Handbook of Water Analysis

Leo M.L. Nollet, Leen S.P. De Gelder

Determination of Volatile Organic Compounds in Water

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# Determination of Volatile Organic Compounds in Water

Iván P. Román Falcó and Marta Nogueroles Moya

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21.1 Introduction

Volatile organic compounds (VOCs) are a group of chemicals that have high vapor pressure at room temperature. Their determination is of prime concern in analysis because VOCs are dangerous to humans and cause environment pollution. Many of these compounds are pollutants, not only contributing to environmental degradation processes such as stratospheric ozone depletion and tropospheric ozone formation, but also contaminating water reservoirs.

It is noteworthy that no agreement on the definition of VOCs exists. U.S. Environmental Protection Agency (EPA) defines VOCs as “any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions” (http://epa.gov/ttn/naaqs/ozone/ozonetech/def_voc.htm) [1]. However, a broader definition is based on volatilization processes related with physical and chemical properties such as vapor pressure and solubility. In those terms, VOCs are defined as organic compounds whose vapor pressure is greater than or equal to 13.3 Pa at 25°C, according to the ASTN test method D3960–90 [2] in the United States. Although in the European Union (EU), VOCs are organic compounds with vapor pressure above 10 Pa at 20°C (European VOC Solvents Directive 1999/13/EC) or any organic compound having an initial boiling point less than or equal to 250°C measured at a standard pressure of 101.3 kPa [3,4]. The partitioning process of a compound between the surface of a liquid and the headspace (HS) is said volatilization. So a volatile compound is an organic chemical which shows a great tendency to pass through the interface to the HS.

Referring to water, VOCs are among the most common pollutants found in groundwater [5]. VOCs often occur in trace levels in surface waters as a result of their volatility, while higher concentration can be found in groundwater. VOCs are components of agricultural products such as fumigants (chloroform, 1,3-dichloropropene, dichloropropane, 1,2-dibromomethane, 1,2-dichloroethane, trichloroethane, naphthalene, 1,2-dichlorobenzene, ethylene dibromide), as herbicides (1,4-dichlorobenzene, 1,2,4-trichlorobenzene) and as solvents for pesticides (xylenes), which contribute to soil pollution and, subsequently water contamination [6]. Great amounts of water are polluted by accidental leaks of ubiquitous petroleum derivatives. Other anthropogenic sources of VOCs include production, handling of solvents, paints, adhesives, deodorants, drugs, dyes, plastics, refrigerants, and so on. Trichloroethylene (used as degreaser) and tetrachloroethylene (industrial solvent) are persistent toxic pollutant. Migration from polymers, such as polymer pipes, polyacrylamide (which is used as flocculants in the treatment plants), polyethylene-teraphthalate, and so on contribute to drinking water pollution with compounds such as acrylamide, vinyl chloride, epichlorohydrin, aldehydes, ketones, esters, chlorinated compounds, and so on [7–9]. Natural sources of VOCs exist, for example, geosmin, 2-methyl isoborneol, trichloroanisoles, volatile organic sulfur compounds (VOSCs) (see Chapter 9) [10–14]. However, biological degradation of natural or anthropogenic compounds can also lead to formation of volatile compounds. Trihalomethanes (THMs: chloroform, bromoform, bromodichloromethane, and dibromochloromethane) are disinfection-by-products (DBP), which in current studies using compliant levels of THMs in water have revealed adverse reproductive effects. Aldehydes, haloketones, haloacetonitriles, haloacetic acids, chloral hydrate, and chloropicrin are other DBP of relevance.

Some VOCs have toxic, carcinogenic, and/or mutagenic effects to human beings, while others are persistent and show bioaccumulation. Besides their toxicity, VOCs are involved in odor and taste problems that are responsible from consumer complaints (due to BTEX, alcohols, aldehydes, trichloroanisoles, 2-MIB, geosmin, VOSCs, fuel oxygenates, etc.).

Leaking underground storage tanks pose significant environmental risks by spilling of petroleum products, such as gasoline, diesel fuel, and lubricating and heating oil [15,16], so testing methods were developed. A subgroup of contaminants related with petroleum pollution is the BTEX group, which consists of benzene, toluene, ethylbenzene, and the three isomers o-, m-, and p-xylene. Compared to the other main group of hydrocarbons present in gasoline, such as aliphatics, BTEX are very soluble in water, permitting their transfer to the groundwater [17]. Concentrations of BTEX have been found in surface water, groundwater, and drinking water from few micrograms per liter to higher concentrations [18–21]. Accidental emissions can lead to higher concentrations in groundwater. Because of the high
concentration of BTEX compounds in petroleum and the massive use of petroleum, products as energy source or solvents, and in the production of other organic chemicals, their presence in water creates a hazard to the environment and public health [22].

Short-chain halocarbons, volatile halogenated organic compounds (VHOCs), are another part of the VOCs group. Many of these compounds are used in the industry. A subset is formed by disinfection by-products such as THMs, haloacetonitriles, and so on. Volatile organic sulfur compounds (VOSCs) lead to unpleasant odor in water by action of microorganisms.

Recently a new group of compounds, such as ketones, alcohols, esters, and ethers, are regulated. Fuel oxygenates group (methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME), tert-butyl alcohol (TBA) and disopropyl ether) are added to gasoline instead of lead as no-knock agents. Fuel oxygenates contamination is a relatively recent concern [23]. MTBE was found responsible for taste and odor problems in drinking water, and there are also concerns about possible adverse health effects. The U.S. EPA recommends monitoring of oxygenate compounds in groundwater at leaking underground storage tank sites, and MTBE has been included in the final Unregulated Contaminant Rule [24,25].

Ketones (such as acetone, 2-butane (MEK), 4-methyl-2-pentane (MIBK), and 2-hexanone), alcohols (1-propanol, 2-propanol, and \( n \)-butanol), vinyl and ethyl acetate are incorporated in regulatory legislation.

### 21.1.1 Physicochemical, Toxicological, and Ecological Aspects

VOC compounds are a widely diverse group of compounds. VOCs are best selected in different groups according to their chemical structure. The characteristics of the group of interest should be known first of all, and further also the sample matrix to determine the best-suited method and the whole analytical procedure to be selected.

Volatile halogenated organic compounds include volatile chlorinated hydrocarbons and THMs. The BTEX compounds represent a homogeneous group of aromatic volatile hydrocarbons with similar physicochemical properties.

A better understanding of VOCs analysis can be achieved by knowing the particular physicochemical properties of each analyte (Table 21.1). Vapor pressure and the solubility provide an idea about the volatility, and hence the best-suited sample preparation technique for extraction among HS, purge and trap, solid-phase microextraction (SPME), and so forth.

The World Health Organization has issued guidelines for drinking water quality [26] on basis of risk assessments. Following analytes, benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichlorethane, hexachlorobutadiene, 1,1,2,2-tetrachlorethane, 1,1,2-trichlorethane, chloroform, 1,2-dibromoethane, tetrachlorethylene, trichlorethylene, and vinyl chloride, have been tentatively classified as known or suspected human or mammalian carcinogens. Giving a detailed guide of toxicological data and guideline values is not the purpose of this chapter, so the reader is referred to international toxicological associations [27–29] and toxicological databases [30–37].

### 21.1.2 Regulations

Over more than a decade, important progress has been made by several regulatory agencies that have put great emphasis on organic chemical regulations regarding water pollution. Several VOCs are included in the EPA Contaminant Candidate List 1 and 2 [38–40] and also in the corresponding European Community Priority Pollutant List I and II, as compounds to be monitored in water due to their health and environmental significance. Additionally, more VOCs (such as 1,1,1,2-tetrachlorethane, 1,1-dichlorethane, 1,2,3-trichlorepropane, 1,3-butadiene, etc.) that are currently not subject to any regulation under the Safe Drinking Water Act (SDWA) are included in Contaminant Candidate List 3, because they are known or anticipated to occur in public water system [41].

In the U.S. EPA Primary Drinking Water Regulations, maximum contamination levels (MCLs) were established for several compounds (for instance, 0.2 \( \mu \)g/L for 1,2-dibromo-3-chloropropene; 5 \( \mu \)g/L for benzene, carbon tetrachloride, 1,2-dichlorethane, trichlorethylene, and tetrachlorethylene; 1 \( \mu \)g/L for toluene, 0.7 \( \mu \)g/L for ethylbenzene, 10 \( \mu \)g/L for total xylenes, and 2 \( \mu \)g/L for vinyl chloride) [42].
### TABLE 21.1

Volatility of Some Organic Compounds

<table>
<thead>
<tr>
<th>CAS Number</th>
<th>Compound</th>
<th>Boiling Point (°C)</th>
<th>Vapor Pressure at 20°C (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>67-64-1</td>
<td>Acetone*</td>
<td>56.2</td>
<td>105 at 8°C</td>
</tr>
<tr>
<td>506-96-7</td>
<td>Acetyl bromide</td>
<td>76</td>
<td>80°F</td>
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<tr>
<td>75-36-5</td>
<td>Acetyl chloride</td>
<td>50.9</td>
<td>175°F</td>
</tr>
<tr>
<td>107-18-6</td>
<td>Allyl alcohol*</td>
<td>97.1</td>
<td>10 at 10°C</td>
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<tr>
<td>300-57-2</td>
<td>Allyl benzene*</td>
<td>156</td>
<td>5°F</td>
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<tr>
<td>106-95-6</td>
<td>Allyl bromide</td>
<td>70</td>
<td>150°F</td>
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<tr>
<td>107-05-1</td>
<td>Allyl chloride (3-chloropropene)</td>
<td>45</td>
<td>400 at 27.5°C</td>
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<tr>
<td>557-40-4</td>
<td>Allyl ether</td>
<td>94</td>
<td>20°F</td>
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<tr>
<td>557-31-3</td>
<td>Allyl ethyl ether</td>
<td>66</td>
<td>150°F</td>
</tr>
<tr>
<td>870-23-5</td>
<td>Allyl mercaptan</td>
<td>67</td>
<td>100 at 15°C</td>
</tr>
<tr>
<td>627-40-7</td>
<td>Allyl methyl ether</td>
<td>55</td>
<td>300°F at 25°C</td>
</tr>
<tr>
<td>1471-03-0</td>
<td>Allyl propyl ether</td>
<td>91</td>
<td>25°F</td>
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<td>Benzaldehyde*</td>
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<td>1-Bromobutane</td>
<td>101.6</td>
<td>40 at 25°C</td>
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<td>29576-14-5</td>
<td>1-Bromo-2-butene</td>
<td>98</td>
<td>70°F</td>
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<td>74-97-5</td>
<td>Bromochloromethane</td>
<td>68</td>
<td>100°F</td>
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<td>762-49-2</td>
<td>1-Bromo-2-fluorooetane</td>
<td>72</td>
<td>110°F</td>
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<tr>
<td>107-82-4</td>
<td>1-Bromo-3-methylbutane</td>
<td>120.5</td>
<td>12 at 15°C</td>
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<tr>
<td>106-94-5</td>
<td>1-Bromopropane</td>
<td>71</td>
<td>100 at 18°C</td>
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<td>7526-3</td>
<td>2-Bromopropane</td>
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<td>Bromotrichloromethane</td>
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<td>50°F</td>
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<td>109-79-5</td>
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<td>123-86-4</td>
<td>Butyl acetate</td>
<td>125</td>
<td>15°F</td>
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<td>71-36-3</td>
<td>n-Butyl alcohol*</td>
<td>117.2</td>
<td>4.4</td>
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<td>78-92-2</td>
<td>Sec-butyl alcohol*</td>
<td>99.5</td>
<td>12</td>
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<tr>
<td>75-65-0</td>
<td>Tert-butyl alcohol*</td>
<td>83</td>
<td>31</td>
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<td>109-69-3</td>
<td>n-Butyl chloride</td>
<td>78.4</td>
<td>80</td>
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<td>78-86-4</td>
<td>Sec-butyl chloride</td>
<td>68</td>
<td>100 at 14°C</td>
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<tr>
<td>507-20-0</td>
<td>Tert-butyl chloride</td>
<td>51</td>
<td>375°F at 30°C</td>
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<tr>
<td>628-81-9</td>
<td>Butyl ethyl ether</td>
<td>91.5</td>
<td>25°F</td>
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<td>123-72-8</td>
<td>Butyraldehyde*</td>
<td>75.7</td>
<td>71</td>
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<td>Butyryl chloride</td>
<td>102</td>
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<td>142-96-1</td>
<td>n-Butyl ether*</td>
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<td>Chloroacetone*</td>
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<td>25°F</td>
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<td>107-14-2</td>
<td>Chloroacetonitrile</td>
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<td>200°F</td>
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<td>Chlorocyclobutane</td>
<td>83</td>
<td>140°F</td>
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<tr>
<td>542-18-7</td>
<td>Chlorocyclohexane</td>
<td>143</td>
<td>10°F</td>
</tr>
<tr>
<td>930-28-9</td>
<td>Chlorocyclopentane</td>
<td>114</td>
<td>60°F</td>
</tr>
<tr>
<td>544-10-5</td>
<td>1-Chlorohexane*</td>
<td>134.5</td>
<td>20°F</td>
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<tr>
<td>543-59-9</td>
<td>1-Chloropentane</td>
<td>108</td>
<td>75°F</td>
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<tr>
<td>75-29-6</td>
<td>2-Chloropropane</td>
<td>35</td>
<td>450°F</td>
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<tr>
<td>540-54-5</td>
<td>1-Chloropropane</td>
<td>46.6</td>
<td>375°F</td>
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### TABLE 21.1 (continued)

Volatility of Some Organic Compounds

<table>
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<th>CAS Number</th>
<th>Compound</th>
<th>Boiling Point (°C)</th>
<th>Vapor Pressure at 20°C (torr)</th>
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<tbody>
<tr>
<td>590-21-6</td>
<td>1-Chloropropene</td>
<td>37</td>
<td>400 at 18°C</td>
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<td>557-98-2</td>
<td>2-Chloropropene</td>
<td>22.5</td>
<td>&gt;700</td>
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<td>95-49-8</td>
<td>2-Chlorotoluene&lt;sup&gt;b&lt;/sup&gt;</td>
<td>159</td>
<td>5&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>123-73-9</td>
<td>2-Butenal (crotonaldehyde)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>104</td>
<td>19</td>
</tr>
<tr>
<td>108-93-0</td>
<td>Cyclohexanol&lt;sup&gt;b&lt;/sup&gt;</td>
<td>161</td>
<td>1</td>
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<tr>
<td>78-75-1</td>
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<td>141.5</td>
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<td>1,3-Dibromopropane&lt;sup&gt;b&lt;/sup&gt;</td>
<td>167</td>
<td>3&lt;sup&gt;e&lt;/sup&gt;</td>
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<td>120</td>
<td>10&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>79-02-7</td>
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<td>90.5</td>
<td>45&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>120</td>
<td>20&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>1,2-Dichlorobutane</td>
<td>123.5</td>
<td>22&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
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<td>1,1-Dichlorobutane</td>
<td>115</td>
<td>16&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>17&lt;sup&gt;°&lt;/sup&gt;</td>
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<td>134</td>
<td>10&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>108</td>
<td>15&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>78-99-9</td>
<td>1,1-Dichloropropane</td>
<td>88</td>
<td>45&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>78-87-5</td>
<td>1,2-Dichloropropane</td>
<td>97</td>
<td>41</td>
</tr>
<tr>
<td>142-28-9</td>
<td>1,3-Dichloropropane</td>
<td>120.4</td>
<td>40&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>594-20-7</td>
<td>2,2-Dichloropropane</td>
<td>69.3</td>
<td>60&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>542-75-6</td>
<td>1,3-Dichloro-1-propene</td>
<td>108</td>
<td>39&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>78-88-6</td>
<td>2,3-Dichloro-1-propene</td>
<td>84</td>
<td>53 at 23°C</td>
</tr>
<tr>
<td>60-29-7</td>
<td>Diethyl ether&lt;sup&gt;&lt;a&gt;*&lt;/sup&gt;&lt;/sup&gt;</td>
<td>34.5</td>
<td>442</td>
</tr>
<tr>
<td>352-93-2</td>
<td>Diethyl sulfide</td>
<td>92</td>
<td>50&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>108-20-3</td>
<td>Diisopropyl ether</td>
<td>69</td>
<td>130</td>
</tr>
<tr>
<td>75-18-3</td>
<td>Dimethyl sulfide</td>
<td>38</td>
<td>420</td>
</tr>
<tr>
<td>141-78-6</td>
<td>Ethyl acetate&lt;sup&gt;&lt;a&gt;*&lt;/sup&gt;&lt;/sup&gt;</td>
<td>77</td>
<td>73</td>
</tr>
<tr>
<td>140-88-5</td>
<td>Ethyl acrylate&lt;sup&gt;&lt;a&gt;*&lt;/sup&gt;&lt;/sup&gt;</td>
<td>100</td>
<td>29</td>
</tr>
<tr>
<td>97-95-0</td>
<td>2-Ethyl-1-butanol&lt;sup&gt;b&lt;/sup&gt;</td>
<td>150</td>
<td>1.8</td>
</tr>
<tr>
<td>105-54-4</td>
<td>Ethyl butyrate</td>
<td>121</td>
<td>11.3</td>
</tr>
<tr>
<td>107-07-3</td>
<td>Ethylen chlorohydrin</td>
<td>128</td>
<td>4.9</td>
</tr>
<tr>
<td>109-94-4</td>
<td>Ethyl formate&lt;sup&gt;&lt;a&gt;*&lt;/sup&gt;&lt;/sup&gt;</td>
<td>54</td>
<td>192</td>
</tr>
<tr>
<td>75-08-1</td>
<td>Ethyl mercaptan</td>
<td>36</td>
<td>440</td>
</tr>
<tr>
<td>97-63-2</td>
<td>Ethyl metacrylate</td>
<td>117</td>
<td>15&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>110-43-0</td>
<td>2-Heptanone&lt;sup&gt;b&lt;/sup&gt;</td>
<td>150</td>
<td>2.6</td>
</tr>
<tr>
<td>106-35-4</td>
<td>3-Heptanone&lt;sup&gt;b&lt;/sup&gt;</td>
<td>148.5</td>
<td>1.4 at 25°C</td>
</tr>
<tr>
<td>123-19-3</td>
<td>4-Heptanone&lt;sup&gt;b&lt;/sup&gt;</td>
<td>144</td>
<td>1.2 at 25°C</td>
</tr>
<tr>
<td>78-84-2</td>
<td>Isobutyraldehyde&lt;sup&gt;a&lt;/sup&gt;</td>
<td>61.5</td>
<td>170</td>
</tr>
<tr>
<td>98-82-8</td>
<td>Isopropylbenzene&lt;sup&gt;b&lt;/sup&gt;</td>
<td>152.5</td>
<td>3.2</td>
</tr>
<tr>
<td>75-29-6</td>
<td>Isopropyl chloride</td>
<td>35.7</td>
<td>450&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>108-21-4</td>
<td>Isopropyl acetate</td>
<td>90</td>
<td>47.5</td>
</tr>
<tr>
<td>108-83-8</td>
<td>Isovalerone (diisobutyketone)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>165</td>
<td>1.7</td>
</tr>
<tr>
<td>513-36-0</td>
<td>Isobutyl chloride</td>
<td>69</td>
<td>100 at 16°C</td>
</tr>
<tr>
<td>590-86-3</td>
<td>Isovaleraldehyde</td>
<td>90</td>
<td>70&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>126-98-7</td>
<td>Methacrylonitrile&lt;sup&gt;a&lt;/sup&gt;</td>
<td>90.3</td>
<td>65 at 25°C</td>
</tr>
<tr>
<td>100-6v6-3</td>
<td>Methoxybenzene (anisole)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>155</td>
<td>5&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>96-33-3</td>
<td>Methyl acrylate&lt;sup&gt;a&lt;/sup&gt;</td>
<td>80</td>
<td>70</td>
</tr>
<tr>
<td>96-34-3</td>
<td>Methyl chloroacetate</td>
<td>130</td>
<td>10&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

continued
The main apolar and polar DBPs, THMs, and haloacetic acids, are regulated under Stage 1 and Stage 2 D/DBP rules by US EPA [39].

