micro-extraction combined with 1024 derivatization, J. Chromatogr. A 1296 (2013) 235-242.
- 1025 111. E. Bizkarguenaga, A. Iparragirre, P. Navarro, M. Olivares, A. Prietoa, A. Vallejo, O. Zuloag, In-port derivatization 1026 after sorptive extractions, J. Chromatogr. A 1296 (2013) 36-46.
- 1027 112. C. F. Poole, Alkylsilyl derivatives for gas chromatography, J. Chromatogr. A 1296 (2013) 2–14.
- 1028 113. A. M. C.Ferreira, M. E.F. Laespada, J. L. P. Pavón, B. M. Cordero, In situ aqueous derivatization as sample 1029 preparation technique for gas chromatographic determinations, J. Chromatogr. A 1296 (2013) 70–83.
- 1030 114. C. F. Poole, Derivatization reactions for use with the electron-capture detector, J. Chromatogr. A 1296 (2013) 1031 15-24.
- 1032 115. L. Hing-Biu, T.E. Peart, J.M. Carron, Gas chromatographic and mass spectrometric determination of some resin 1033 and fatty acids in pulpmill effluents as their pentafluorobenzyl ester derivatives. J. Chromatogr. A 498 (1990) 1034 367-379.
- 1035 116. J. Wu, H. K. Lee, Injection Port Derivatization Following Ion-Pair Hollow Fiber-Protected Liquid-Phase 1036 Microextraction for Determining Acidic Herbicides by Gas Chromatography/Mass Spectrometry, Anal. Chem. 1037 78 (2006) 7292-7301.
- 1038 117. P. Husek, P. Simek, Alkyl chloroformates in sample derivatization strategies for GC analysis. Review on a 1039 decade use of the reagents as esterifying agents, Curr. Pharm. Anal. 2 (2006) 23-43.
- 1040 118. R. Cervini, G. Day, A. Hibberd, G. Sharp, A. Froud, Investigation of a Novel, Sol-Gel Derived Stationary Phase for 1041 Gas Chromatography, LC GC Eur. 14 (2001) 564-569.
- 1042 119. http://www.restek.com/Pages/faq gcc (21.07.2017)
- 1043 120. https://www.chromspec.com/assets/Literature/rk 2015 gc columns.pdf (21.07.2017)
- 1044 121. L.M.L. Nollet, Chromatographic Analysis of the Environment, Third Edition, CRC Press, 2005.
- 1045 122. J. Beihoffer, C. Ferguson, Determination of Selected Carboxylic Acids and Alcohols in Groundwater by GC-1046 MS, J. Chromatogr. Sci. 32 (1994) 102-106.
- 1047 123. E. Senturk, M. Ince, O.G. Engin, Treatment efficiency and VFA composition of a thermophilic anaerobic contact 1048 reactor treating food industry wastewater, J. Hazard. Mater. 176 (2010) 843-848.
  - 124. D.W. Lou, X. Lee, J. Pawliszyn, Extraction of formic and acetic acids from aqueous solution by dynamic headspace-needle trap extraction Temperature and pH optimization, J. Chromatogr. A 1201 (2008) 228–234.
  - 125. E. Alkaya, S. Kaptan, L. Ozkan, S. Uludag-Demirer, G.N. Demirer, Recovery of acids from anaerobic acidification broth by liquid–liquid extraction, Chemosphere 77 (2009) 1137–1142.
  - 126. A. Banel, A. Jakimska, M. Wasielewska, L. Wolska, B. Zygmunt, Determination of SCFAs in water using GC-FID. Selection of the separation system, Anal. Chim. Acta 716 (2012) 24–27.
  - 127. M.C. Pietrogrande, D. Bacco, M. Mercuriali, GC-MS analysis of low-molecular-weight dicarboxylic acids in atmospheric aerosol: comparison between silulation and esterification derivatization procedures, Anal. Bioanal. Chem. 396 (2010) 877-885.
  - 128. R.P. Eganhouse, J. Pontolillo, R. B. Gaines, G. S. Frysinger, F.L. P. Gabriel, H.-P. E. Kohler, W. Giger, L. B. Barber, Isomer-Specific Determination of 4-Nonylphenols Using Comprehensive Two-Dimensional Gas Chromatography/Time-of-Flight Mass Spectrometry, Environ. Sci. Technol. 43 (2009) 9306–9313.
  - 129. C. Zhang, R.P. Eganhouse, J. Pontolillo, I. M. Cozzarelli, Y.Wang, Determination of nonylphenol isomers in landfill leachate and municipal wastewater using steam distillation extraction coupled with comprehensive