In Europe, the council Directive 98/83/CE (Drinking Water Directive) establishes the parameters and the parametric values to ensure the quality of drinking water supplied to the citizen [43]. VOCs regulated by 98/83/CE are acrylamide (0.10 μg/L), benzene (1.0 μg/L), 1,2-dichloroethane (3.0 μg/L), epichlorohydrin (0.1 μg/L), trichloroethylene and tetrachloroethylene (total amount 10 μg/L), THMs (total amount 100 μg/L from 2009), and vinyl chloride (0.5 μg/L).

Water pollution by discharges of certain dangerous substances is regulated by Directive 76/464/EEC in inland surface waters, territorial waters, inland coastal waters and ground water [44]. By this way, the Directive introduced the concept of List I and List II substances, listed in the Annex of the Directive. The purpose of the Directive is to eliminate the pollution from list I and to reduce the pollution from list II substances.

An ambitious water policy in the European Union started with the Water Framework Directive (WFD) in 2000 [45], but more specific legislation was needed regarding the priority substances. In 2008, the Directive 2008/105/EC was adopted with the aim of achieving good surface water chemical status, laying down environmental quality standards (EQS) for priority substances and certain other pollutants [46]. In 2007, the first stage in the implementation of the Water Framework Directive reported that the results were worst than expected of national water protection efforts illustrating the current

### Table 21.1 (continued)

<table>
<thead>
<tr>
<th>CAS Number</th>
<th>Compound</th>
<th>Boiling Point (°C)</th>
<th>Vapor Pressure at 20°C (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>74-95-3</td>
<td>Methylene bromide</td>
<td>98</td>
<td>36</td>
</tr>
<tr>
<td>78-93-3</td>
<td>Methyl ethyl ketone</td>
<td>79.6</td>
<td>77.5</td>
</tr>
<tr>
<td>74-88-4</td>
<td>Methyl iodide</td>
<td>42.5</td>
<td>400 at 25°C</td>
</tr>
<tr>
<td>563-80-4</td>
<td>Methyl isopropyl ketone</td>
<td>97.5</td>
<td>42 at 25°C</td>
</tr>
<tr>
<td>108-10-1</td>
<td>Methyl isobutyl ketone</td>
<td>119</td>
<td>6</td>
</tr>
<tr>
<td>80-62-6</td>
<td>Methyl methacrylate</td>
<td>101</td>
<td>38 at 25°C</td>
</tr>
<tr>
<td>557-17-5</td>
<td>Methyl propyl ether</td>
<td>38.5</td>
<td>400 at 22.5°C</td>
</tr>
<tr>
<td>107-87-9</td>
<td>2-Pentanone</td>
<td>101</td>
<td>13³</td>
</tr>
<tr>
<td>96-22-0</td>
<td>3-Pentanone</td>
<td>102</td>
<td>13</td>
</tr>
<tr>
<td>109-60-4</td>
<td>α-Propyl acetate</td>
<td>102</td>
<td>25</td>
</tr>
<tr>
<td>103-65-1</td>
<td>α-Propylbenzene</td>
<td>159</td>
<td>2.5</td>
</tr>
<tr>
<td>107-19-7</td>
<td>Propargyl alcohol</td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>123-38-6</td>
<td>Propionaldehyde</td>
<td>49</td>
<td>235</td>
</tr>
<tr>
<td>107-12-0</td>
<td>Propionitrile</td>
<td>97</td>
<td>40 at 22°C</td>
</tr>
<tr>
<td>107-03-9</td>
<td>α-Propyl-mercaptan</td>
<td>68</td>
<td>150³</td>
</tr>
<tr>
<td>79-03-8</td>
<td>Propionyl chloride</td>
<td>80</td>
<td>85³</td>
</tr>
<tr>
<td>917-00-3</td>
<td>1,1,1-Trichloroacetone</td>
<td>149</td>
<td>5³</td>
</tr>
<tr>
<td>76-02-8</td>
<td>Trichloroacetyl chloride</td>
<td>118</td>
<td>10³</td>
</tr>
<tr>
<td>10403-60-8</td>
<td>2,2,3-Trichlorobutane</td>
<td>144</td>
<td>5³</td>
</tr>
<tr>
<td>96-18-4</td>
<td>1,2,3-Trichloropropane</td>
<td>156</td>
<td>2</td>
</tr>
<tr>
<td>2567-14-8</td>
<td>1,1,2-Trichloropropylene</td>
<td>118</td>
<td>20³</td>
</tr>
<tr>
<td>354-58-5</td>
<td>1,1,1-Trichloro-2,2,2-trifluoroethane</td>
<td>46</td>
<td>275³</td>
</tr>
<tr>
<td>76-13-1</td>
<td>1,1,2-Trichloro-1,2,2-trifluoromethane</td>
<td>48</td>
<td>270</td>
</tr>
<tr>
<td>110-62-3</td>
<td>Valeraldehyde</td>
<td>103</td>
<td>50 at 25°C</td>
</tr>
<tr>
<td>108-05-4</td>
<td>Vinyl acetate</td>
<td>72</td>
<td>83</td>
</tr>
<tr>
<td>593-60-2</td>
<td>Vinyl bromide</td>
<td>15.8</td>
<td>&gt;700</td>
</tr>
<tr>
<td>109-93-3</td>
<td>Vinyl ether</td>
<td>28</td>
<td>&gt;600³</td>
</tr>
</tbody>
</table>

a Poor purging efficiency because of moderate solubility in water.
b Compounds show high retention times on GC chromatography.
c Vapor pressure estimated.
“distance to target” of national water protection efforts. Moreover, river basin management plans were due by December 2009 to bring further real improvements for the whole water system in the form of programs of measures, which must be operational by 2012 and deliver the environmental objectives of the Directive by 2015.

Sensitive and accurate analytical methods need to be developed in order to detect concentrations under the maximum permitted levels.

21.1.3 Analytical Process

The chemical measurement process is constituted by several steps: field sampling, sample handling, laboratory sample preparation, separation and quantitation, data handling and statistical evaluation, results interpretation and conclusion suggestion, and finally the required action [47].

21.1.3.1 Sampling and Preservation of Samples

The sample must be representative. Agitation should be avoided to minimize volatile-analyte losses. Duplicate samples should be collected and kept in an insulated container stocked with ice. The sample should be held at low temperature (4°C) and lower vapor pressure during transport and storage and analyzed as soon as possible. All samples must be analyzed within 14 days of collection. Physical, chemical, and biological processes may change the composition during transport and storage steps. An appropriate container must be used in order to avoid physical processes due to adsorption or diffusion into/through the container walls. Plastic containers may act as a sorbent, so glass containers are more suitable. Amber bottles and vials are apposite to avoid photo-degradation and Teflon cap or septa to prevent contamination. In addition, the bottle must be filled completely to have no HS. It is advisable to add sodium thiosulfate or ascorbic acid to treated water in order to prevent additional formation of halogenated compounds after sample collection [48–52]. Degradation by microorganisms may be minimized by lowering temperature, using a biocide (such as HgCl₂) or change sample pH to an acid or basic extreme [48,49].

21.1.3.2 Analytical Methods

Some traditional sample preparation techniques are time and tiresome, multiple steps procedures and use toxic solvents. The challenge of analytical chemistry is to develop coupled techniques with interfaced instruments and automated solvent-free procedures which give fast and reliable results.

Depending on the nature of analyte(s) of interest, sample preparation processes will be quite different. Several techniques have been reported in the literature for analysis of VOCs in water, but among all those, a suitable technique should accomplish three basic requirements:

• Detect a large number or analytes within a single run, with low costs and efficiently.
• Detect all compounds with the required limits of detection at or below μg/L levels—with high intra-day precision.
• Avoid false positives/negatives by unequivocally assuring the presence of analytes.

The technique of choice for the analysis of VOCs in water is gas chromatography (GC). Mass spectrometry is also applied in multicomponent analysis but suffers from some drawbacks. Because of the low concentrations in water (from ng/L to μg/L) and the established guideline values, extraction/preconcentration steps are indispensable/essential prior to the analysis. Two separate steps can be distinguished in the analytical scheme.

In the first step, the extraction/concentration process is carried out. The analytical chemist is challenged to develop a sample preparation technique coupled to the separation instruments allowing a fast and easy analysis without loses or contamination risks.

Each technique has its strength for specific analytes and analyte-matrix combination (measurand). Analytical procedures of VOCs can be classified according to the sample preparation technique. First of all it is worth mentioning that the analytes can be extracted from the liquid phase or from its HS (vapor
phase above the liquid). The extraction and/or preconcentration can be made by a gas, a liquid, or a solid. Organic compounds with high volatilities are often extracted by a gas. The most popular gas–liquid extraction methods for volatile compounds in water are static HS, purge and trap (P&T), and to a less extent close-loop stripping analysis (CLSA). In solid–liquid extraction a solid adsorbent (or a liquid absorbent phase linked to a solid support) is responsible for the extraction such as SPME, membrane extraction or stir bar sorptive extraction (SBSE). Membrane extraction techniques are also based on solid porous or absorbents and are widely applied in mass spectrometry and less in gas chromatography. Liquid–liquid extraction (LLE) has several drawbacks such as high limits of quantitation, large consumption of solvents, and consists of laborious and time-consuming procedures. Miniaturization/automation of the extraction process (liquid-phase microextraction [LPME] and single-drop microextraction [SDME]), renews the interest in liquid–liquid extraction SPME, SDME, and LPME can be performed in the HS getting cleaner extracts and avoiding fiber damages in SPME or avoiding drop detachment.

The second step is gas chromatographic analysis. The reader is referred to the next section for all the information related to columns, detectors, and operational conditions of the gas chromatograph for VOCs analysis.

### 21.1.3.3 Detectors, Columns and Gas Chromatography Conditions

#### 21.1.3.3.1 Detectors

Several detectors are used for VOCs analysis by GC: flame ionization detector (FID), photo ionization detector (PID), electron capture detector (ECD), electrolytic conductivity detector (ELCD), mass spectrometer detector (MSD or MS) and Fourier transform infrared detector (FTIRD). Readers are directed to in-depth reviews [53–55]. Current trends and developments in GC analysis of VOCs have been recently reviewed by the group of Dewulf [3,56]. Mass spectrometer detectors allow low detection limits in single/selected ion monitoring (SIM) and a qualitative confirmation by full scan mode or by means of other ion selected as qualifier.

Using a single column, retention times are not unique for every analyte. Coelutions are very common creating complex chromatograms that are difficult to interpret. Hence, a dual-column configuration or specific detectors (such as MSD) are required. In dual-column configuration, the sample band passes through a guard column, and is splitted between two different selectivity columns. The second analytical column is used for confirmatory purposes. However, the sensitivity is reduced to half.

Detectors can be connected in parallel, in series or in tandem to enhance the information about the sample. In parallel configuration, the eluting sample is split equally between two detectors, so half sensitivity is obtained in each detector. This configuration is used, for instance, with ECD and with the next explanation you will see that fits better an “and” FID (and so “in combination with MSD” should be deleted) to analyze BTEX and VHOCs simultaneously. There was a “not” missing, so the sentence without it made no sense at all. So, our proposal is to keep it like that: when other detection systems are not available such as MSD. When a series configuration is used the first detector must be no-destructive (e.g., PID). The eluting sample passes through the first detector and next reaches the second one. The main disadvantage lies in a broadening obtained in the peak from the second detector due to the dead volume in the connection between detectors. In tandem systems, two detectors (e.g., MS/MS) are connected without dead volume. The first detector is the base for the next detection.

#### 21.1.3.3.2 Columns

Different parameters affect column efficiency. The smaller is the internal diameter (i.d.), the better is the separation efficiency. However, sample capacity is decreased by decreasing the i.d. resolution efficiency increases with the square root of the column length, but the analysis time is increased and the carrier gas pressure must be increased to maintain the flow rate in the column. The thicker is the film, the longer the analytes are retained and the longer is the analysis time. For very volatile analytes is advisable to use long, thick film columns.

Column selection is based on the compound list, detector used and analytical method. Different columns have been used for VOCs separation as shown in Tables 21.2 through 21.5. Standardized analytical methods suggest the chromatographic column to be used.
### TABLE 21.2
Analysis of Volatile Organic Compounds by HS Extraction Techniques

<table>
<thead>
<tr>
<th>Extraction Technique</th>
<th>Analytes</th>
<th>Extraction Conditions</th>
<th>Extraction Instrument, Chromatographic Column and Detector</th>
<th>Figures of Merit and Remark</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS</td>
<td>34 VOCs</td>
<td>8 mL of sample. 12 mL of serum vials. Vials are heated in a water bath at 45°C for 40–45 min. 500 μL of the HS are removed with a gas-tight syringe and injected.</td>
<td>Chromatographic column: HP-VOC, 60 m × 0.32 mm i.d. 1.8 μm film thickness. Detector: MSD</td>
<td>Four sample preparation technique are compared (LLE, direct aqueous injection and P&amp;T). LODs ranged from 0.05 to 0.6 μg/L for CHCl3. Mean recoveries ranged from 34% (1,1-dichloropropene, carbon tetrachloride) to 128% (bromobenzene).</td>
<td>[171]</td>
</tr>
<tr>
<td>HS</td>
<td>Disinfection by-products (DBP)</td>
<td>8 mL of sample. 10 mL flat base HS vials. Vials are heated in a water bath at 45°C for 40 min. 500 μL of the HS are removed with a gas-tight syringe and injected.</td>
<td>Chromatographic column: HP-VOC, 60 m × 0.32 mm i.d. 1.8 μm film thickness. Detector: MSD</td>
<td>LODs 0.2 μg/L for CHCl3, 0.1 μg/L for CHBr3 and 0.05 μg/L for CHBrCl and CHBr3CI. LODs 5 μg/L for dichloroacetonitrile, 0.5 μg/L for trichloroaconitriole, 20 μg/L for bromochloroacetonitrile, 5 μg/L for 111-trichloropropane, 2.5 μg/L for 1,1-dichloropropane, 0.5 μg/L for chloropicrin. Others DBP were not recovered. Recovery range: 88.4–99.1% for THMs.</td>
<td>[172]</td>
</tr>
<tr>
<td>HS</td>
<td>53 VOCs (VHOCs, BTEX, alkylybenzenes, naphthalene,…)</td>
<td>Salt addition: KCl. Time of loop filling: 0.1 min</td>
<td>HS system: HP 7694 HS autosampler. Chromatographic column: DB-1701, 30 m × 0.32 mm i.d. Detector: MSD</td>
<td>Linearity: 0.5–100 μg/L. Mean correlation coefficient: 0.995. Not figures of merit available.</td>
<td>[5]</td>
</tr>
<tr>
<td>P&amp;T (needle-trap)</td>
<td>18 VOCs</td>
<td>Sample volume: 5 mL. Vial volume: 20 mL. Temperature 50°C. Extraction time: 30 min with agitation</td>
<td>Chromatographic column: TR-Meta. VOC 30 m × 0.25 mm i.d. 1.5 μm film thickness Detector: MSD (scan mode)</td>
<td>LODs: 0.01–0.03 μL/L. Linearity: LOQ = 50 μg/L (r² &gt; 0.96). RSDs: 2–13% (n = 3); 15–25% between NTD (n = 5). Recoveries: 50–98%.</td>
<td>[169]</td>
</tr>
</tbody>
</table>

continued
<table>
<thead>
<tr>
<th>Extraction Technique</th>
<th>Analytes</th>
<th>Extraction Conditions</th>
<th>Extraction Instrument, Chromatographic Column and Detector</th>
<th>Figures of Merit and Remark</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>P&amp;T</td>
<td>Dimethylsulfide (DMS), dimethyltrisulfide (DMTS), 2-isopropyl-3-methoxypyrazine (IPMP), 2-isobutyl-3-methoxypyrazine (IBMP), 2-methylisoborneol (MIB), β-cyclocitrinal, geosmin (GSM) β-ionone</td>
<td>Sample volume: 25 mL Trap: #07 Purge gas: N2 Purge flow: 40 mL/min Purge time: 12 min Sample temp. 55°C Desorp. temp. 180°C Desorp. time: 4 min (He)</td>
<td>P&amp;T system: a 4551A autosampler (OI Analytical Company, USA), a #07 trap (OI Analytical Company, USA) Chromatographic column: HP-5MS UI 30 m × 0.25 mm i.d., 0.25 μm film thickness Detector: MSD (SIM mode)</td>
<td>LODs (S/N = 3): &lt;1.5 ng/L Linearity: 1–500 ng/L (r &gt; 0.999, n = 8) RSDs: 3.38–8.59% (n = 5) Recoveries: 80.54–114.91%</td>
<td>[173]</td>
</tr>
<tr>
<td>P&amp;T</td>
<td>19 VOCs</td>
<td>Sample volume: Trap: Purge gas: He Purge flow: 40 mL min⁻¹ Purge time: 13 min Purge temp. Desorp. temp. 250°C Desorp. flow 300 mL min⁻¹ Desorp. time: 2 min</td>
<td>P&amp;T system: a 4552 Archon autosampler (Varian Instruments)-Velocity XPT (Teledyne Tekmar Instruments, OH, USA) Chromatographic column: VF-5 ms 30 m × 0.25 mm i.d., 0.25 μm film thickness Detector: QqQ-MSD</td>
<td>Recoveries: 73–124% Precision: &lt;24% LOQs: 0.1 μg/L</td>
<td>[174]</td>
</tr>
<tr>
<td>P&amp;T</td>
<td>VHOCs, BTEX, fuel oxygenates, geosmin, and 2-methylisoborneol</td>
<td>Sample Volume: 10 mL Trap: 2/3 Tenax GR and 1/3 Carbosieve S III Preconditioning: temp 60°C 500 rpm, 5 min. Purge flow: 60 strokes of 1 mL at 0.1 mL/s Desorp. temp. 300°C Desorp. flow: 10 μL/s (He)</td>
<td>Optic 3 programmed temperature vaporization injector with cryofocusing unit (Axel Semrau, Sprockhövel, Germany), and a Combi-PAL autosampler (Axel Semrau). Chromatographic column Restek Rtx-VMS 60 m × 0.32 mm i.d., 1.8 μm film thickness MSD (Scan mode).</td>
<td>LODs 0.001–0.07 μg/L Linearity: 0.1–2.1 μg/L for 1,4-dioxane to 0.002–4 μg/L for CHBrCl (r &gt; 0.998) RSDs: 5.1–8.9% (n = 49–84) Recoveries: 88–117% Extraction yield 7–50%</td>
<td>[175]</td>
</tr>
</tbody>
</table>
P&T Fuel oxygenates
Sample Volume: 25 mL
Trap: VOCARB 3000
Purge gas: N2
Purge flow: 40 mL/min
Purge time: 11 min
Purge temp. RT
Desorp. temp. 250°C
Desorp. time: 2 min

P&T THM
Sample Volume: 25 mL
Trap: VOCARB 4000
Purge gas: He
Purge flow: 40 mL/min
Purge time: 11 min
Purge temp. 30°C
Desorp. temp. 250°C
Desorp. time: 4 min

P&T 2,4,6-Trichloroanisole
Sample volume: 6 mL
Trap: Tenax GR
Purge gas: He
Purge flow: 0.3 L/min
Purge time: 30 min
Purge temp. 50°C
Desorp. temp. 280°C Curie Temp.
Desorp. time: 0.2 s

P&T Chlorofluorocarbons
CCl₃F (CFC-12), CCl₂F₂ (CFC-11) and C₂Cl₃F₃ (CFC-113)
Sample volume: 34 mL
Trap: molecular Unibeads 2S 80/100 mesh
Purge gas: He
Purge flow: 30 mL/min
Purge time: 270 s
Purge temp. Cryotrap temp. −78°C
Desorp. temp. 100°C
Desorp. time: 120 s

P&T AQUAtek 70 autosampler and a Velocity XPT. Chromatographic column: Restek Stabilwax (60 m × 0.32 mm i.d., film thickness 1 μm) GC-IRMS interfaced by a combustion oven
GC-Combustion 3Isotope-ratio-MSD for, C MAT 253 isotope ratio mass spectrometer for H

Method LODs for carbon isotope analysis 28, 5, and 375 μg/L, respectively for MTBE, TAME, and TBA;
Method LODs for hydrogen isotope analysis 25, 50, and 1250 μg/L, respectively for MTBE, TAME, and TBA

Comparison of samples by principal component analysis and cluster analysis

The separation of CFC-11, CFC-12 and CFC-113 occurs on the GC main column (80/100 mesh Carbopack B held in the GC oven at 140°C). ECD

Labmade P&T system. te-eluting compounds. The separation of CFC-11, CFC-12 and CFC-113 occurs on the GC main column (80/100 mesh Carbopack B held in the GC oven at 140°C). ECD

LODs (S/N = 3): 0.04 ng/L
Linearity: 0.12–120 ng/L (r² = 0.986, n = 6)
RSDs: <8.5% (n = 3)

Chlorofluorocarbons

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### TABLE 21.2 (continued)
Analysis of Volatile Organic Compounds by HS Extraction Techniques

<table>
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<th>Extraction Technique</th>
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<th>References</th>
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<tr>
<td>P&amp;T</td>
<td>17 Vocs</td>
<td>Sample volume: Trap: Carbox-pack B and Carbosieve III Purge gas: He Purge flow: Purge time: 12 min Purge temp: 60°C Desorp. temp: 260°C Desorp. time: 4 min</td>
<td>P&amp;T system: O.I. analytical P&amp;T concentrator (model 4560). OV-624 column 75 m × 0.25 mm i.d.</td>
<td>LODs: 0.32–2.39 μg/L Linearity: 5–35 μg/L ($r^2 &gt; 0.996$–0.999, $n = 7$), for acetone 60–240 μg/L RSDs: 2–13.4% ($n = 5$) Accuracies: 0.3–23.5% Recoveries: 80.54–114.91%</td>
<td>[180]</td>
</tr>
<tr>
<td>P&amp;T</td>
<td>THM, trichloroethylene, tetrachloroethylene, benzene and 1,2-dichloroethane</td>
<td>Sample volume: 5 mL Trap: VOCARB 3000 Purge gas: He Purge flow: 40 mL/min Purge time: 11 min Purge temp: RT Desorp. temp: 250°C Desorp. time: 1 min</td>
<td>Velocity XPT P&amp;T Sample Concentrador. VF-5 ms 30 m × 0.25 μm i.d., 0.25 μm film thickness</td>
<td>LODs: 0.008–0.7 μg/L Linearity: 2.5–100 μg/L THM, others 0.25–10 μg/L ($r^2 &gt; 0.994$–0.9996, $n = 8$) RSDs: 1–12% ($n = 10$) Recoveries: 80–119%</td>
<td>[181]</td>
</tr>
<tr>
<td>P&amp;T</td>
<td>THM</td>
<td>Sample volume: flow rate 2.5 mL/min 15 min Trap: TENAX-GR trap Purge gas: He Purge flow: 30 mL/min Purge temp: 65°C Desorp. temp: Desorp. time:</td>
<td>Pervaporation through a silicone capillary membrane contained within a gas extraction cell (GEC) followed by preconcentration using an adsorbent trap. Restek MXT-1 (30 m × 0.53 mm i.d., film thickness 1.50 μm (or 20 m × 0.53 mm i.d., film thickness 5.0 μm. Dry electrolytic conductivity detector</td>
<td>LODs: &lt;1.0 μg/L Linearity: 0.7–50 μg/L (except for CHBr,Cl 0.3–50 μg/L) ($r^2 0.994–0.999$ quadratic fit except CHBr3) RSDs: 1.2–2.8% ($n = 10$) Recoveries: 110–128%</td>
<td>[182]</td>
</tr>
</tbody>
</table>
Determination of Volatile Organic Compounds in Water

**P&T VOSCs: Methanethiol, DMS, DMDS.**
- Sample volume: 25 mL (diluted with 25 mL HCl)
- Trap: Tenax/silica gel/carbon molecular sieve (OI Analytical #10), Purge gas: Purge flow: Purge time: 10 min Purge temp: 20°C Desorp. temp: 190°C Desorp. time: 4 min
- P&T concentrator (O.I. Analytical 4560, College Station, Texas), and a vial autosampler (Tekmar-Dohrmann SOLATek 72, Mason, Ohio)
- DB-VRX 60 m × 0.25 mm film thickness 1.40 μm
- LODs: 4.8, 2.8, and 1.2 lg/L for methanethiol, DMS, and DMDS, respectively.
- Linearity: 5–500 μg/L ($r^2 > 0.99$)
- Recoveries: 81% for methanethiol, 100% for DMS, and 92% for DMDS

**P&T 2-Isopropyl-3-methoxypyrazine, 2-isobutyl-3-methoxypyrazine, 2-methylisoborneol, 2,4,6-trichloroanisole, geosmin**
- Sample volume: 20 mL
- Trap: Tenax trap
- Purge gas: He
- Purge flow: 35 mL/min
- Purge time: 20 min
- Salt addition: 5 g
- Desorp. temp: 250°C
- Desorp. time: 4 min
- Tekmar 3100 P&T concentrator and Aquatek 70 liquid autosampler
- DB-624 75 m × 0.53 mm i.d., film thickness 3 μm
- LODs: 0.2–2 ng/L
- Linearity: 10–200 ng/L
- RSD < 8%
- Recoveries: 80–103%

**P&T THM**
- Sample volume: 100 mL
- Trap: Rtx-5MS 30 m × 0.25 mm, film thickness 0.25 μm
- LODs: 1 μg/L
- Linearity: 0–80 μg/L
- RSDs: 2.63–30.35%

**P&T MTBE, MTBA, and BTEX**
- Sample volume: 5 mL
- Trap: Tenax-sigel-CMS 4560 adsorbent trap (O.I. Analytical)
- Purge gas: He
- Purge flow: 30 mL/min
- Purge time: 30 min
- Purge temp: 60°C
- Desorp. temp: 180°C
- Desorp. time: 4 min
- P&T system: PTI 4560 sample concentrator (O.I. Analytical TX, USA)
- Chromatographic column: HP-1, 60 m × 0.25 mm i.d., 1 μm film thickness
- Detector: quadrupole-MSD
- P&T optimization by experimental design (Optimal parameters: extrn. temp. 60°C, extrn. time: 30 min, no-salt addition)
- LODs: 2.6–23 ng/L
- Repeatability 4.4% at the highest conc. and 12% at the lowest conc.
- Linearity: Mandel’s fitting test
- Reproducibility (3-days): ANOVA test

continued
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<th>Extraction Technique</th>
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<tr>
<td>P&amp;T VHOCs (including THMs, 1,1,1-trichloroethane, tetrachloromethane, 1,1,2-trichloroethylene, and tetrachloroethylene)</td>
<td>Sample volume: 10 mL&lt;br&gt;Trap: Cold trap (a portion of a HP-1 column (15 cm × 0.53 mm, 2.65 μm))&lt;br&gt;Purge gas: He&lt;br&gt;Purge flow: 10 mL/min&lt;br&gt;Purge time: 10 min&lt;br&gt;Purge temp.: ATa&lt;br&gt;Trap temp. adsorp.: −100°C&lt;br&gt;Desorp. temp.: 200°C&lt;br&gt;Desorp. time:</td>
<td>P&amp;T system: Chrompack CP-4010&lt;br&gt;P&amp;T thermal desorption system (Midelburg, The Netherlands) equipped with a Chrompack Cryo-bath condenser&lt;br&gt;Chromatographic column: HP-5MS, 30 m × 0.25 mm i.d., 0.25 μm film thickness&lt;br&gt;Detector: quadrupole-MSD (SIM mode)</td>
<td>The effect of purge time, sample volume&lt;br&gt;LOD in the order of ng/L units</td>
<td>[187]</td>
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<tr>
<td>P&amp;T 27 VOCs (including BTEX, THMs, di- and trichlorobenzenes and hexachloro-1,3 butadiene...)</td>
<td>Sample volume: 60 mL&lt;br&gt;Trap: See Extraction instrument&lt;br&gt;Purge gas: He&lt;br&gt;Purge flow: 50 mL/min&lt;br&gt;Purge temp.: 45°C&lt;br&gt;Purge time: 20 min&lt;br&gt;Desorp. temp.: 275°C&lt;br&gt;Desorp. time: 15 min&lt;br&gt;Cryo. cooling −150°C Cryof. heated at 800°C until 260°C (kept 6 min)</td>
<td>P&amp;T system: water P&amp;T off-line and desorption on-line to GC. Sample vessel: (3.4 i.d., height 20 cm). Custom-made sorbent trap containing 17 cm Tenax TA, 6 cm Carboxen 1000 and 1 cm carboxen 1001 (Supelco, Bellerfonte, PA, USA). Chromatographic column: Rtx-502, 60 m × 0.32 mm i.d. 1.8 μm film thickness&lt;br&gt;Detector: quadrupole-MSD (SIM mode)</td>
<td>LODs: ranged from 0.15 ng/L to 6.57 ng/L for all VOCs, except for CH₂Cl₂ (0.15 ng/L), CH₂Cl₂ (19.74 ng/L), benzene (20.43 ng/L). Precision: &lt;12.9%, except for CH₂Cl₂ (103.1%) and benzene (26.0%). Accuracy: ranged from 82.9% to 103.9% (except for CH₂Cl₂, 54.4%, and benzene, 66.9%).&lt;br&gt;Migration study; From high density polyethylene (HDPE) 6 classes of compounds are found (antioxidants, esters, aldehydes, terpenoids and aromatic hydrocarbons). From cross bonded polyethylene (PEX): oxygenates and mainly MTBE. From Polystyrene chloride: hesanal, octanal, nonanal and decanal. From Threshold odor number (TON) HDPE and PEX show odor (TON ≥ 4)</td>
<td>[59]</td>
<td></td>
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<tr>
<td>P&amp;T VOCs migrated from pipes</td>
<td>Sample volume: 1000 mL&lt;br&gt;Trap: Tenax GR Adsrobent (60–80 mesh, Altech)&lt;br&gt;Purge gas: N₂&lt;br&gt;Purge flow: 100 mL/min&lt;br&gt;Purge time: 60 min&lt;br&gt;Purge temp.: 40°C&lt;br&gt;Trap temp. adsorp.: 55°C&lt;br&gt;Desorp. temp.: 180°C&lt;br&gt;Desorp. time: 4 min</td>
<td>P&amp;T system: ATD-400 instrument (Perkin Elmer) equipped with a Peltier cryofocussing Tenax GR trap. is used for trap desorption.&lt;br&gt;Chromatographic column: Chrompack CP Sil 13 CB, 25 m × 0.25 mm i.d. 1.2 μm film thickness.&lt;br&gt;Detector: quadrupole-MSD</td>
<td>LODs: ranged from 0.15 ng/L to 6.57 ng/L for all VOCs, except for CH₂Cl₂ (0.15 ng/L), CH₂Cl₂ (19.74 ng/L), benzene (22.05 ng/L), and 1,4-CH₂Cl₂ (20.43 ng/L). Precision: &lt;12.9%, except for CH₂Cl₂ (103.1%) and benzene (26.0%). Accuracy: ranged from 82.9% to 103.9% (except for CH₂Cl₂, 54.4%, and benzene, 66.9%).&lt;br&gt;Migration study; From high density polyethylene (HDPE) 6 classes of compounds are found (antioxidants, esters, aldehydes, terpenoids and aromatic hydrocarbons). From cross bonded polyethylene (PEX): oxygenates and mainly MTBE. From Polystyrene chloride: hesanal, octanal, nonanal and decanal. From Threshold odor number (TON) HDPE and PEX show odor (TON ≥ 4)</td>
<td>[8]</td>
<td></td>
</tr>
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</table>
Determination of Volatile Organic Compounds in Water

P&T 40 VOCs

Sample volume: 13 mL
Trap: both Tenax and Tenax-silicaGel-Charcoal
Purge gas: He
Purge flow: 35 mL/min
Purge time: 11 min
Purge temp. –
Desorp. temp. 225°C
Desorp. time: 3 min
Desorp. flow: 3 mL/min
Bake 8 min at 270°C

P&T system: Tekmar 3100 and Aquatek 70 Liquid Autosampler (Tekmar-Dohrmann)
Chromatographic column: DB-624 75 m × 0.53 mm i.d. 3 μm film thickness,
Detector: MSD (detection in SIM and Scan modes)
The injector was set in the splitless mode, and He flow was decreased from 3 to 1 mL/min in 1 min.
Sample volume and purge flow is optimized.
LODs: 0.002–0.1 μg/L
r 0.97–0.99
Precision: RSDs 2.1–10.5%

P&T 14/41 VOCs

Sample volume: 5 mL
Trap: Both VOCARB 3000 (see next reference for P&T conditions) and Tenax-silica gel-charcoal
Purge gas: He
Purge flow: 40 mL/min
Purge time: 11 min
Purge temp. AT
Desorp. temp. 180°C (preheat 175)
Desorp. time: 3 min
Desorp. flow: 30 mL/min
Bake 220°C for 10 min

P&T system: Hewlett Packard P&T concentrator 7695
Chromatographic column: HP-VOC, 60 m × 0.32 mm i.d. 1.8 μm film thickness,
Detector: ECD and MSD
LODs: 0.02–0.05 μg/L
Recoveries: from 85% for (1,1,1-trichloroethane) to 124%
(1,1,2-trichloroethane, CHBr3).
41 VOCs analyzed by P&T-GC-MSD
LODs: 0.01–0.25 μg/L
Recoveries: from 46% (n-propylbenzene) to 160% (CH2Cl2)
VOCs included in List I and II from 76/464/EEC Directive are analyzed in surface and treated wastewater in Greece

P&T 41 VOCs

Sample volume: 5 mL
Trap: VOCARB 3000
Purge gas: He
Purge flow: 44 mL/min
Purge time: 11 min
Purge temp. AT
Desorp. temp. 250°C (preheat 245)
Desorp. time: 3 min
Desorp. flow: 30 mL/min
Bake 260°C for 8 min

P&T system: Hewlett Packard P&T concentrator 7695
Chromatographic column: HP-VOC, 60 m × 0.32 mm i.d. 1.8 μm film thickness,
Detector: MSD

Four sample preparation technique are compared (LLE, direct aqueous injection and P&T)
14 VOCs analyzed by P&T-GC-ECD
LODs: 0.02–0.05 μg/L
Recoveries: from 85% for (1,1,1-trichloroethane) to 124%
(1,1,2-trichloroethane, CHBr3).
41 VOCs analyzed by P&T-GC-MSD
LODs: 0.01–0.25 μg/L
Recoveries: from 46% (n-propylbenzene) to 160% (CH2Cl2)
VOCs included in List I and II from 76/464/EEC Directive are analyzed in surface and treated wastewater in Greece

continued
### TABLE 21.2 (continued)

**Analysis of Volatile Organic Compounds by HS Extraction Techniques**

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<tr>
<td>P&amp;T</td>
<td>Disinfection by-products (DBP)</td>
<td>Sample volume: 5 mL Trap: VOCARB 3000 Purge gas: He Purge flow: 44 mL/min Purge time: 11 min Purge temp. AT Desorp. temp. 250°C (preheat 245) Desorp. time: 3 min Desorp. flow: 30 mL/min Bake 260°C for 8 min</td>
<td>P&amp;T system: Hewlett Packard P&amp;T concentrator 7695 Chromatographic column: HP-VOC, 60 m x 0.32 mm i.d. 1.8 μm film thickness, Detector: MSD</td>
<td>P&amp;T is appropriate for THMs analysis. LODs (0.01 μg/L for CHCl₃, CHBr₂Cl and CHBr₃ and 0.05 μg/L for CHBrCl₃) LODs 0.5 μg/L for dichloroacetonitrile, 1 μg/L for trichloroacetonitrile, 2 μg/L for bromochloroacetonitrile, 3 μg/L for 1,1,1-trichloropropanone and 10 μg/L for 1,1-dichloropropanone. Others DBP were not recovered.</td>
<td>[172]</td>
</tr>
<tr>
<td>P&amp;T</td>
<td>58 VOCs (VHOCs, Chlorobenzenes, chlorotoluene, volatile aromatic hydrocarbons, volatile eters, ...)</td>
<td>Sample volume: 25 mL Trap: Cold trap Purge gas: He Purge flow: 10 mL/min Purge time: – Purge temp. 50°C Trap temp. adsorp. –120°C Desorp. temp. 220°C Desorp. time: – Desorp. flow: – mL/min</td>
<td>P&amp;T system: Chrompack P&amp;T and multisampler. Cold trap of fused-silica capillary tubing (length 25 cm x 0.53 mm i.d.) coated by CP Sil 8 CB 5 μm film thickness. Chromatographic column: CP Sil 5 CB, 50 m x 0.32 mm i.d. 1.2 μm film thickness, Detector: ion-trap-MSD</td>
<td>LODs ranged from 0.001 to 0.01 μg/L r ≥ 0.99 Review of the results of the main rivers in the Netherlands.</td>
<td>[189]</td>
</tr>
<tr>
<td>P&amp;T</td>
<td>BTEX, n-pentane, n-hexane, cyclohexane, n-heptane, dichloromethane, trichloromethane, tetrachloromethane, 1,2-dichloroethane, acetone, ether, ethyl acetate, and n-propanol</td>
<td>Sample volume: – Trap: purified multi-walled carbon nanotubes, carbopack B and VOCARB 3000 were compared Purge gas: N₂ Purge flow: 40 mL/min Purge time: 11 min Purge temp.C Trap temp. adsorp. 35°C Desorp. temp. 250°C Desorp. time: – Desorp. flow: –</td>
<td>P&amp;T system: ENCON P&amp;T system (EST Co, OH, USA) Chromatographic column: DB-624, 70 m x 0.53 mm i.d. 3 μm film thickness, Detector: FID</td>
<td>Purified multi-walled carbon nanotubes were evaluated as adsorbent for P&amp;T. This material had higher breakthrough volumes than carbopack B. The recoveries obtained with this material ranged from 80 to 110%, and were not affected by the humidity of the purge gas.</td>
<td>[159]</td>
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<tr>
<td>P&amp;T</td>
<td>55 VOCs</td>
<td>25 mL</td>
<td>–</td>
<td>He</td>
<td>40 mL/min</td>
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<tr>
<td>P&amp;T</td>
<td>Geosmin and 2-MIB</td>
<td>20 mL</td>
<td>Tenax-silica gel-SP2100</td>
<td>He</td>
<td>45 mL/min</td>
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<tr>
<td>P&amp;T</td>
<td>BTEX</td>
<td>2.0 mL (P&amp;T 5 mL)</td>
<td>N2 20 psi (spray by N2) and 0.5 bar (spray extraction chamber)</td>
<td>N2</td>
<td>30 mL/min</td>
</tr>
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In the light of the results, the authors suggest that weighted second-order models for calibration curves must be used, to define properly LODs and measure unknown samples.