.059

.060

.061

.062

- 1063 two-dimensional gas chromatography/time-of-flight mass spectrometry, J. Chromatogr. A 1230 (2012) 110-1064 116.
- 1065 130. C.F. Poole, N. Lenca, Gas chromatography on wall-coated open-tubular columns with ionic liquid stationary 1066 phases, J. Chromatogr. A 1357 (2014) 87-109.
- 1067 131. C. Ragonese, D. Sciarronea, P. Q. Tranchida, P. Dugo, L. Mondello, Use of ionic liquids as stationary phases in 1068 hyphenated gas chromatography techniques, J. Chromatogr. A 1255 (2012) 130–144.
- 1069 132. L. Vidal, M.-L. Riekkola, A. Canals, Ionic liquid-modified materials for solid-phase extraction and separation: A 1070 review, Anal. Chim. Acta 715 (2012) 19-41.
- 1071 133. G. Boczkaj, A. Przyjazny, M. Kamiński, New procedures for control of industrial effluents treatment 1072 processes, Ind. Eng.Chem. Res. 53 (2014) 1503-1514.
- 1073 134. C. M. Hussain, C. Saridara, S. Mitra, Self-Assembly of Carbon Nanotubes via Ethanol Chemical Vapor 1074 Deposition for the Synthesis of Gas Chromatography Columns, Anal. Chem. 82 (2010) 5184–5188.
- 1075 135. A. V. Herrera-Herrera, M. Á. González-Curbelo, J. Hernández-Borges, M. Ángel Rodríguez-Delgado, Carbon 1076 nanotubes applications in separation science: A review, Anal. Chim. Acta 734 (2012) 1–30.
- 1077 136. D. Merli, A. Speltini, D. Ravelli, E. Quartaronec, L. Costa, A. Profumo, Multi-walled carbon nanotubes as the gas 1078 chromatographic stationary phase: Role of their functionalization in the analysis of aliphatic alcohols and 1079 esters, J. Chromatogr. A 1217 (2010) 7275-7281.
- 1080 137. G. R. Verga, A. Sironi, W. Schneider, J. Ch. Frohne; Selective determination of oxygenates in complex samples 1081 with the O-FID analyzer. J. High Resol. Chromatogr., 11 (1998) 248.
- 1082 138. ASTM D 5599: Standard Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography 1083 and Oxygen Selective Flame Ionization Detection.
- 1084 139. Polish Standard PN-EN 1601:2001: Liquid petroleum products, unleaded gasoline - Determination of 1085 oxygenated organic compounds and total organic oxygen content by gas chromatography (O-FID).
- 1086 140. R. Bro, PARAFAC. Tutorial and applications. Chemometr Intell. Lab. 38 (1997) 149-171.
- 1087 141. R. Tauler, Multivariate curve resolution applied to second order data, Chemometr Intell. Lab. 30 (1995) 133-1088 146.
- 1089 142. M.M. Galera, M.D.G. Garcia, H.C. Goicoechea, The application to wastewaters of chemometric approaches to 1090 handling problems of highly complex matrices, TrAC 26 (2007) 1032-1042.
  - 143. M. Shahpar, S. Esmaeilpoor, Advanced QSRR Modeling of Organic Pollutants in Natural Water and Wastewater in Gas Chromatography Time-of-Flight Mass Spectrometry, Chem. Method. 2 (2018) 1-22.
  - 144. K.A. Schug, I. Sawicki, D.D. Carlton Jr, H. Fan, H.M. McNair, J.P. Nimmo, P. Kroll, J. Smuts, P. Walsh, D. Harrison, Vacuum ultraviolet detector for gas chromatography, Anal. Chem. 86 (2014) 8329–8335.
  - 145. I.C. Santos, K.A. Schug, Recent advances and applications of gas chromatography vacuum ultraviolet spectroscopy. J. Sep. Sci. 40 (2017) 138-151.
  - 146. B. Gruber, T. Groeger, D. Harrison, R. Zimmermann, Vacuum ultraviolet absorption spectroscopy in combination with comprehensive two-dimensional gas chromatography for the monitoring of volatile organic compounds in breath gas: a feasibility study, J. Chromatogr. A 1464 (2016) 141-146.
  - 147. H. Fan, J. Smuts, L. Bai, P. Walsh, D.W. Armstrong, K.A. Schug, Gas chromatography-vacuum ultraviolet spectroscopy for analysis of fatty acid methyl esters, Food Chem. 194 (2016) 265-271.
  - 148. B.M. Weber, P. Walsh, J.J. Harynuk, Determination of hydrocarbon group-type of diesel fuels by gas chromatography with vacuum ultraviolet detection, Anal. Chem. 88 (2016) 5809-5817.
  - 149. H. Fan, J. Smuts, P. Walsh, D. Harrison, K.A. Schug, Gas chromatography-vacuum ultraviolet spectroscopy for multiclass pesticide identification, J. Chromatogr. A 1389 (2015) 120-127.