Purge efficiency for 2-MIB of 19% and for geosmin of 84%.

Linearity: P&T and S&T: 10–50 μg/L
S&T LODs: ranged from 0.93 to 1.71 μg/L
P&T LODs: ranged from 0.51 to 1.88 μg/L
S&T R² better than 0.990
P&T R² better than 0.996
S&T RSDs (%) 0.7–7.3%
P&T RSDs (%) 0.6–6.3%

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\( ^a \) AT, ambient temperature.
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<td>HS-SPME</td>
<td>10 Chlorobenzenes (Volatile chloro-, dichloro- and trichlorobenzenes)</td>
<td>SPME fiber coated with 100-μm PDMS</td>
<td>Chromatographic column: DB-1, 30 m × 0.32 mm 0.25 μm film thickness, Detection: MSD</td>
<td>LOD below 0.006 μg/L. Linearity ranged from 0.02 to 20 μg/L. RSDs ranged from 1.19% to 8.19%. Recovery &gt; 90%,</td>
<td>[223]</td>
</tr>
<tr>
<td>HS-SPME</td>
<td>23 VOCs</td>
<td>SPME fiber coated with 75 μm CAR/PDMS, Sample volume: 4 mL (10 mL) Vial volume: 10 mL (20 mL) Salt addition: 0.4 g (1 g) Extraction time: 30 min Extraction temp. 50°C Desorp. temp. 280°C Desorp. time: 5 min</td>
<td>Chromatographic column: BP624 30 m × 0.25 mm i.d., 1.4 μm film thickness Detection: MS-MS (SRM and pseudo-SRM)</td>
<td>LOQs (S/N = 3): &lt;0.1 μg/L Linearity: 0.05–1 μg/L (low conc. level), 1–25 μg/L (intermediate) and 10–100 μg/L (high conc. level) (r &gt; 0.99) RSDs: &lt;20% Recoveries: 70–120%</td>
<td>[224]</td>
</tr>
<tr>
<td>HS-SPME</td>
<td>VOSC DMS, DMDS, DMTS</td>
<td>SPME fiber coated with 100 μm PDMS Sample volume: 15 mL Vial volume: 20 mL Salt addition: 2.5 g Na2SO4 Extraction time: 5 min Extraction temp. 30°C Desorp. temp. 200°C Desorp. time: 2 min</td>
<td>Chromatographic column: ZB-5 30 m × 0.25 mm i.d., 1.0 μm film thickness Detection: MSD</td>
<td>LODs: 50–240 ng/L. Linearity (r² &gt; 0.988). RSDs: 3–7% Recoveries: 94–122%</td>
<td>[225]</td>
</tr>
<tr>
<td>HS-SPME</td>
<td>23 VOCs (THMs, BTEX, MTBE, epichlorohydrin, vinyl chloride and chlorinated solvents)</td>
<td>SPME fiber coated with 75 μm Carboxen-PDMS Sample volume: 10 mL Vial volume: 20 mL Extraction time: 15 min Extraction temp. 20°C Desorp. temp. 250°C</td>
<td>Chromatographic column: CP Select 624 CB 30 m × 0.25 mm i.d., 1.4 μm film thickness Detection: MSD (Scan, extracted ion chromatogram)</td>
<td>LODs: 0.06–0.17 μg/L. Linearity 0.25–5 μg/L (r² 1.000–0.993). RSDs: 8.59–16.53% Recoveries: 85–125.2% (except tetrachloroethylene drinking water 145%)</td>
<td>[226]</td>
</tr>
</tbody>
</table>
Determination of Volatile Organic Compounds in Water

Inside needle capillary adsorption trap (INCAT) or in-tube extraction

- BTEX Sorbent Porapak Q
  - Sample volume: 8 mL
  - Vial volume: 16 mL
  - Salt addition: 0.4 g (1 g)
  - Extraction time: 20 min (0.4 mL/min)
  - Extraction temp. 40°C
  - Desorp. temp. 270°C

- Chromatographic column: DB-1 30 m × 0.53 mm i.d., 3 μm film thickness. FID
- LOQs 0.019–0.125 μg/L
- Linearity: 0.2–100 (or 200 depending on BTEX) μg/L (r² 0.998–0.999)
- RSDs: <20%
- Recoveries: 70–120%

HP-SPME

- BTEX
  - SPME fiber coated with 100-μm PDMS
  - Extraction time: 7 min
  - Extraction temp. 25°C
  - Desorp. temp. 180°C for 3 min (1.5 valve closed)

- Chromatographic column: CP-SIL 13 CB, 25 m × 0.32 mm 1.2 μm film thickness, Detection: FID

HP-SPME

- 26 VOCs (THMs, BTEX, MTBE, Geosmin, 2-MIB, 1,4-dioxane, trichloroethylene, tetrachloroethylene, carbon tetrachloride, 1,2-dichloroethane, ...)

- SPME fibers coated with CAR/PDMS, DVB/PDMS and 100-μm PDMS
  - 100-μm PDMS was the best fiber to obtain a wide linearity range for the target compounds.
  - Sample volume 10 mL
  - Vial volume: 20 mL
  - Extraction time: 30 min
  - Extraction temp. 60°C
  - NaCl addition 3 g
  - Desorp. temp. 270°C for 1 min

- Automatic SPME device (MPS2) (Gerstel GmbH, Müllheim a/d Ruhr, Germany).
- Chromatographic column: DB-1, 60 m × 0.25 mm i.d. 1.0 μm film thickness
- Detection: MSD

- LODs: ranged from 0.01 to 0.05 μg/L for 22 VOCs, 0.01 μg/L for MTBE, 1.2 μg/L for 1,4-dioxane, 0.6 ng/L for 2-MIB and 0.3 ng/L for geosmin.
- Recoveries in river water of 22 VOCs at 1 μg/L ranged from 93.7 to 104.0% with RSDs ranged from 1.7 to 9.5%
- Recoveries of 1,4-dioxane, 2-MIB and geosmin at 5 μg/L, 10 ng/L and 10 ng/L were 109.1, 95.9 and 97.4% respectively with 2.0, 5.6 and 1.8% of RSDs
- Linearity ranged from 0.1 to 100 μg/L for 21 VOCs and MTBE, 0.1 to 50 μg/L for m,p-xylene, 5 to 100 μg/L for 1,4-dioxane, and 1 to 100 ng/L for 2-MIB and geosmin.

continued
<table>
<thead>
<tr>
<th>Extraction Technique</th>
<th>Analytes</th>
<th>Extraction Conditions</th>
<th>Chromatographic Column and Detector</th>
<th>Figures of Merit and Remark</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS-SPME</td>
<td>Fuel oxygenates and BTEX</td>
<td>SPME fiber coated with 65-μm PDMS-DVB is selected</td>
<td>Chromatographic column: HP-1, 30 m x 0.32 mm 0.25 μm film thickness, Detection: FID</td>
<td>Experimental design to optimize LODs: ranged from 0.02 (toluene, ethylbenzene and xylenes) to 1.1 μg/L (MTBE). RSDs from 2.6% (benzene) to 8.5% (ethylbenzene).</td>
<td>[229]</td>
</tr>
<tr>
<td>HS-SPME</td>
<td>BTEX, Chlorobenzenes (chlorobenzene, dichlorobenzene and trichlorobenzene) and styrene</td>
<td>SPME fiber coated with 7 and 100 μm PDMS, 85 μm PA, PDMS/DVB and PDMS/DVB/CAR were tested.</td>
<td>Chromatographic column: DB-624, 30 m x 0.53 mm i.d. 3 μm film thickness, Detection: FID</td>
<td>HS-SPME is compared with CLSA. The best analytical conditions: PDMS/DBV/CAR fiber using a HS-SPME at 50°C for 20 min without stirring. LODs ranged from 15 ng/L (benzene) to 260 ng/L (trichlorobenzene). Extraction optimization: Salt addition, extraction time and desorp. Temp. Method tested in different matrixes: surface, tap and mineral water. LODs 14 ppt RSDs ranged from 2 to 8 μg/L. Recovery ranged from 96% to 104% Linearity: 0.05–20 ppb with r = 0.999</td>
<td>[230]</td>
</tr>
<tr>
<td>HS-SPME</td>
<td>MTBE</td>
<td>SPME fiber coated with 30 μm DVB/CAR/PDMS, Sample volume: 10 mL Vial volume: 20 mL Salt addition: 2.5 g Extraction time: 15 min Extraction temp. AT Desorp. temp. 250°C Desorp. time: 4 min</td>
<td>Chromatographic column: VOCOL, 30 m x 0.25 mm 1.5 i.d. film thickness Detection: MSD (SIM used for quantitation)</td>
<td></td>
<td>[231]</td>
</tr>
</tbody>
</table>
### SPME and HS-SPME

**Polar VOCs (methanol, ethanol, n-propanol, i-butanol, n-butanol, methyl acetate, ethyl acetate and butyl acetate)**

- **SPME**
  - Fiber coated with 85 μm PA
  - Direct SPME:
    - Sample volume: 1.3 mL
    - Vial volume: 2 mL
    - Salt addition: 0.35 g/mL
    - Extraction time: 20 min
    - Extraction temp. AT
    - Desorp. temp. 250°C
    - Desorp. time: 2 min
  - Chromatographic column: SPB-5, 60 m × 0.53 mm i.d. 5 μm film thickness
  - Detection: FID
  - Linearity: 4.25–425 ppm
  - RSDs ranged from 0.6 to 6.0%

- **HS-SPME**
  - Sample volume: 1.3 mL
  - Vial volume: 4 mL
  - Salt addition: 0.35 g/mL
  - Extraction time: 10 min
  - Extraction temp. 50°C
  - Above mentioned desorp. condition
  - Chromatographic column: HP-5MS, 30 m × 0.25 mm i.d. 0.25 μm film thickness
  - Detection: MSD (SIM)
  - LODs range from 0.022 to 0.16 ng/L
  - Linearity from 0.1, 0.2 or 0.5 to 100 ng/L
  - Recovery: 89% to 109% at 1 ng/L
  - RSD: 0.80 to 3.7% at 1 ng/L

### SBSE

**Off-flavor compounds (geosmin, 2-MIB and 2,4,6-trichloroanisole)**

- **Stir bar**: 10 mm length, coated with 500 μm layer of PDMS
- The selected mode was SBSE versus HS sorptive extraction.
- Extraction temp.: 25°C
- Extraction times: 60, 120, and 240 min, respectively for 20, 40, and 60 mL of sample

- Chromatographic column: HP-5MS, 30 m × 0.25 mm i.d. 0.25 μm film thickness
- Detection: MSD (SIM)
- Extraction LODs range from 0.022 to 0.16 ng/L
- Linearity from 0.1, 0.2 or 0.5 to 100 ng/L
- Recovery: 89% to 109% at 1 ng/L
- RSD: 0.80 to 3.7% at 1 ng/L
### Table 21.4
Analysis of VOCs by Membrane Extraction Techniques

<table>
<thead>
<tr>
<th>Extraction Technique</th>
<th>Analytes</th>
<th>Extraction Conditions</th>
<th>Chromatographic Column and Detector</th>
<th>Figures of Merit and Remark</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynamic membrane extraction</td>
<td>BTEX, chlorobenzene and trichloroethylene</td>
<td>Membrane material: silicone fiber i.d. 700 μm, o.d. 800 μm; Length: 30 cm; Sample temp. 15–20°C; Sample volume: 9.3–280 mL; Contact time 560 s; Stripping gas: air; Stripping gas flow: 55–60 mL/min; Desorp. temp. 350°C; Desorp. time: 180 s</td>
<td>Chromatographic column: DB-624, 10.3 m x 0.2 mm i.d.; 1.12 μm film thickness; Detection: FID</td>
<td>The combination of dynamic membrane extraction with mobile gas chromatograph allows field analysis of VOCs. LODs ranged from 0.1 to 1.0 μg/L using a water flow-rate of 30 mL/min. Linear range depended on the water flow-rate: 5–250 μg/L (1 mL/min), 1–50 μg/L (10 mL/min) and 1–20 μg/L (30 mL/min) with ( r &gt; 0.992 ). Reproducibility: RSDs &lt; 10% (except trichloroethene ~12%) and flow-rate independent.</td>
<td>[237]</td>
</tr>
<tr>
<td>HS-MESI</td>
<td>Benzene, toluene, ethylbenzene, o-xylene and trichloroethylene</td>
<td>Membrane material: 4 cm-long hollow fiber silicone membrane. i.d. 700 μm, Wall thickness: 165 μm; Sample temp. 25°C; Sample volume: 1 L; Trapping time 4 min; Stripping gas: air; Desorp. temp. 350°C; Desorp. time: 2 s</td>
<td>Chromatographic column: SPB-5, 5 m x 0.32 mm i.d.; 1 μm film thickness; Detection: FID</td>
<td>The system is composed by a membrane extraction probe, a sorbent interface and GC. Linearity: 1 μg/L to 5 mg/L ( r^2 ) ranged from 0.9831 to 0.9998. RSDs below 7%.</td>
<td>[239]</td>
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</tbody>
</table>
## TABLE 21.5
Analysis of Volatile Organic Compounds by Solvent Extraction Techniques

<table>
<thead>
<tr>
<th>Extraction Technique</th>
<th>Extraction Conditions</th>
<th>Chromatographic Column and Detector</th>
<th>Figures of Merit and Remark</th>
<th>References</th>
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</thead>
<tbody>
<tr>
<td>HS-SDME</td>
<td>Extracting solvent: Toluene, n-hexane, n-heptane were tested. Toluene was selected. Internal standard 1,4-DBB Vial volume 15 mL Drop volume 2.5 μL Sample volume 10 mL Stirring 1000 rpm Salt addition: NaCl 30% (w/v) Extraction temp. 22°C Extraction time 5 min</td>
<td>HP-5MS, 30 m × 0.25 mm i.d. 0.25 μm film thickness, Detection: MSD (SIM for acquisition and quantitation). Scan mode was used to identification of all target compounds based in the MS spectra and retention times</td>
<td>LODs from 0.003 to 0.031 μg/L ( r ) from 0.9901 to 0.9971 (except for hexachlorobenzene ( r = 9886 )) Recoveries from 84 to 99% in tap water and from 82 to 102% in well water RSDs from 2.1 to 13.2% ( (n = 5) )</td>
<td>[265]</td>
</tr>
<tr>
<td>SDME</td>
<td>Extracting solvent: hexane Vial volume—mL Drop volume: 2 μL Sample volume:—mL Extraction temp.:25°C Extraction time: 15 min SPME fiber coated with 100 μm PDMS</td>
<td>SB-1, 60 m × 0.25 mm i.d. 0.25 μm film thickness, Detection: ECD</td>
<td>Comparison of SPME (100 μm PMDS fiber) with SDME for the extraction of THMs. The same conditions were applied in both extractions (temperature, time and sample volume). LODs obtained for SDMEs are 8–10 times higher than SPME. ( r^2 ) from 0.979 to 0.997 for SDME and from 0.992 to 0.996 for SPME RSDs &lt; 5.1% for SDME and &lt; 3.4% for SPME</td>
<td>[270]</td>
</tr>
<tr>
<td>HS-SDME</td>
<td>Extracting solvent: 1-octanol, decane, and dodecane were tested. Decane was selected. Vial volume 8 mL Drop volume 2 μL containing the derivatizing agent Sample volume 4 mL Stirring 1100 rpm Extraction temp. 30°C Extraction time 6 min</td>
<td>HP-5MS, 30 m × 0.25 mm i.d. 0.25 μm film thickness, Detection: MSD (SIM mode)</td>
<td>Extraction and derivatization optimization: solvent, extraction temp., extraction time, stirring rate, drop volume and HS volume. LODs ranged from 7.3 to 10.6 μg/L ( r^2 ) from 0.995 to 0.998 Recoveries ranged from 84 to 92% RSDs ranged from 7.3 to 10.6%</td>
<td>[98]</td>
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continued
### TABLE 21.5 (continued)

Analysis of Volatile Organic Compounds by Solvent Extraction Techniques

<table>
<thead>
<tr>
<th>Extraction Technique</th>
<th>Analytes</th>
<th>Extraction Conditions</th>
<th>Chromatographic Column and Detector</th>
<th>Figures of Merit and Remark</th>
<th>References</th>
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</thead>
<tbody>
<tr>
<td>HS-SDME</td>
<td>MTBE</td>
<td>Extracting solvent: benzyl alcohol</td>
<td>Chromatographic column: DB-5, 20 m × 0.53 mm i.d. 1.5 μm film thickness, Detection: FID</td>
<td>Extraction optimization: solvent, extraction time, salt concentration, sample and microdrop volumes, stirring rate, sample and microsyringe needle temperature. LODs 0.06 μg/L Linearity: 0.1–500 μg/L r² 0.999 Recoveries 103–107% RSDs 4.88%</td>
<td>[95]</td>
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<td></td>
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<td>Internal standard toluene</td>
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<td>Vial volume 10 mL</td>
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<td>Drop volume 2 μL</td>
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<td>Sample volume 6 mL</td>
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<td>Stirring 1000 rpm</td>
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<td>Salt addition: NaCl 30% (w/v)</td>
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<td>Extraction temp. 35°C</td>
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<td>Extraction time 7.5 min</td>
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<td>Microsyringe needle temp. –6°C</td>
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<tr>
<td>HS-SDME</td>
<td>BTEX</td>
<td>Extracting solvent: (n)-hexadecane</td>
<td>Chromatographic column: HP-5, 30 m × 0.25 mm i.d. 1.0 μm film thickness, Detection: FID</td>
<td>Extraction optimization: extraction temp., extraction time, stirring rate, drop volume and HS/sample volume. LODs ranged from 0.72 to 5.0 μg/L r² from 0.9991 to 0.9994 RSDs ranged from 6.9 to 9.6% without internal standard, and from 2.7 to 5.9% with internal standard</td>
<td>[96]</td>
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<td></td>
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<td>Internal standard: ethyl acetate</td>
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<td>Vial volume 2 mL</td>
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<td>Drop volume 1 μL</td>
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<td>Sample volume 1.5 mL</td>
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<td>Stirring 1200 rpm</td>
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<td>Extraction temp. 23°C</td>
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<td>Extraction time 6 min</td>
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<tr>
<td>HS-SDME</td>
<td>BTEX</td>
<td>Extracting solvent: 1-octanol</td>
<td>Chromatographic column: Restek XTI-5, 30 m × 0.25 mm i.d. 0.25 μm film thickness, Detection: quadrupole-MSD (SIM used to determine LODs) For kinetic studies: Chromatographic column: SPB-1, 30 m × 0.32 mm i.d. 0.25 μm film thickness, Detection: FID</td>
<td>Kinetic study of the extraction: determination of the diffusion coefficients. Evaluation of stirring rate. r² 0.99 for benzene and 0.98 for toluene, ethylbenzene and (o)-xylene. RSDs ranged from 9 to 11% for extraction time 1 min. RSDs decreased to 1–2% for extraction time 5 min (closer to equilibrium)</td>
<td>[272]</td>
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<tr>
<td></td>
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<td>Internal standard: decane</td>
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<td>Vial volume 1 mL</td>
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<td>Drop volume 1 μL</td>
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<td>Sample volume 0.5 mL</td>
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<td></td>
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<td>Stirring 1000 rpm</td>
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<td></td>
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<td>Extraction temp. 25°C</td>
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<td>Extraction time 5 min</td>
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</tbody>
</table>
Determination of Volatile Organic Compounds in Water

**HS-SDME THMs**

Extracting solvent: xylene, ethylene glycol, and 1-octanol were tested. 1-octanol was selected.
Internal standard: hexachloroethane
Vial volume 40 mL
Drop volume 1 μL
Sample volume 25 mL
Salt addition: 0.3 g/mL
Stirring: 800 rpm
Extraction temp. 20°C
Extraction time 10 min

Chromatographic column: HP-5, 30 m × 0.32 mm i.d.
1 μm film thickness,
Detection: ECD

Extraction optimization: HS volume, extraction time, stirring rate, salt addition and extraction temperature.
LODs ranged from 0.15 (CHBr₂Cl and CHBr₂Cl₂) to 0.4 μg/L
r² ranged from 0.9980 to 0.9992
Recoveries ranged from 101 to 112%.
RSDs at 10 μg/L <10%

**HS-SDME Geosmin**

Extracting solvent: 1-octanol, 1-hexanol, and benzonitrile were tested. 1-hexanol was selected.
Internal standard: 1-decene
Vial volume 7 mL
Drop volume 1.5 μL
Sample volume 5 mL
Salt addition: saturated
Stirring max stirring rate
Extraction temp. 40°C
Extraction time 15 min

Chromatographic column: HP-5MS, 30 m × 0.25 mm i.d. 0.25 μm film thickness
(splitless injection)
Detection: quadrupole-MSD
(SIM mode for quantitation)

Extraction optimization (one-at-the-time): solvent selection, drop volume, extraction temp., stirring rate, ionic strength, sample volume and extraction time.
LODs 0.8 μg/L
r² > 0.998
RSDs < 5%

**HS-HF-LPME Dimethylselenide (DMSe) and dimethyldiselenide (DMDSe)**

Extracting solvent: 1-decanol. Ethyl benzene as internal std
Vial volume 15 mL
Drop volume 3 μL
Sample volume 10 mL
Stirring 1000 rpm
Extraction temp. 30°C
Extraction time 5 min
Sampling continuous mode at a speed of 20 μL/min at 0°C

Chromatographic column: DB 624 60 m × 0.25 mm i.d., 1.4 μm film thickness
Detection: MSD

LODs: 65 ng/L DMSe 57 ng/L DMDSe
Linearity: 0.5–590 μg/L (r² 0.98) for DMSe, 0.4–480 μg/L (r² 0.99) for DMDSe
RSDs 4.8% for DMSe, 3.9% for DMDSe
Enrichment factors: 1250 for DMSe and 1170 for DMDSe

continued
### TABLE 21.5 (continued)

<table>
<thead>
<tr>
<th>Extraction Technique</th>
<th>Analytes</th>
<th>Extraction Conditions</th>
<th>Chromatographic Column and Detector</th>
<th>Figures of Merit and Remark</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF-LPME</td>
<td>BTEX</td>
<td>Extracting solvent: 1-octanol</td>
<td>Chromatographic column: CP-Sil 24CB</td>
<td>LODs: 7 μg/L for all (except 30 μg/L for benzene)</td>
<td>[294]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Drop volume 3 μL</td>
<td>30 m × 0.32 mm i.d., 0.25 μm film thickness</td>
<td>Linearity: 50–20,000 μg/L (r² &gt; 0.9972)</td>
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<td></td>
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<td>Sample volume 5 mL</td>
<td>Detection: FID</td>
<td>RSDs 2.02–4.61% (n = 5)</td>
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<tr>
<td></td>
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<td>Stirring 800 rpm</td>
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<td>Enrichment factors: 41.47–128.01</td>
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<td>Extraction temp. 22°C</td>
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<td>Extraction time 25 min</td>
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<td></td>
<td></td>
<td>Without salt addition</td>
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<tr>
<td>Dynamic-HS-LPME</td>
<td>9 Alcohols (methanol,</td>
<td>Extracting solvent: hexyl acetate, n-octanol, o-xylene, and n-decane were tested. n-octanol was selected.</td>
<td>Chromatographic column: DB-5MS, 60 m × 0.25 mm i.d. 0.1 μm film thickness, Detection: MSD</td>
<td>Extraction optimization: sampling volume, solvent volume, sample temp., syringe plunger withdrawal rate and ionic strength. LODs ranged from 1 to 97 μg/L (GC-MS scan mode) r² ranged from 0.9723 to 0.9999 RSD ranged from 5.5 to 9.3% (except for methanol 16.4%)</td>
<td>[295]</td>
</tr>
<tr>
<td></td>
<td>ethanol, 2-propanol,</td>
<td>Vial volume 4 mL</td>
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<tr>
<td></td>
<td>tert-butanol, 1-propanol, 2-butanol, 1-butanol, 2-pentanol and 1-pentanol)</td>
<td>Drop volume 0.8 μL</td>
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<td>Sampling volume: 5 μL</td>
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<td>Sample volume 2 mL</td>
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<td>Salt addition: NaCl saturated</td>
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<td>Stirring 1500 rpm</td>
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<td>Extraction temp. 60°C</td>
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<td>Number of extraction cycles: 80</td>
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<td></td>
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<td>Plunger withdrawal rate: 1.4 μL/s</td>
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<tr>
<td>Fiber in tube-LPME</td>
<td>Substituted benzenes</td>
<td>Extracting solvent: chloroform, n-octanol and hexane were tested. Hexane was selected.</td>
<td>PTFE fibers (20 μm diameter, curled, Tongchuang Co., Beijing, China) and PTFE tube with 2 mm i.d. and 3 mm o.d. (Tianjin 9th Factory for Plastics, Tianjin, China) were employed.</td>
<td>LODs ranged 0.3-5.0 μg/L r²: 0.9982–0.9991 Recoveries: 86–101% in river water and from 86–99% in wastewater RSDs: 3.6–8.1% Enrichment factors: 224–361</td>
<td>[296]</td>
</tr>
<tr>
<td></td>
<td>(toluene, ethylbenzene, p-xylene, o-xylene, 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene)</td>
<td>Fiber type: PTFE (28 mg)</td>
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<td>Tube length: 10 mm</td>
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<td>Vial volume: 10 mL</td>
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<td>Solvent volume 16 μL</td>
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<td>Sample volume 8 mL</td>
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<td>Salt addition: without addition</td>
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<td>Stirring: 600 rpm</td>
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<td>Extraction time 15 min</td>
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</tbody>
</table>
Continuous flow-LPME VHOCs (chloroform, carbon tetrachloride, trichloroethylene and tetrachloroethylene)

Extracting solvent: \( n \)-pentane, \( n \)-hexane, cyclohexane, toluene and xylene were tested. Hexane was selected.

Drop volume 3 \( \mu \)L
Flow rate of sample: 1 mL/min
Sample volume 5 mL
Salt addition: without addition

Chromatographic column:
HP-5, 30 m × 0.25 mm i.d.
0.25 \( \mu \)m film thickness,
Detection: \( \mu \)ECD

A organic drop is suspended means of a syringe in a chamber through the samle flows. Extraction optimization: solvent selection, drop size, flow rate of sample and sample volume.

LODs ranged from 0.001 to 0.02 \( \mu \)g/L
\( r^2 \) ranged from 0.9939 to 0.9998
Recoveries ranged from 84 to 99%
RSDs ranged from 2.0% to 4.6%
Enrichment factors: 9.3–19.1

IL-SDME Chlorobenzenes

Extracting solvent: IL: 1-butyl-3-methylimidazolium hexafluorophosphate:
Vial volume: 15 mL
Solvent volume 5 \( \mu \)L
Sample volume 10 mL
Stirring: 1580 rpm
Extraction time 37 min
Salt addition: 30% (w/w) NaCl

HPLC: Phenomenex Luna C18 column
(150 mm × 4.6 mm, 5 \( \mu \)m particle size). PDA wavelength 210 nm.

LODs ranged from 0.102 to 0.203 \( \mu \)g/L
\( r^2 \) ranged from 0.9981 to 0.9997
Recoveries ranged from 60.8 to 120.6%
RSDs ranged from 1.6% to 5.1%

IL-SDME Chlorobenzenes

Extracting solvent: IL: 1-hexyl-3-methylimidazolium hexafluorophosphate:
Vial volume: 15 mL
Solvent volume 5 \( \mu \)L
Sample volume 10 mL
Stirring: 1580 rpm
Extraction time 37 min
Salt addition: 30% (w/w) NaCl

LODs ranged from 1 to 4 ng/L
\( r^2 \) ranged from 0.998 to 0.9995
Recoveries ranged from 90 to 113%
RSDs ranged from 3.0% to 5.2%

IL-SDME BTEX

Extracting solvent: IL: 1-methyl-3-octylimidazolium hexafluorophosphate:
Solvent volume 2 \( \mu \)L
Sample volume 8 mL
Stirring: 750 rpm
Extraction time 30 min
Salt addition: 300 g/L NaCl

GC-MS: A Gerstel TDS 2 thermodesorption system couple to Agilent 6890 N gas chromatograph coupled with an Agilent 5973 MS detector. Analytical Column: DB-624 30 m, 0.25 mm I.D., 1.4 \( \mu \)m film thickness
GC-MS with a lab-made interface for desorption in the injection port.
Analytical column: 30 m × 0.25 mm i.d.
(0.25 \( \mu \)m film thickness)

LODs ranged from 22 to 91 ng/L
\( r^2 \) ranged from 0.995 to 0.9997
Recoveries ranged from 88 to 103%
RSDs ranged from 3.0% to 5.25%

continued
<table>
<thead>
<tr>
<th>Extraction Technique</th>
<th>Analytes</th>
<th>Extraction Conditions</th>
<th>Chromatographic Column and Detector</th>
<th>Figures of Merit and Remark</th>
<th>References</th>
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</thead>
<tbody>
<tr>
<td>LPME-SFO, DLLME-SFO</td>
<td>Benzene, ethylbenzene, toluene, o-xylene</td>
<td>LPME-SFO: Extracting solvent: 1-undecanol, n-heptane internal std. Vial volume 12 mL. Drop volume 20 μL. Sample volume 8 mL. Stirring 400 rpm. Extraction time 60 min. After extraction placed in ice-bath for 5 min.</td>
<td>Chromatographic column: EquityTM-5 (30 m × 0.53 mm i.d., film thickness 1.5 μm)</td>
<td>LODs: 0.15–0.31 μg/L for LPME-SFO, and 0.10–0.35 for DLLME-SFO Linearity: up to 10 mg/L (r 0.997–0.998) RSDs &gt;12% Recoveries: 94.6–105.9% Enrichment factors: 87–290</td>
<td>[299]</td>
</tr>
<tr>
<td>US-DLLME</td>
<td>MTBE</td>
<td>Extracting solvent: benzyl alcohol. Drop volume 100 μL. Sample volume 10 mL. Extraction temp. 25 ± 3°C Extraction time 30 s Centrifugation at 3500 rpm (5 min) Then, placed in ice-bath for 5 min.</td>
<td>A 40 kHz and 0.138 kW US water bath. Chromatographic column: HP-5 (30 m × 0.32 mm i.d. film thickness 0.25 μm). FID</td>
<td>LOD: 0.05 μg/L Linearity: 0.1–500 μg/L (r² = 0.998) RSD: 6.6% Enrichment factor: 1450</td>
<td>[284]</td>
</tr>
<tr>
<td>DLLME</td>
<td>Trichlorobenzenes, 2,4,6-trichlorophenol</td>
<td>Extracting solvent: chlorobenzene Vial volume 25 mL. Drop volume 10 μL (disolved in 0.5 mL acetone) Sample volume 10 mL Centrifugation at 4000 rpm (15 min)</td>
<td>Chromatographic column: HP-5 MS 30 m × 0.25 mm i.d., 0.25 μm film thickness Detection: MSD</td>
<td>LOD: 2–6 μg/L RSDs: 2.3–7.8% Enrichment factors: 315–456 Recoveries 92.5–104.3%</td>
<td>[300]</td>
</tr>
</tbody>
</table>
**US-DLLME**  
### Aldehydes: acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde  
- **Extracting solvent:** chlorobenzene  
- **Ethylbenzene as Internal std**  
- **50 µL of O-2,3,4,5,6-(pentafluorobenzyl) hydroxylamine for derivatization**  
- **Solvent volume 20 µL (dissolved in 1 mL of EtOH)**  
- **Sample volume 5 mL**  
- **Ultrasound time 2 min**  
- **Centrifugation at 6000 rpm (3 min)**  

### Chromatographic column:  
**HP-5MS 30 m × 0.25 mm i.d., 0.25 µm film thickness**  
- **Detection:** MSD  
- **LODs:** 0.16–0.23 µg/L  
- **Linearity:** 0.8–160 µg/L  
- **(r² 0.9983–0.9993)**  
- **RSDs:** 1.8–10.2%  
- **Recoveries:** 85–105%

---

**US-DLLME**  
### Geosmin, 2-methylisoborneol  
- **Extracting solvent:** tetrachloroethylene  
- **Drop volume 8 µL**  
- **Sample volume 12 mL**  
- **Extraction temp. 20°C**  
- **Extraction time 3 min**  
- **Centrifugation at 2300 rpm (3 min)**  

### Chromatographic column:  
**Meta.X5 30 m × 0.25 mm i.d., 1.0 µm film thickness**  
- **Detection:** IT-MSD  
- **LODs:** 2 ng/L for geosmin, 9 ng/L for 2-MIB  
- **Linearity:** 10–1000 for geosmin, 50–1000 for 2-MIB  
- **(r = 0.9988–0.9994)**  
- **RSDs:** <11%  
- **Recoveries:** 70–113%

---

**TCIL-DLPME**  
### 5 Chlorobenzenes: dichlorobenzenes and trichlorobenzenes  
- **Extracting solvent:** 1-butyl-3-methylimidazolium hexafluorophosphate  
- **Tube volume 12 mL**  
- **Drop volume 75 µL**  
- **Sample volume 5 mL**  
- **Heating time: 4 min**  
- **Extraction temp. 50°C**  
- **Extraction time 20 min ice cooled**  
- **Centrifugation: at 3000 rpm 25 min**  

### HPLC column ODS-H C18  
(250 mm × 4.6 mm i.D., 5 µm). Mobile phase H2O/ACN 24:76 flow rate 1 mL/min  

- **LODs:** 0.05–0.1 µg/L  
- **Linearity:** 0.5–300 µg/L for dichlorobenzenes 0.5–500 for trichlorobenzenes  
- **(r² > 0.992)**  
- **RSD <9.2%**  
- **Enrichment factors:** 187–298

---

**DLLME**  
### MTBE  
- **Extracting solvent:** trichloromethylene  
- **n-hexane as Internal std**  
- **Tube volume 10 mL**  
- **solvent volume 42 µL (Disperser 0.3 mL MeOH)**  
- **Sample volume 10 mL**  
- **Salt addition: 5% (w/v)**  
- **Centrifugation at 4500 rpm 3 min**

### Chromatographic column:  
**HP-1MS, 30 m × 0.25 mm i.d. 0.25 µm film thickness,**  
- **Detection:** MSD (SIM)  
- **LOD:** 0.3 ng/L  
- **Linearity:** 0.001–370 µg/L  
- **RSDs:** 2.7% with internal std, 3.1% without internal std.  
- **Recoveries:** 100–105%

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**continued**
### Table 21.5 (continued)

**Analysis of Volatile Organic Compounds by Solvent Extraction Techniques**

<table>
<thead>
<tr>
<th>Extraction Technique</th>
<th>Analytes</th>
<th>Extraction Conditions</th>
<th>Chromatographic Column and Detector</th>
<th>Figures of Merit and Detector</th>
<th>References</th>
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</thead>
<tbody>
<tr>
<td>DLLME</td>
<td>BTEX</td>
<td>Extracting solvent: CS2 Drop volume 25 μL (Disperser 1 mL ACN) Sample volume 5 mL</td>
<td>Chromatographic column: BP-5, 30 m × 0.22 mm i.d. 0.25 μm film thickness, Detection: FID</td>
<td>LODs: 0.1–0.2 μg/L</td>
<td>[303]</td>
</tr>
<tr>
<td>DLLME</td>
<td>1,2-Dichlorobenzene, 1,2,4-trichlorobenzene, tetrahydroxyethylene, hexachlorobutadiene</td>
<td>Extracting solvent: 2-dodecanol Solvent volume 10 μL (in 0.5 mL acetone as disperser) Sample volume 5 mL Centrifugation for 5 min at 6000 rpm Ice bath for 5 min</td>
<td>Chromatographic column: HP-5MS (for GC-MS) DB-5MS (for GC-ECD), 30 m × 0.22 mm i.d. 0.25 μm film thickness, Detection: MSD (SIM), ECD</td>
<td>LODs: 0.005–0.05 μg/L (GC/ECD), 0.005–0.047 μg/L (GC-MS) Linearity: 0.01–500 μg/L for GC-ECD (r² 0.996) 0.02–500 μg/L for GC-MS (r² 0.996) RSDs: 4.3–8.7% Recoveries: 81–102% Enrichment factor: 174–246</td>
<td>[289]</td>
</tr>
<tr>
<td>DLLME</td>
<td>Chlorobenzenes</td>
<td>Extracting solvent: chlorobenzene, 1,4-dibromobenzene as Internal std Vial volume 10 mL Solvent volume 9.5 μL (0.5 mL of acetone) Sample volume 5 mL Centrifugation for 2 min at 5000 rpm</td>
<td>Chromatographic column: ZB-1701, 15 m × 0.25 mm i.d. 0.25 μm film thickness, Detection: ECD</td>
<td>LODs: 65 ng/L DMSs 57 ng/L DMDs Linearity: 0.05–100 μg/L Dichlorobenzenes, 0.002–20 μg/L for trichlorobenzenes and tetrachlorobenzenes, 0.001–4 μg/L for penta and hexachlorobenzenes RSD: 0.52–2.8 Enrichment factors: 711–813 Recoveries: 71.1–81.3</td>
<td>[304]</td>
</tr>
<tr>
<td>DLLME</td>
<td>THM</td>
<td>Extracting solvent: CS2 1,2-dibromopropane as Internal std Solvent volume 20 μL (0.5 mL of acetone) Sample volume 5 mL Centrifugation for 1 min at 6000 rpm</td>
<td>Chromatographic column: CP-Sil 13CB, 25 m × 0.32 mm i.d. 1.2 μm film thickness, Detection: ECD</td>
<td>LODs: 0.005–0.040 μg/L Linearity: 0.01–50 μg/L RSDs: 1.3–5.9% Recoveries: 92.2–107.8% Enrichment factors: 116–355</td>
<td>[305]</td>
</tr>
</tbody>
</table>
Determination of Volatile Organic Compounds in Water

Diphenyl/dimethyl polysiloxane columns (e.g., VOCOL®, Rtx-Volatiles, HP-VOC®, Rtx-502.2) were the first columns used to analyze VOCs. Although these are low bleeding phases and oxidation resistant, their main drawback is the incomplete resolution of very volatile compounds (such as bromomethane and chloroethane). The columns based on cyanopropylphenyl/dimethylpropyl polysiloxane phases (commonly known as “624”) are designed to perform EPA Method 624, but are also used in Method 524.2 Rev. IV and Method 8260B. The main advantage is the complete separation of highly volatile compounds such as vinyl chloride.