.103

.104

.105

- 1106 150. C. Qiu, J. Cochran, J. Smuts, P. Walsh, K. A. Schug, Gas chromatography-vacuum ultraviolet detection for
   classification and speciation of polychlorinated biphenyls in industrial mixtures, J. Chromatogr. A 1490 (2017)
   1108 191–200.
- 1109 151. L. Skultety, P. Frycak, C. Qiu, J. Smuts, L. Shear-Laude, K. Lemr, J. X. Mao, P. Kroll, K.A. Schug, A. Szewczak,
   1110 C.Vaught, I. Lurie, V. Havlicek, Resolution of isomeric new designer stimulants using gas chromatography 1111 Vacuum ultraviolet spectroscopy and theoretical computations, Anal. Chim. Acta 971 (2017) 55-67.
- 1112 152. M.S. Zhang, A.M. Wang, Determination of trace phenol in water with bromide derivatization and gas 1113 chromatography. Chinese J. Anal. Chem. 27 (1999) 63-65.
- 1114 153. US Environmental Protection Agency, Determination of carbonyl compounds in drinking water by
   pentafluorobenzylhydroxylamine derivatization and capillary gas chromatography with electron capture
   detection, Office of Research and Development, US EPA, Method 556, 1998.
- 1117 154. W.H. Steinecker, K. Miecznikowski, P. J. Kulesza, Z. D. Sandlinc , J.A. Cox, Amperometric detector for gas
   1118 chromatography based on a silica sol-gel solid electrolyte, Talanta 174 (2017) 1–6.
- 1119 155. J.S. Brown, S.M. Bay, D. J. Greenstein, W. R. Ray, Concentrations of Methyl-Tert-Butyl Ether (MTBE) in Inputs
   1120 and Receiving Waters of Southern California, Mar. Pollut. Bull. 42 (2001) 957–966.
- 1121 156. M Castillo, D Barceló, Characterization of organic pollutants in industrial effluents by high-temperature gas
   1122 chromatography–mass spectrometry, TrAC 18 (1999) 26–36.
- 1123 157. T. Reemtsma, A. Putschew, M. Jekel, Industrial wastewater analysis: a toxicity-directed approach, Waste
   1124 Manag. 19 (1999) 181-188.
- 1125 158. C. Achten, A. Kolb, W. Puttmann, Methyl tert-Butyl Ether (MTBE) in River and Wastewater in Germany.
  1126 Environ. Sci. Technol. 36 (2002) 3652-3661.
- 1127 159. G. Boczkaj, A. Fernandes, Wastewater treatment by means of Advanced Oxidation Processes at basic pH
   1128 conditions: A review, Chem. Eng. J. 320 (2017) 608-633.
- 1129 160. M. Gagol, A. Przyjazny, G. Boczkaj, Wastewater treatment by means of advanced oxidation processes based
   1130 on cavitation a review, Chem. Eng. J. 338 (2018) 599-627.
- 1131 161. C.B. Oman, C. Junestedt, Chemical characterization of landfill leachates 400 parameters and compounds.
   1132 Waste Manage. 28 (2008) 1876–1891.
  - 162. T. Yamamoto, A. Yasuhara, H. Shiraishi, O. Nakasugi, Bisphenol A in hazardous waste landfill leachates. Chemosphere, 42 (2001) 415-418.
  - 163. A. Yasuhara, H. Shiraishi, M. Nishikawa, T. Yamamoto, O. Nakasugi, T. Okumura, K. Kenmotsu, H. Fukui, M. Na gas, Y. Kawagoshi, Organic components in leachates from hazardous waste disposal sites.Waste Manage. Res., 17 (1999) 186-197.