Rtx®-VRX, and more recently, Rtx®-VGC and Rtx®-VMS columns were developed by means of computer-assisted stationary phase design (CASPD). The main drawback of Rtx®-VRX column is the poor resolution of chloroform and bromodichloromethane from other target analytes. Rtx®-VGC and Rtx®-VMS columns were designed to overcome this disadvantage for analysis with PID/ELCD. The Rtx®-VMS column separates the EPA Method 8260B compounds in less than 18 min [57].

For quality control and method validation the reader is directed to Refs. [58–60].

21.2 HS Extraction Techniques

21.2.1 Static HS

In static HS, the sample is introduced in a closed system (generally a septum sealed vial) at a given temperature, for a period of time in which volatiles are transferred from the liquid phase to the gas phase above it until the equilibrium is reached. The first reported application of static HS with GC date from 1958 [91].

Since then the technique has been used successfully and instrumentation has allowed automation of the extraction process. Two different modes exist: a manual injection with an appropriate syringe and one with a HS autosampler. In any case, an aliquot of the gaseous phase is taken with either a gas-tight syringe or an equivalent device and injected in the gas chromatograph. Static HS in the GC analysis of VOCs in aqueous and solid samples is still used and new autosamplers were developed [92–94]. More recently, companies have developed a robotic autosampler for both liquid injection and HS sampling for introduction in the GC system. Moreover, other techniques are performed in HS mode such as HS-SPME or HS-SDME [95–98].

Theoretical aspects:

For quantitative HS gas analysis, parameters affecting the equilibrium in the system must be taken into consideration as well as the sample matrix. Theoretical aspects of the thermodynamic equilibrium have been studied by different authors [99–102]. The distribution constant of the solute in the gas–liquid-phase system can be defined as the ratio of the concentration in the liquid phase (\(C_l\)) to that in the gaseous phase (\(C_g\)) [55]:

\[
K = \frac{C_l}{C_g}
\]

This constant is dependent upon the analyte, the composition of the phases, the pressure and the temperature of the system. The distribution coefficient can be obtained experimentally by a method reported in Refs. [103,104]. Nevertheless, the pressure and gas-phase composition are parameters with no practical interest in the optimization of the static HS analysis, because the sample is loaded in a sealed bottle/vial with ambient air filling the HS, and the pressure in the system is generally a parameter fixed by the selected temperature.

21.2.1.1 Factors Affecting the Technique

The HS sensitivity can be expressed as the ratio:

\[
S = \frac{A}{C^0_l} = \frac{f V_g C_g}{C^0_l}
\]
where $A$ is the peak area for the analyte and $C_L^0$ is the starting concentration of the sample, $f$ is the detector response factor, and $V_g$ is the volume of the gas-phase injected. By using the definition of the partition coefficient and the mass balance, the next equation can be derived [55,104]

$$S = f \frac{V_g}{K + \beta}$$

Hence, the main factors affecting the analysis sensitivity are the **analyte partition coefficient** and the **ratio phase** ($\beta = V_g/V_l$), which describes the degree of filling of the HS vial, as was established by Ettre and Kolb [104]. The partition coefficient $K$ can be lowered by changing the **temperature** at which the vial is equilibrated or by changing the composition of the sample matrix (salt addition or modifier addition). Lowering the phase ratio (i.e., larger volume sample) will yield higher responses.

For analytes with high partition coefficients (e.g., alcohols, dioxan, etc.), temperature has a greater influence than the phase ratio, because analytes are transferred into the HS by heating [105]. The sample is heated by immersing the vial in a water bath, in an oven, on a heated plate, or by means of a microwave-assisted system [93]. However, possible damages on the sample vial or the seal restrict the increasing of the temperature 20°C below the boiling point of the solvent, 80°C in the case of water. To avoid sample condensation over the syringe walls it is necessary to maintain the syringe at least 10°C over the sample equilibration temperature by placing the syringe in a heated device between injections. For all these reasons, a sample equilibration temperature of 60–80°C is a good compromise between sensitivity and practical considerations. When automated HS autosampler systems are used it is easier to work with temperatures around 80–90°C, maintaining the sample loop and transfer lines at higher temperatures to avoid condensation before injection.

For analytes with low partition coefficients, such as BTEX, trichloroethylene, ortetrachloroethylene, the **phase ratio** $\beta$ determines the sensitivity. The concentration of the analytes in the gaseous phase can be increased, by adding a salt to the sample, which is known as the “salting-out effect.” Salt addition buffers the matrix effect due to the salt content in the sample. Furthermore, saturation by an inorganic salt, such as Na$_2$SO$_4$, NaCl, or Na$_2$CO$_3$, increases the concentration of analytes in the vapor phase and is a practical way of increasing the sensitivity [106]. Salt addition should not exceed the saturation point, in order to avoid absorption of the analytes over the precipitated salts.

Sample agitation reduces the time needed to reach equilibrium. A magnetic stirrer is a simple and effective way to agitate the sample, manual agitation or the most effective ultrasonic agitation can also be used for this purpose.

In conclusion, sample preparation in static HS analysis can be optimized by saturating the sample with an inorganic salt and heating the sealed sample vial while agitating the condensed phase during the required time to reach equilibrium. Although analysis can be carried out in nonequilibrium conditions, the maximum sensitivity and also the highest precision for HS analysis occurs when sample and HS are in equilibrium. The nature of the sample matrix affects the rate of diffusion of volatile components from the sample to the HS. Therefore, the analyst should consider the sample matrix when deciding on the length of the equilibration period. Low-viscosity fluids equilibrate faster than high-viscosity ones.

Both manual procedures and automated devices for gas sample injection have been developed: manual injection using gas-tight syringes [107], sample injection using a loop in a HS autosampler with electro-pneumatic systems [5], automated injection by means of an autosampler equipped with gas-tight syringes and automated injection by means of a static-HS autosampler equipped with a trap to preconcentrate and focus the VOCs [108–110].

Manual injection with gas-tight syringes is an in-expensive method giving good results with careful handling. The syringe temperature must always be higher than that of the sample to avoid losses by condensation in the inner walls of the syringes. Once the vial septum is pierced, the syringe should be filled slowly and emptied back into the sample flask at least four times to minimize losses resulting from adsorption. Finally, in order to avoid memory effects between injections, it is important to clean the syringe by removing the plunger and passing a current of nitrogen through the interior while maintaining it at the operation temperature.
Modern, fully automated HS autosamplers are commercially available. These autosamplers allow full programming of the different parameters, such as equilibration time, equilibrium temperature, mixing power, and gas sample size. The main advantages of these systems are better precision, the minimization of memory effects, and the reduction of time. Nowadays, these autosamplers allow multiple uses with different extraction techniques.

21.2.1.2 HS Limitations and Advantages

Preliminary qualitative analysis can be performed manually with a gas-tight syringe. For water quality control, HS autosamplers are commercially available enabling the analysis of all sample matrices (gas, liquid, and solid) up to 100 samples, so the analysis cost for a single sample is kept low. The HS vials filled in the sampling point can be sealed and directly placed in the autosampler for analysis, so that analyte losses and laboratory contamination during sample handling is avoided. Foaming samples or samples containing unexpected high concentrations do not usually lead to carry-over effects.

Matrix effects can lead to systematic errors in quantitative analysis, for this reason matrix standardization by salt addition and internal standard are required. Water vapor from water samples can enter the column, affecting the integrity of the early eluting peak, and can reach the detector, so special care must be paid to the stability of the ion sources when a mass spectrometer is used for quantitative analysis [55]. The sensitivity is limited by the partition coefficient and can be increased by rising the temperature or by multiple-HS extractions, in which case cryofocussing is necessary. The other alternative is standard addition. Damages on the sample vial or the seal restrict the temperature increase to avoid vial burst, putting the instrument out of operation and making a necessary cleanup. The air filling the HS can lead to an undesirable reaction with oxygen degradation of the analytes. In addition, the air can damage the column materials. Blank and standards prepared in the lab can be contaminated by lab atmosphere leading to systematic errors. The degradation of organic compounds (such as trihaloacetic acids by decarboxylation) leads to the formation of THMs upon heating of aqueous solutions at 60°C for 30 min [111].

21.2.2 Purge and Trap

P&T, the so-called dynamic HS, could be defined as a HS gas analysis in which volatiles are stripped from the sample with an inert gas, trapped into a solid sorbent, and thermally desorbed into a gas chromatograph. Since the first attempts by Swinnerton and Linneborn in 1967 and the development of the popular system pioneered by Bellar and Lichtenberg [112], P&T has been widely used in environmental analysis for volatile organic pollutants in water [112–128] and has been extended to foods [129], clinical applications [130], and other matrices [131,132]. P&T is the most widely used technique for the routine quality control of organic volatiles in any kind of water and is the official method required in many countries.

The P&T technique is recommended as an extraction technique for VOCs in several Standard Methods (Table 21.6). The U.S. Environmental Protection Agency (EPA) has proposed, different standard protocols for the analysis of volatiles in water using P&T. These methods can be used for most of VOCs that have boiling points below 200°C and are insoluble or slightly soluble in water. The type of sample matrix being analyzed determines which configuration of extraction technique is implemented. The 500 series EPA methods are addressed to potable waters, while the 600 series refer to analysis of wastewater. The analytical methods for determining hazardous waste are known as the 8000 series methods (US EPA SW-846).

The P&T consists of three separate processes: (1) an aliquot of sample is stripped with a purge gas (generally He or N₂), (2) simultaneously the analytes swept by the gas stream are trapped into a solid sorbent (Figure 21.1 left) (3) analytes are thermally desorbed into the gas chromatograph (Figure 21.1 right). The P&T system consists of a purge vessel, a sorbent trap, a six port-valve, and a transfer line. It operates basically in six steps:

- Standby step
- Purge wet step
- Purge dry step
## Standardized Methods for VOCs Analysis in Water Samples

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<th>EPA Method Reference</th>
<th>Sample Preparation Technique</th>
<th>Detector Types</th>
<th>Sample Matrix</th>
<th>Ref.</th>
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<tr>
<td>VOCs</td>
<td>502.2, 8021</td>
<td>P&amp;T, direct injection, headspace</td>
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<tr>
<td>Purgeable halogenated organics</td>
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<td>PID, ELCD</td>
<td>Waste water, solid wastes</td>
<td>[62,63]</td>
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<tr>
<td>Purgeable aromatic organics</td>
<td>602, 8020</td>
<td>Purge and headspace for screening</td>
<td>PID</td>
<td>Drinking water, trap, waste water, solid wastes</td>
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<tr>
<td>VOCs using MSD</td>
<td>524.2, 624, 8240, 8260</td>
<td>P&amp;T, direct injection, headspace</td>
<td>MSD</td>
<td>Drinking water, waste water, solid wastes</td>
<td>[66–69]</td>
</tr>
<tr>
<td>VOCs using 5973 MSD</td>
<td>524.2, 624, 8240, 8260</td>
<td>P&amp;T, direct injection, headspace</td>
<td>MSD (5973)</td>
<td>Drinking water, waste water, solid wastes</td>
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<tr>
<td>EDB and DBCP</td>
<td>504.1, 8011</td>
<td>Microextraction with Hexane</td>
<td>ECD</td>
<td>Drinking water, solid wastes</td>
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<tr>
<td>Acrylonitrile and acrolein</td>
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<tr>
<td>Chlorinated disinfection by-products</td>
<td>551.1</td>
<td>Liquid extraction, derivatization</td>
<td>ECD</td>
<td>Drinking water</td>
<td>[74]</td>
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<tr>
<td>Halogenated acetic acids and dalapon</td>
<td>552.0, 552.1, 552.2, 552.3</td>
<td>Liquid extraction, derivatization</td>
<td>Liquid-liquid microextraction, derrivatization</td>
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<td>Carbonyl compounds</td>
<td>556, 556.1</td>
<td>Derivatization, liquid-liquid extraction</td>
<td>ECD</td>
<td>Drinking water and raw source water</td>
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<tr>
<td>Acrylamide</td>
<td>8052</td>
<td>Derivatization, liquid–liquid extraction</td>
<td>ECD</td>
<td>Drinking water and raw source water</td>
<td>[80]</td>
</tr>
<tr>
<td>VOCs</td>
<td>1624B</td>
<td>P&amp;T</td>
<td>Isotope dilution-MSD</td>
<td>Water</td>
<td>[81]</td>
</tr>
<tr>
<td>VOCs</td>
<td>8265</td>
<td>Direct sampling</td>
<td>Ion trap mass spectrometry (without chromatographic separation)</td>
<td>Water</td>
<td>[82]</td>
</tr>
</tbody>
</table>

### Analyte Type Reference
- **Earthy-musty-smelling compounds and U.S. EPA priority pollutants**: 6040B
- **Volatile organic compounds (VOCs)**: 6040C, 6200
- **Taste and odor–causing compounds**: 6040D
- **Trihalomethanes and chlorinated organic solvents**: 6232
- **1,2-Dibromoethane (EDB) and 1,2-dibromo-3-chloropropane (DBCP)**: 6231
- **Halogenated acetic acids and trichlorophenol**: 6251B
- **Disinfection by-products: Aldehydes**: 6252

### Sample Preparation Technique
- **CLSA**: 6040B
- **P&T**: 6040C, 6200
- **SPME**: 6040D
- **P&T, LLE**: 6232
- **LLE, P&T (6200), CLSA (6040)**: 6231
- **Liquid-liquid microextraction**: 6251B
- **O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine derivatization and LLE.**: 6252
Determination of Volatile Organic Compounds in Water

21.2.2.1 P&T and Desorption Processes: Factors Affecting the Technique

21.2.2.1.1 Purge

The kinetics of purging volatiles in water have been studied in depth by Lin et al. [137]. Purge efficiency can be defined as the quantity of analytes purged from a sample with a defined volume of purge gas [55]. The recovery can be calculated as the ratio of the peak area for an analyte from P&T analysis to that from direct injection. The efficiency depends upon several factors such as purge volume, sample temperature, purge vessel, matrix, and the properties of analytes.

1. **Sample volume:** A 5 mL purging vessel is recommended if the GC instrument has adequate sensitivity to obtain the required method detection limits; otherwise, a 25 mL purging vessel should be used. It is noteworthy that the purge is not exhaustive, so it should be considered that higher the sample volumes the more difficult will be to extract quantitatively [138].

2. **Purge vessel:** Vessels of 25 and 5 mL are most commonly used. Three types of purge vessels are generally used in P&T: frit spargers, fritless spargers, and needle spargers. The frit spargers produce fine and uniform bubbles with large surface area increasing the efficiency. Although frit spargers are more efficient, fritless spargers are advisable for not-clean water, waste water, and complex matrix samples because solid particles from the sample can obstruct the frit. Needle spargers are used for analysis of soils, sludges, solid samples, or waste samples, which can dirty the P&T device. A closed system for P&T is regulated in EPA method 5035, in which the sample is purged by a needle sparger [139].

3. **Extraction temperature:** Heating the sample during the purge period favors the extraction efficiency [138,140]. Extractions obtained at 40°C versus 25°C increase by a factor of 1.5–2.5 for high-boiling-point polar compounds included in EPA method 524.2 [141]. Fuel oxygenates are extracted by heating because of their solubility in water (EPA Method 5030C). Excessive
moisture is transferred to the trap during the purge step, especially when heating the sample, subsequently to the chromatographic column and the detector [119], but recent P&T instruments make use of a moisture control system to overcome this drawback [142–144].

4. Stripping gas volume: The purge volume is the product of the purge flow rate and the purge time. Since a flow rate of 40 mL/min is considered as optimal, changes in purge volume can be accomplished by changing the purge time. A purge time of 11 min is recommended giving a total stripping volume of 440 mL. Extraction of analytes with high boiling points can generally be improved by increasing the total extraction volume [145], but losses of the most volatile organics are possible due to breakthrough problems.

Recently, the purge cycle efficiency was studied showing that the purge extraction is not quantitative under standard conditions [138]. Additionally, volatiles can be removed by a current of the inert gas passing over the surface of the liquid phase (with or without agitation), which is called “sweeping.” With this purge system, the foaming of wastewater samples is sometimes a serious problem. The foam can climb through the apparatus to the sorbent trap, causing several problems, such as deactivation of the trap and the introduction of thermal decomposition products from labile, nonvolatile materials. For samples that do not form highly persistent foam it is possible to reduce the foam by decreasing the purge flow or by inserting a mechanical barrier to the foam. When this is insufficient, alternatives are (1) applying heat to dissipate the foam, and (2) adding silicone-based commercial antifoam emulsions [146,147].

21.2.2.1.2 Trap

Trapping efficiency is affected by several factors, including the vapor pressure of the compound, the surface area of the adsorbent, and thermodynamic interactions between the analyte and the adsorbent [141].

1. Adsorption temperature: To minimize breakthrough, the trap temperature should be near to 25°C (room temperature). Room temperature must be maintained from run to run to obtain reproducible results. New P&T instruments do not go on with the next analysis until the initial programmed temperature is reached. Also cryogenic traps are used.

2. Solid adsorbent: In the choice of the proper adsorbent, the primary concern is the ability of the materials to efficiently retain VOCs during the purge time and subsequently release the analytes. Sorbents that trap and desorb efficiently will help to provide high recoveries, sharp peaks, and good resolution. Each adsorbent material has a specific trapping capability for a set of compounds with similar adsorptive properties. The properties of adsorbent materials used to make a trap are detailed in Table 21.7. Since VOCs include a wide-ranging group of compounds, a suitable trap may be composed by several different beds of adsorbent. The trap is built up from the weakest adsorbent in the inlet bed to the strongest sorbent in the innermost adsorbent bed.

The sorbent materials used to make the traps are mainly Tenax®, silica gel, activated charcoal, graphitized carbon black (GCB or Carbopack®), carbon molecular sieves (carbosieve such as Carbosieve-SIII®) and Vocarb.

Sorbents for P&T can be classified as:

1. Carbon sorbents: Activated carbon was used in the first applications of trapping volatiles with solid sorbents [148,149] due to its high specific surface and thermal stability (up to 700°C). Vocarb is a hydrophobic activated carbon, so vapor water is badly adsorbed and is quickly dry purged. Although, some degradation has been noted on brominated compounds and 2-chloroethyl vinyl ether (degraded in Vocarb 4000®, but not in Vocarb 3000®) when higher desorption temperatures are used [139]. Charcoal is a hydrophobic adsorbent stronger than Tenax and silica gel. It is used to trap very volatile compounds such as freons which are not retained in Tenax and silica gel. However, it traps CO₂ which interferes with early-eluting compounds in GC-MS. Carbon molecular sieves (Carbosieve-SIII®) are hydrophobic adsorbents alternative
TABLE 21.7
Trapping Adsorbent Materials

<table>
<thead>
<tr>
<th>Adsorbent Material</th>
<th>Surface Area (m²/g)</th>
<th>Type of Adsorbent</th>
<th>Type of Compounds</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon and graphitized sorbents</td>
<td>Coconut charcoal</td>
<td>900</td>
<td>Strong</td>
<td>Very volatile compounds</td>
</tr>
<tr>
<td>Graphtized Carbon Black (GCB) or Carbopack® adsorbent</td>
<td>10–100</td>
<td>Weak</td>
<td>Same range or VOCs than Tenax</td>
<td>Alternative to Tenax</td>
</tr>
<tr>
<td>Carbon Molecular Sieves (Carbosieve®-SIII)</td>
<td>50–800</td>
<td>Strong</td>
<td>Ideal for highly volatile compounds</td>
<td>Alternative to silica gel and charcoal</td>
</tr>
<tr>
<td>Carboxen®-1000 Adsorbent</td>
<td>1200</td>
<td>Strong</td>
<td>Traps Freons compounds Permanent gases Light hydrocarbons</td>
<td>Designed to be used as the innermost adsorbent bed.</td>
</tr>
<tr>
<td>Vocarb®</td>
<td>Strong</td>
<td>Very volatile compounds</td>
<td>Used in series after GCB and carbon molecular sieves.</td>
<td></td>
</tr>
<tr>
<td>Silica gel</td>
<td>Silica gel</td>
<td>200–800</td>
<td>Medium</td>
<td>VOCs: Polar and highly volatile compounds</td>
</tr>
<tr>
<td>Porous polymers</td>
<td>Tenax (poly(2,6-diphenyl-p-phenylene oxide))</td>
<td>50</td>
<td>Weak</td>
<td>Non polar compounds</td>
</tr>
<tr>
<td>Chromosorb®</td>
<td>15–800</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porapak</td>
<td>225–840</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amberlite (Divinylbenzene copolymers)</td>
<td>100–750</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

to silica gel and charcoal and have excellent thermal stability. Carboxen®-1000 adsorbent is a strong adsorbent used as the innermost adsorbent bed. Its retention capacity is similar to Carboxsieve-SIII®. Carboxen®-1000 is stable up to 300°C. Graphtized carbon blacks (GCBs or Carbopak®, Carbotrap, etc.) is a hydrophobic adsorbent with similar trapping capacity to Tenax [150–152]. GCBs are available in different pore sizes.

2. Inorganic sorbents based on silica and alumina: Silica gel is a stronger adsorbent than Tenax adsorbent. Adsorbent properties of silica gel are ideal for trapping polar and highly volatile compounds. However, silica gel is an hydrophilic adsorbent and retains water vapor, which will not be removed by dry purge [57].

3. Porous polymer sorbents: Porous polymers in spite of their smaller specific active surface compared to carbon and graphitized sorbents are excellent adsorbents for nonpolar compounds. Tenax is a (hydrophobic) porous polymer resin based on 2,6-diphenylene oxide, is by far the most widely used trapping organic polymer for VOCs [140,153–155]. Very volatile VOCs and polar compounds like alcohols are poorly retained, so a stronger adsorbent bed is required.
Thermal stability of Tenax is limited by thermal degradation to aromatic compounds (toluene, benzene, benzaldehyde, acetophenone, benzophenone, and other aldehydes and ketones) [57,139], so sensitivity for brominated compounds decreases as the polymer degrades. Tenax should not be heated above 200°C to avoid degradation. Moreover, Tenax degrades by organic acids present in the samples. Two grades of Tenax adsorbents exist: Tenax®-GC and Tenax®-TA (trapping agent). Even after thermal conditioning, aliphatic and aromatic hydrocarbons and certain ghost peaks have been reported in the blanks when Tenax-GC is used [156,157]. Tenax-TA is a modified purer form, which is more recommended for P&T applications, since better blank chromatograms are obtained with Tenax TA than with Tenax GC [158]. Other polymeric sorbents used for P&T are Chromosorb, Porapak, and Amberlite XAD series.

4. Nanomaterials: Nanotubes have been used as sorbents in P&T [159].

General precautions with any of these polymeric materials must be taken in order to avoid various detrimental effects on the performance of the polymer [157]: first, oxidizing atmospheres when working at high temperatures; second, heavy organic molecules deposited on the surface of the polymeric sorbent that could modify either its chemical structure or its adsorptive properties, and finally, not heating the polymer over its maximum permitted temperature, generally specified by the manufacturer.

The trap consists of a stainless-steel tube (it may be a deactivated glass tube) whose length and internal diameter varies from 5 to 25 cm and from 2 to 5 mm, respectively, filled with a packed column of sorbents. Different traps are commercially available with different fillings each one designed for a set analytes. For example, if dichlorodifluoromethane (boiling point −29°C) has to be analyzed the trap should contain charcoal or a similar sorbent. Table 21.8 summarizes the sorbent contained in different traps commercially available.

21.2.2.1.3 Desorption

Once VOCs have been purged and trapped, the trap is heated desorbing the trapped-VOCs to the gas chromatograph through a narrow band to avoid tailing chromatographic peaks. The faster the heating is, the quicker the analytes are desorbed [160–163]. Desorption time is inversely proportional to the flow rate and the trap temperature:

1. **Time of desorption** should be as short as possible (generally 4 min). Most of the VOCs are desorbed during the first minute.

2. **Desorption temperature:** As mentioned above, previous to the desorption step, the trap is pre-heated to desorb VOCs at a temperature approximately 5°C below the desorption temperature. The desorption temperature depends on the adsorbents with which the trap is made (from 180°C to 250°C). While traps containing Tenax are not recommended to heat over 200°C, a trap made of GCB, carbon molecular sieves, and Vocarb can desorb at 250°C (recommended desorption and bake temperatures are listed in Table 21.8).

3. **Flow rate:** Low desorption flow rate can produce tailing peaks. When using a narrow capillary column, the desorption flow rate entails a problem, because of the high flow rate used to desorb in the P&T device (~40 mL/min) in contrast with the typical flow rates of carrier gas used in a narrow-bore capillary column ranging from 1 to 10 mL/min. Hence, they are not compatible with the fast desorb flow rates from common P&T systems. Splitting the sample at the injection port or cryofocussing (i.e., retaining analytes in a secondary trap) will provide compatibility and focus the sample at the column inlet.

When a cryofocussing injector interface is used, the trap is desorbed at only 1–2 mL/min and VOCs are focused in the inlet of a short section of narrow-bore column. VOCs are cooled to −160°C, using liquid nitrogen, on a short length of the uncoated fused silica tubing [66]. Although peak shape and resolution is improved by cryofocussing, large amounts of liquid nitrogen are consumed (increasing the analysis cost and requiring liquid nitrogen tanks in the lab). Once trap desorption is completed, the interface is heated rapidly (1000°C/min) under a stream of carrier gas, transferring the analytes to the
### Table 21.8
List of Traps Used for P&T Extraction

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1 or A</td>
<td>Tenax</td>
<td>Everything down to methylene chloride</td>
<td>Yes</td>
<td>2–6 min</td>
<td>220°</td>
<td>225°</td>
<td>230°</td>
<td>7–10 min</td>
<td>230° 1 h</td>
<td>Low response on brominated compounds, a high back pressure, an outgassing of benzene, toluene and ethyl benzene</td>
</tr>
<tr>
<td>2 or B</td>
<td>Tenax silica gel</td>
<td>Everything except the freons</td>
<td>No</td>
<td>n/a</td>
<td>220°</td>
<td>225°</td>
<td>230°</td>
<td>10–12 min</td>
<td>230° 1 h</td>
<td>Low response on brominated compounds, a high back pressure, an outgassing of benzene, toluene and ethyl benzene</td>
</tr>
<tr>
<td>3 or C</td>
<td>Tenax silica gel charcoal</td>
<td>Everything including freons</td>
<td>No</td>
<td>n/a</td>
<td>220°</td>
<td>225°</td>
<td>230°</td>
<td>10–12 min</td>
<td>230° 1 h</td>
<td>Low response on brominated compounds, a high back pressure, an outgassing of benzene, toluene and ethyl benzene</td>
</tr>
<tr>
<td>4 or D</td>
<td>Tenax charcoal</td>
<td>Traps everything down to methylene chloride and gases</td>
<td>No</td>
<td>n/a</td>
<td>220°</td>
<td>225°</td>
<td>230°</td>
<td>10–12 min</td>
<td>230° 1 h</td>
<td>Low response on brominated compounds, a high back pressure, an outgassing of benzene, toluene and ethyl benzene</td>
</tr>
<tr>
<td>5 or E</td>
<td>OV-1 Tenax silica gel charcoal</td>
<td>Everything including freons</td>
<td>No</td>
<td>n/a</td>
<td>220°</td>
<td>225°</td>
<td>230°</td>
<td>10–12 min</td>
<td>230° 1 h</td>
<td>Low response on brominated compounds, a high back pressure, an outgassing of benzene, toluene and ethyl benzene</td>
</tr>
<tr>
<td>6 or F</td>
<td>OV-1 Tenax silica gel</td>
<td>Everything except the freons</td>
<td>Yes</td>
<td>2–6 min</td>
<td>220°</td>
<td>225°</td>
<td>230°</td>
<td>10–12 min</td>
<td>230° 1 h</td>
<td>Low response on brominated compounds, a high back pressure, an outgassing of benzene, toluene and ethyl benzene</td>
</tr>
<tr>
<td>7 or G</td>
<td>OV-1 Tenax</td>
<td>Everything including freons</td>
<td>Yes</td>
<td>2–6 min</td>
<td>220°</td>
<td>225°</td>
<td>230°</td>
<td>10–12 min</td>
<td>230° 1 h</td>
<td>Low response on brominated compounds, a high back pressure, an outgassing of benzene, toluene and ethyl benzene</td>
</tr>
<tr>
<td>8 or H</td>
<td>Carbopak B; Carbosieve SIII</td>
<td>Everything including freons</td>
<td>Yes</td>
<td>11 min</td>
<td>245°</td>
<td>250°</td>
<td>260°</td>
<td>7–10 min</td>
<td>270° 20–30 min</td>
<td>High back pressure and a low response on chlorinated compounds</td>
</tr>
<tr>
<td>Supelco Vocabor 4000 or I</td>
<td>Carbopak C; Carbopak B; Carboxen 1000; Carboxen 1001</td>
<td>Everything except 2-chloro-ethyl vinyl ether</td>
<td>yes</td>
<td>1–3 min</td>
<td>245°</td>
<td>250°</td>
<td>270°</td>
<td>7–10 min</td>
<td>270° 4 h</td>
<td>Unknown</td>
</tr>
<tr>
<td>Supelco Vocabor 3000 or K</td>
<td>Carbopak B; Carboxen 1000; Carboxen 1001</td>
<td>Everything including freons</td>
<td>yes</td>
<td>1–3 min</td>
<td>245°</td>
<td>250°</td>
<td>270°</td>
<td>12–15 min</td>
<td>280° 4 h</td>
<td>Unknown</td>
</tr>
<tr>
<td>Alltech Tenax gr graphpak-D</td>
<td>Tenax gr graph pac-d</td>
<td>Everything including freons</td>
<td>Yes</td>
<td>1–4 min</td>
<td>245°</td>
<td>250°</td>
<td>260°</td>
<td>12 min</td>
<td>270° 1 h</td>
<td>Unknown</td>
</tr>
<tr>
<td>Supelco BTEX or J</td>
<td>Carbopak B; Carbopak C</td>
<td>Everything down to benzene (it does not trap meth)</td>
<td>Yes</td>
<td>1–3 min</td>
<td>245°</td>
<td>250°</td>
<td>260°</td>
<td>7–10 min</td>
<td>270° 1 h</td>
<td>High back pressure</td>
</tr>
<tr>
<td>Supelco Modified BTEXTRAP or L or M</td>
<td></td>
<td></td>
<td></td>
<td></td>
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analytical column in a narrow band. This interface is proposed in EPA method 524.2. The main advantage of this interface is that all the volatiles from the sample are transferred to the column offering the highest sensitivity. Problems with detector saturation or blockage of the interface by frozen water from the trap should be controlled.

An alternative is splitting the sample at the injection port, which implies a decrease in the analysis sensitivity. However, ion-trap GC-MS and recently developed quadrupole MS systems allow high split ratios maintaining the sensitivity, due to their higher sensitive detectors. Older quadrupole GC-MS requires to use a 25 mL vessel (instead of a 5 mL vessel) to compensate the sensitivity loss by splitting the sample.

The use of microwave-assisted systems instead of electrical ovens has improved the desorption efficiency in P&T extraction [164–167], permitting an increase in the heating rate. A complete desorption can be accomplished in 2 or 3 s increasing the sensitivity without artifacts from secondary reactions or degradation of thermolabile compounds [168].

Special care must be taken for water-soluble analytes (such as ketones, alcohols, etc.) which are advisable to purge at an elevated temperature of 80°C. Despite of the boiling points and vapor pressure of fuel oxygenated compounds (such as methyl-t-butyl ether, ethyl-t-butyl ether, ethyl-butyl alcohol, etc.) are often encountered problems as a result of their high solubility in water. Thus, the method performance must be checked. The use of an appropriate analytical column and heating to 80°C rather than ambient temperature are proposed modification in EPA method 5030c.

Some variations have been performed recently such as the coined HS and trap. Other techniques are in the border between the P&T and SPME such as the recently developed needle in trap [169,170].

21.2.2.2 P&T Limitations and Advantages

Glass purge vessels must be cleaned, especially the vessels with frit. Highly contaminated samples can lead carry-over effect, even if the baking out is performed adequately. Cryofocussing or splitting ratio is necessary, increasing the operating expenses or losing sensitivity. The P&T instrumentation and autosampler imply an investment for analysis of purgeable VOCs.

21.3 Sorptive Extraction Techniques

The sorptive extraction techniques are solvent-free techniques used to extract and preconcentrate analytes from the sample in a sorbent, which can be a high-molecular-weight polymeric liquid or a high porosity solid sorbent. Analytes are absorbed or adsorbed, or both, depending on if the sorbent is a polymeric liquid or a porous solid [192]. Polymers behave like a liquid or a gum above their glass transition temperature, so they show similar properties as organic solvents [193].

SPME and SBSE are the most implemented in water quality control laboratories. Other sorptive extraction techniques (such as open-tubular trapping, gum-phase trapping extraction, or equilibrium gum-phase extraction) are reviewed [193].

21.3.1 Solid-Phase Microextraction

SPME was developed by Pawliszyn and coworkers in 1987 [194–196]. The reader may find for further information on the historical evolution, principles, and commercially available devices of SPME in an excellent review by the pioneer of the technique [197]. SPME is based on a partitioning equilibrium of the solutes between the sorbent phase and the aqueous and/or gas matrix. A small amount of sorbent phase is dispersed on a solid support which will be exposed to the sample for a predetermined time. Different implementations were developed such as suspended particles, coated-stirrer, vessel walls, discs, stirrer or membranes, although the fiber and in-tube are explored theoretically and experimentally in depth. The former consists of a thin, fused silica fiber coated with sorbent on its surface and mounted in a modified gas chromatography syringe, which protects the fiber and allows handling. The latter, in-tube implementation consists of an internally coated tube or capillary. The analytes are extracted by sorption when it is immersed in the water sample (direct SPME) or in the HS above the sample (HS-SPME).
21.3.1.1 Extraction: Absorption

The absorption process is the most important step. In direct-SPME, the fiber is introduced directly into the sample, and so analytes are retained in the fiber. This extraction mode is specially suited for separating low volatile analytes. In the case of HS-SPME, a fiber in the needle tip of a microsyringe is exposed to the HS above a sample. Next, the fiber is retracted into the microsyringe and injected directly into the gas chromatograph. This extraction technique has been successfully applied to determine volatile compounds as BTEX in water samples. Because low volatile compounds, such as proteins or humic matter, are not absorbed in the fiber, the extraction is more specific. Another possibility, SPME using a protector membrane, this system is used to avoid fiber worsening when very complex and dirty samples have to be extracted and HS SPME cannot be applied. However, this extraction mode is applied mainly for semivolatile and nonvolatile compounds, since membrane extraction is slow and VOCs are extracted by means of HS-SPME.

For theoretical aspects of SPME the reader is directed to Refs. [197–201].

21.3.1.1.1 Parameters Affecting the Extraction

The parameters of interest for SPME are the ones increasing the concentration of the analyte in the fiber.

1. Polymeric coating of the fiber: The choice of polymeric coating depends on the analyte characteristics. Specific coatings, discussed later, have been developed for a range of applications. Coating selection and design is based on the chromatographic experience. The thickness is another characteristic parameter of the fiber coating. The thicker is the fiber coating the more sensitive is the technique. Nevertheless, larger equilibrium and desertion times are required when using thick coatings, even carry-over effects may appear. Hence, the thickness coating which provides the required sensitivity and LOD should be used to reduce the extraction time.

2. Extraction temperature: The extraction temperature is a very important parameter in SPME optimization, because it is involved in the extraction kinetics, and hence in the sensibility and selectivity. Two opposite effects are due to temperature: the analyte diffusion is enhanced by rising the extraction temperature and in addition in HS-SPME, the analyte transfer to the HS is favored by increasing the temperature. In contrast, the absorption step is an exothermic process, the distribution constant decrease by increasing the temperature [202]. A refrigerated SPME device which allows heating the sample and internally cooling the fiber with liquid CO₂ was developed by Pawliszyn and coworkers improving the diffusion and the absorption [203].

3. Extraction time: At the equilibrium time, the lowest detection limits and higher reproducibility are obtained. Compounds with lower diffusion coefficients require longer equilibration times.

4. Agitation: The diffusion layer at the sample matrix–sorbent interface is reduced by agitation, so the equilibrium is reached faster [204]. In direct SPME, the fiber should be off-centered, because in the center the sample moves slowly. Agitation can be accomplished by magnetic stirring, fast sample flow, fiber movement, vial movement, or sonication [205,206].

5. Wind speed: Wind speed or air bulk movement significantly affects the VOC mass transfer process from the bulk air to the fiber in nonequilibrium extraction. The VOC mass loading on the fiber increases as the wind speed increases to a certain speed. Then the boundary layer is decreased.

6. Salting-out effect: The solubility of nondissociated analytes decreases by salt addition. In HS-SPME, the addition of salt, usually sodium chloride or sodium sulfate increases the partition coefficient between the aqueous and the gaseous phase. Also the partition coefficient between the water sample and the coating rises by adding salt. After the analysis, the fiber must be washed because it becomes more fragile [207].

7. Sample pH: pH should be considered when dissociable analytes are analyzed, such as volatile organic acids. The maximum sensitivity is obtained when the pH is adjusted to 2 pH unit below for acids (or two pH units above for basic compounds) the analyte pKₐ. Buffers are recommended to achieve reproducible results. HS-SPME is recommended when an extreme pH is used in order to avoid fiber damage.
8. **Sample volume:** Sample volume is directly related to the sensitivity. As the sample volume increases also the extracted amount increases to a certain degree. Generally, typical 2-mL GC autosampler vials are used for direct SPME.