  - 164. E.M. Siedlecka, J. Kumirska, T. Ossowski, P. Glamowski, M. Gołębiowski, J. Gajdus, Z. Kaczyński, P. Stepnowski, Determination of Volatile Fatty Acids in Environmental Aqueous Samples. Pol. J. Environ. Stud. 17 (2008) 351– 356.
  - 165. A.M. Sulej-Suchomska, Ż. Polkowska, Z. J. Kokot, M. de la Guardia, J. Namieśnik, Determination of antifreeze substances in the airport runoff waters by solid-phase microextraction and gas chromatography-mass spectrometry method. Microchem. J. 126 (2016) 466–473.
  - 166. F. Delfino, D. Dube. Persistent contamination of ground water by phenol. J. Environ. Sci. Health. 43 (1976) 345-355.
  - 167. L. Mandaric, M. Celic, R. Marcé, M. Petrovic Introduction on Emerging Contaminants in Rivers and Their Environmental Risk. In: Petrovic M., Sabater S., Elosegi A., Barceló D. (eds) Emerging Contaminants in River Ecosystems. The Handbook of Environmental Chemistry, 2005. Springer, Cham.
  - 168. J. Michałowicz, W. Duda, Phenols Sources and Toxicity. Polish J. of Environ. Stud. 16 (2007) 347-362.

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1135

1136

1137

1138

1139

1140

1141

1142

1143

1144 1145

.146

.147

.148

.149

1150	169. K. Ito, Y. Takayama, M. Ikedo, M. Mori, H. Taoda, Q. Xu, W. Hu, H. Sunahara, T. Hayashi, S. Sato, T. Hirokawa,
1151	K. Tanaka, Determination of some aliphatic carboxylic acids in anaerobic digestion process waters by ion-
1152	exclusion chromatography with conductimetric detection on a weakly acidic cation-exchange resin column. J.
1153	Chromatogr. A, 1039 (2004) 141–145.
1154	170. G. Boczkaj, M. Momotko, D. Chruszczyk, A. Przyjazny, M. Kamiński, Novel stationary phases based on
1155	asphaltenes for gas chromatography, J. Sep. Sci. 39 (2016) 2527-2536.
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# 1163 Tables

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# **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 <sub>2</sub> )	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 <sub>2</sub> )	-	10	220	Tenax TA	-	-	-	[45]
Acetone	12	-	60	4	260	Carbopack B / Carbosieve III	0.32 - 2.39 μg/L	< 13.4	-	[43]

**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	CHCl₃	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 <sub>4</sub>	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 <sub>8</sub> MIM][PF <sub>6</sub> ]	-	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-HSO₄	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]
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ratio)				
(MeOH-				
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**Table 3** Compilation of various types of solid-phase extraction procedures in the determination of O-VOCs in wastewater samples.

Extraction technique	Analytes	Sorbent	Derivatizati on	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 microspher es	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	formaldehy de	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- Hexylimida zolium) 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-	-	50°C / 15 min	260°C / 3 min	-	FID	0.47 – 9.01 μg/L	< 9.1	90 - 103	[104 ]
	phenols, aldehydes	PDMS-CAR-	-	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 <sub>3</sub> ), PCI-MS (CH <sub>4</sub> )	6 - 675 μg/L (FID), 2 - 6 μg/L (NCI-MS), 10 - 115 μg/L (PCI- MS)	< 16	-	[93]
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**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

# **Table5**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 <sub>6</sub> [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 <sub>16</sub> [44]
Phenols	4-chlorophenol [11], <i>n</i> -pentadecane [59,61], 1,1,3,3-tetramethoxypropane [29], N,N-diisopropylformamide [29], bisphenol-d <sub>16</sub> [79], [ $^{13}C_6$ ]-pentachlorophenol [82], phenol-d <sub>5</sub> [87], 2-chlorophenol-d <sub>4</sub> [87], 2,4-dimethylphenol-d <sub>3</sub> [87], 4-chloro-3-methylphenol-d <sub>2</sub> [87], 2,4-dichlorophenol-d <sub>3</sub> [87], 2-nitrophenol-d <sub>4</sub> [87], 2,4,6-trichlorophenol-d <sub>2</sub> [87], 4-nitrophenol-d <sub>4</sub> [87], 2,4-dinitrophenol-d <sub>3</sub> [87], pentachlorophenol- $^{13}C_6$ [87], 2-methyl-4,6-dinitrophenol-d <sub>2</sub> [87]
Carboxylic acids	2-ethylbutyric acid [37,90,93], margaric acid [51], heneicosanoic acid [52], anthracene-d <sub>10</sub> [53], 2- chlorobenzoic acid [64-65], triphenylphosphate [85]

**Table6**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 – 22900 μg/mL	o-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	MTBE	DHS-GC-MS	3 – 25 μg/mL	methyl <i>tert</i> -butyl ether (3 – 25 μg/mL)	[44]
wastewater	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 $\mu\text{g/L}),$ bisphenol A (7.94 $\mu\text{g/L})$	[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 <sub>3</sub> )	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	-	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- <i>tert</i> -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 $\mu$ g/mL), stearic acid (3.4 $\mu$ g/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, ketonesand 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	-	p-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)	
	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	МТВЕ	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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1203 Figures



Figure 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).



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).



1216Figure 3 Schematic diagram of the procedure for the determination of volatile oxygenated organic1217compounds in wastewater samples using gas chromatography ( $^{D}$  – detectors used for the determination1218of O-VOCs after derivatization).

		Advantages	Disadvantages	Recommendation	
	FID	- Inexpensive and widely available - Linear response of 10 <sup>6</sup> - Low maintenance requirements	- Lack of selectivity toward O-VOCs - Destructive	NO	
Detectors	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	<ul> <li>Not able to distinguish between isomers of a compound having the same m/z ratio</li> <li>Most easily interfaced with a low flow rate system</li> </ul>	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 <sup>6</sup> - 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	<ul> <li>Specific for halogens containing derivatives</li> <li>Selective for halogens, nitro groups, peroxides, quinonese</li> </ul>	- Large response to water - To obtain high sensitivity derivatization is required - Radioactive, - Easily contaminated	NO	
	PID	- Linear response of 10 <sup>7</sup> - 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	
	sulfur ds A	PD	Derivatization is required     Quadratic response to sulfur (need     of linearization)     Quenching	NO	
	ective for compoun	- High sensitivity after derivatization	Derivatization is required     Expensive     Quadratic response to sulfur (need     of linearization)	NO	
	Sele	CD	- Derivatization is required - Expensive	NO	

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