9. **HS volume:** In HS-SPME, the total amount of analyte is distributed among the fiber coating, the HS and the sample. The smaller the HS is, the higher the concentration of analyte in the HS is, so that the diffusion toward the fiber is enhanced [208]. From a kinetic point of view, the smaller is the HS volume/sample volume ratio, the faster is the analyte transport from the sample to the fiber.

10. **Vial shape:** In HS-SPME, it is necessary to use vials with small diameters and high heights to contain the fiber. However, in HS-SPME, the mass transfer is affected by the interface area. In addition, convection depends on the vial shape when the sample is stirred.

11. **Time between the extraction and the analysis** should be reduced in order to avoid analyte losses especially for more volatile compounds.

12. **Derivatization processes:** The derivatization carried out before or during the extraction can increase the technique sensibility and selectivity. Different derivatization techniques are discussed in Refs. [47,197]. However, it should be used only when necessary, since SPME becomes more complex. Formaldehyde exposed to a previously doped fiber with the derivatizing agent \( o-(2,3,4,5,6\text{-pentafluorobenzyl})\)hydroxylamine, is converted into the oxime derivative [209]. Haloacetic acids, which are disinfection by-products, have been successfully derivatized to ethyl/methyl esters [210,211].

13. **Solvent addition:** Solvent addition to solids and sludges enhances the diffusion from the solid sample to the fiber coating but needs further research. Solvent addition to aqueous samples usually reduces the extracted amount of analytes [207].

The choice of fiber-coating type should be based on the analyte properties: polarity and volatility. Commercially available fibers with different coatings are enumerated in Table 21.9 with some recommended applications from Supelco.

Polydimethylsiloxane (PDMS) is a very viscous-liquid polymeric phase. Diffusion coefficients are higher than other sorbents. This phase is nonpolar. It shows a great affinity for apolar compounds, but can also be used to extract moderately polar compounds.

Polyacrylate (PA) is a low-density solid polymer which allows analyte diffusion. However, diffusion coefficients are lower than for PDMS, so extraction times are longer. PA is a suitable coating for extraction of polar compounds.

Mixed phases were developed with complementary properties to PA and PDMS covering a higher range of polarities and extracting analytes by both adsorption and absorption. These phases are based on porous microspheres of a solid sorbent such as DVB or Carboxen, immersed in a coating of PDMS or Carbowax (CW) which hold the microspheres on the fiber (e.g., carbowax/divinylbenzene (CW/DVB) fibers, PDMS/DVB fibers, carboxen/PDMS, and carbowax/templated resin, CW/TPR). Mixed phases are more suitable for volatile species. For analysis of polar compounds, the selectivity can be modified changing the liquid polymer from PDMS to Carbowax (for compounds such as alcohols and ketones). When analytes with different properties are analyzed, the choice of fiber coating should be based on the coating which provides the required sensitivity for the most difficult analyte to extract [192].

For alcohols and polar compounds, PEG fiber is recommended. Ionic liquid coating for SPME fiber was developed for the determination of BTEX in paints, which are mixed with water and methanol to extract the analytes [212].

### 21.3.1.2 Desorption

Although SPME can be coupled with HPLC and CE, analyses of VOCs are performed by GC. Once analytes have been extracted, either by direct-SPME, HS-SPME, or membrane-SPME, the polymeric fiber is desorbed in the GC injector. The fiber is withdrawn into the needle, and, after piercing the GC septum, the fiber is released inside the glass insert, where thermal desorption occurs.
Parameters Affecting the Desorption

As mentioned above, the affinity of analytes toward the fiber decreases as temperature increases, and simultaneously analytes are removed by the flow of the carrier gas. Hence, the analytes are released by increasing the temperature at a set column flow rate which determines the desorption time. The main parameters affecting the desorption process are [1,198]:

1. **Injector type**: A splitless injector is used. SPME is a solvent-free technique. It is not necessary to reduce the solvent volume introduced to preserve the column. A GC inlet liner of low volume should transfer desorbed analytes to the chromatographic column inlet. The effect of the inlet liner diameter on the broadening of VOCs peaks is reported by Okeyo and Snow [213]. Peak broadening of the most volatile compounds is avoided using smaller diameter liners. Less volatile compounds are not broadening and the peaks are not affected by the liner diameter.

2. **Desorption temperature**: By increasing the desorption temperature, the diffusion coefficient of the analytes in the fiber is enhanced, while the distribution constant between the fiber and the carrier gas decreases. Generally, the desorption temperature is set at the maximum temperature depending on the stability of the selected fiber coating, so temperature ranges from 150°C to 250°C. However, higher desorption temperatures are required when compounds of high-molecular weight are present in the sample to avoid carry-over effect. The carry-over effect can be reduced by desorption times.

3. **Desorption time**: Depends on the temperature (1 or 2 min usually are enough). However, longer desorption times are required with high-molecular compounds.

4. **Fiber location in the injector**: The fiber location in the injection port is a parameter to consider because the temperature is not uniform.

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TABLE 21.9
Fiber Coatings Commercially Available for SPME Use, by Polarity

<table>
<thead>
<tr>
<th>Fiber Coating</th>
<th>Film Thickness (μm)</th>
<th>Maximum Temperature (°C)</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nonpolar Fibers</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polydimethylsiloxane (PDMS)</td>
<td>100</td>
<td>280</td>
<td>Nonpolar compounds (VOCs, PAHs, etc.)</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>280</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>340</td>
<td></td>
</tr>
<tr>
<td><strong>Polar Fibers</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polycrystalline (PA)</td>
<td>85</td>
<td>320</td>
<td>Polar compounds (pesticides and phenols)</td>
</tr>
<tr>
<td>Carbowax-divinylbenzene (CW-DVB)</td>
<td>65</td>
<td>265</td>
<td>Polar organic compounds</td>
</tr>
<tr>
<td>Carbowax-templated resin (CW-TPR)</td>
<td>50</td>
<td>—</td>
<td>Anionic surfactants</td>
</tr>
<tr>
<td><strong>Bi-Polar Fibers</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polydimethylsiloxane-divinylbenzene (PDMS-DVB)</td>
<td>65</td>
<td>270</td>
<td>Aromatic hydrocarbons, solvents, etc.</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Carboxen-polydimethylsiloxane (Carboxen-PDMS)</td>
<td>75</td>
<td>320</td>
<td>Aromatic hydrocarbons, solvents, etc.</td>
</tr>
<tr>
<td>Divinylbenzene-Carboxen-PDMS</td>
<td>30</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td><strong>Others Polar Fibers</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carboxax (PEG)</td>
<td>60</td>
<td>300</td>
<td>Alcohols and polar compounds</td>
</tr>
</tbody>
</table>

---

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5. **Initial column temperature and column dimensions**: The initial column temperature should be low enough to focus the sample band. Sometimes this is not possible without cryogenics. Columns with thicker film are used to aid in retaining VOCs analytes.

Inter-laboratory studies were carried out for the validation of SPME quantitative analysis of VOCs in aqueous samples [214]. Comparable repeatability, reproducibility, and accuracy were obtained for both SPME and reference methods (P&T and HS). Better precision was found for HS-SPME than direct SPME.

### 21.3.1.3 SPME Limitations and Advantages

SPME shows several advantages over other classical extraction techniques such as high sensitivity and lower detection limit, good precision, relatively low cost, simplicity and ease of use, minimal solvent usage, short preconcentration time, and the possibility of automation.

The fiber quality depends on the manufacturer and its performance can vary from batch to batch, so optimization before use is necessary. The fiber is fragile and can be damaged by high molecular weight compounds irreversible sorbed on the fiber from the samples. The extraction process can be relatively slow because it relies on sufficient stirring or diffusion to bring the analytes into the fiber. Longer desorption times and blank GC runs are required when carry-over effect is possible. Salt addition and suspended matter can damage the fiber during agitation and can lead to changes in sorption properties. Peak tailing is sometimes observed, due to the slower desorption of analytes in the bulk of the sorbents than those in the surface layers [195]. Formation of bubbles on the fiber surface affects the mass transfer rate. The sorbent amount coating the fiber is limited, and so the extraction efficiencies. The fibers are expensive and have a limited life time. The fibers are degraded by using them, losing partially the stationary phase, and hence other compounds may coelute with the target analytes [215].

### 21.3.2 Stir Bar Sorptive Extraction

A quite recent development in sorptive extraction is SBSE. It is based on the sorptive enrichment of the water samples with the sensitivity of packed PDMS beds in conjunction with the application range of SPME in terms of volatility [216]. A stir bar is encased in a glass jacket, which is coated with a 1 mm layer of PDMS absorbent. Two Twister™ are available from Twister, Gerstel GMBH.: 10 mm length × 3.2 mm o.d. (with 55 μL of PDMS used for 1–50 mL sample volume) and 40 mm length × 3.2 mm o.d. (with 219 μL used for 100–250 sample volume) PDMS-coated stir bars [216]. The efficiencies obtained with SBSE are higher than with SPME, due to the higher absorbent volume used in SBSE (typically 0.5 μL in SPME versus 55–219 μL in SBSE). A modification was made to the conventional stir bars for SBSE with a dual-phase system PDMS and active carbons [217].

The extraction process occurs by stirring the immersed stir bar in the aqueous sample at a specified speed for a predefined time. After the extraction, the Twister is removed from the water sample, introduced in a glass tube (4 mm i.d. × 187 mm length) which is placed in a thermal desorption unit where the analytes are thermally desorbed and transferred to the GC. Alternatively, liquid desorption can be used. The octanol-water partition coefficient is in fact proportional to the PDMS–water partition coefficients, so that the absorption is the sorption mechanism of PDMS [218].

### 21.3.2.1 SBSE Advantages and Limitations

SBSE has some operational drawbacks in the removing from the sample, rinsing and drying the stir bars, which are usually performed manually. SBSE yields theoretical recoveries under 90% for analytes with log $K_{ow} < 2$, which implies a limitation of the technique [216]. Both SBSE and SPME are compared in the analysis of malodor wastewater due to characteristic polar compounds from animal-rearing facilities. PA fibers are the best suited for the analysis of polar compounds. SBSE achieved more reproducible results than SPME for aromatic polar compounds [219]. However, SBSE is implemented in quality control labs allowing the analysis of VOCs in more complex aqueous samples such as wines [220] or whiskys [221]. An important advantage is that SBSE and SPME are well suited for multiresidue analysis.
The twister desorption is slower than SPME, because of the higher thickness of the stir bar coating. Hence, desorption is combined with a cold trapping and reconcentration. Two desorption systems are commercially available. These systems are mounted in chromatographs equipped with a programmed-temperature vaporizer injector. The analytes are cryofocused in the programmed-temperature vaporizer with liquid nitrogen [222]. The instrumental cost and the nitrogen consumption suppose an economical drawback.

## 21.4 Membrane Extractions

Membrane extraction (ME) techniques are a set of solvent-free extractions which have gained popularity for VOC analysis in water. The sample is in contact with one side of the membrane surface, called feed or donor side. Analytes permeate selectively (according to their membrane affinity) through the membrane to the other side, called permeate or acceptor side, where they are retained by an acceptor phase. This process is called pertraction (permeation-extraction).

Different extraction techniques have been developed. These techniques have been classified as porous and nonporous, based on their structure, as a flat (like a paper sheet with <1 μm thickness) or hollow fiber (200–500 μm i.d.) configuration. Other classification refers to the number of phases involved in the extraction (one-, two-, or three-phase extraction techniques) [233]. A distinction can be based on the nature of the acceptor phase: liquid membrane extractions, where the acceptor phase is a liquid, such as supported liquid membrane extraction (SLM), microporous membrane liquid–liquid-extraction (MMLLE, the so-called membrane-assisted solvent extraction, membrane-based extraction, or membrane-based stripping), gas diffusion, and so on [233–236], and techniques with a “gas/vacuum” as acceptor phase, in which the analytes are retained in a sorbent trap (membrane extraction sorbent interface, MESI) [237–240] or introduced in a gas chromatograph by a thermal membrane desorption (TMD) [241]. They may also be directly introduced in the mass spectrometer by a driving force based on the pressure difference (such as membrane introduction in mass spectrometry, MIMS) [1,242–246]. Most recently, MIMS has been combined with a proton transfer reaction–mass spectrometer (PTRMS) [247] and used to measure directly VOCs in water [248].

Analytes can be extracted from the water sample or from its HS. The pervaporation is the extraction of VOCs from an aqueous matrix through a semipermeable membrane to a gas phase, while the permeation is the extraction of volatiles from a gas donor phase (the HS of an aqueous or solid) to a gas acceptor phase. These processes are governed by the diffusion laws. The membranes typically used are made up of hydrophobic, nonporous PDMS polymer; although microporous membranes (such as polypropylene or Teflon) have been used for pervaporation.

Flat membranes were developed first, but hollow fiber membranes gain in popularity. Hollow fiber membranes provide higher surface area per volume and can be packed in a small volume. Two different configurations are implemented with hollow fiber: membrane in sample (MIS) and sample in membrane (SIM). In the former, the hollow fiber is introduced in the water sample and a gas stream (or the vacuum) removes the analytes from the other side. In the latter, the water flows “through” or “over” the hollow fiber, while the stripping gas flows countercurrent on the other side. SIM configuration provides higher extracting efficiency than MIS [1].

The main factors affecting the extraction are those involved in the mass transfer of analytes from the water toward the membrane (or toward the sample HS and then toward the membrane) and through it. When the water flow rate reaches the same value as the gas flow rate, then the upper limit of extracted-analyte is obtained [249]. The temperature increase yields in higher diffusion coefficients in water and in the PDMS fiber, and hence a higher extraction efficiency. The upper extraction temperature is determined by the membrane damage or the increase of water solubility in the membrane [242]. Thinner membranes provide faster mass transfer. The larger the sample volumes put in contact with the membrane, the higher the instrumental response. An alternative introduction technique is pulse introduction membrane extraction (PIE), which is a nonsteady state and avoids the usage of a large volume of sample [250].

MESI, TMD, and MIMS suffer from a limited range of applications limited to apolar volatile compounds. The limitation results from the usage of PDMS membrane. MESI, TMD, and P&T were compared by Matz et al. [241]. P&T offers a simple set-up, high throughput, and good sensitivity, but it suffers in poor extraction of polar compounds and the trapped water which induces chromatographic problems.
MESI does not suffer from trapped water, but its memory effect is the main drawback. On the other hand, TMD is adequate for polar compounds and does not show the advantage of water exclusion.

21.5 Solvent Extraction Techniques

21.5.1 Liquid–Liquid Extraction

The classical LLE technique is still in use because it is implemented in standard methods and because the simplicity of the instrumentation [251]. Recently, LLE combined with large volume injection has become an alternative for trace analysis due to the availability of these injection systems which allow injecting up to 100 μL of liquid–liquid extract [252–254]. Unfortunately, LLE technique has many limitations and drawbacks from analytical and environmental points of view. Large volumes of generally toxic organic solvents, which should be extremely pure, are used. Analytes can coelute with the extraction solvent interfering the determination. Large quantities of sample are required to attain the detection limits. With some samples, the initial solvent extraction step results in the formation of an emulsion and hence prolongs the extraction process. The extraction is usually laborious and time consuming with many sources of errors. In the last few years, a considerable scientific interest is focussed in developing miniaturized solvent extraction techniques to avoid these limitations.

The miniaturization can be performed by two different approaches: by reducing the dimension of the stabilized LLE procedure or by developing new extraction techniques and devices. In the former case, the aim lies in the maximum reduction of the ratio between the organic solvent and the sample volumes, so that a better preconcentration factor is obtained. The organic solvent must be water immiscible and the analytes solubility in the organic solvent should be higher than in the aqueous phase.

21.5.2 Single-Drop Microextraction

SDME is evolved from the miniaturization of the traditional LLE. Liu and Dasgupta reported the first sodium dodecyl sulfate extraction on a chloroform drop of 1.3 μL [255]. At the same time, Jeannot and Cantwell suspended a 8 μL drop of n-octane in a Teflon rod to extract 4-methyl-acetophenone [255]. P&T has limitations when the group of VOCs is not purgeable (e.g., their high water solubility or their degradation in the desorption step), so SDME becomes an interesting alternative cheaper than SPME or SBSE. In this method, a single liquid drop of a few microliters is used as a collection phase. The organic solvent must have a sufficiently high surface tension to form a drop which can be exposed to the analyte solution. Once the extraction is finished, the single drop is injected into the GC. Although, several methodologies are developed they can be classified by two different approaches. Based on the sampling mode, the SDME can be performed in direct contact to the water sample or in its HS. Based on the extraction, SDME can be performed in static-mode suspending the drop in the syringe needle or in dynamic mode, in which the drop is exposed to the sample and retracted several times.

Steps of SDME process are:

1. The magnetic stirrer is switched on to agitate the aqueous sample solution.
2. A specific volume of organic solvent is drawn into the syringe with the needle tip out of the solution and the plunger is depressed by 1–2 μL.
3. The needle is then inserted through the septum of the sample vial.
4. The plunger is depressed to expose the organic drop to the stirred aqueous solution or its HS for a period of time.
5. The drop is retracted into the microsyringe.
6. The syringe is drawn out of the vial and subsequently injected in a chromatograph.

In dynamic-SDME, steps 4 and 5 are repeated several times.

The reader can find further information on the theoretical aspects of SDME in Refs. [96,255,256].
21.5.2.1 Factors Affecting the Technique

Factors affecting the SDME are described in a review by Psillakis and Kalogerakis [97,256]:

1. **Extracting solvent**: To achieve the required selectivity, the most adequate solvent should be chosen. The rule “like dissolves like” can be a good approach. Different water-immiscible solvents with different polarity and water solubility can be tested. The solvent must satisfy some basic requirements: high surface tension to form a drop, selectivity, extraction efficiency, low volatility, incidence in the drop loss, rate of drop dissolution, solvent toxicity, and its peaks should be well separated from the analyte peaks [257]. Recently, ionic liquids have been used as extracting phase avoiding the problems of conventional solvents due to their volatility [258–261].

2. **Extraction time**: The maximum sensitivity is achieved at the equilibrium, in which case, as pointed out in SPME, the results are more reproducible and less influenced by experimental errors. However, SDME is not an exhaustive technique, so precise and accurate results can be attained by strict control of the predefined time. The extraction time can be matched with the chromatographic cycle time to obtain the maximum sample throughput [257,262]. An extracted amount of analyte – time plot may allow determining the optimum extraction time. Short extraction time should be chosen with conventional solvents, however, with ionic liquids longer times can increase the amount extracted.

3. **Sample agitation**: The higher is the extraction rate, the higher is the sensitivity, since the agitation reduces the diffusion layer thickness. However, the agitation rate has an upper limit due to the drop dislodgement and dissolution. The use of small stir bars is recommended.

4. **Salt addition**: Unexpected results have been obtained when a salt is added. The salt addition reduced the extraction of chlorobenzenes and the majority of nitroaromatic explosives by SDME [97,263–265]. However, the salt addition enhances the sensitivity when alcohols, MTBE, and chlorobenzenes are analyzed by HS-SDME [97]. The results obtained by NaCl addition are better than by KNO₃ addition [97,263,264], but Na₂SO₄ is not tested.

5. **Drop volume**: Increasing the drop volume results in a sensitivity enhancement. However, a large drop volume involves a greater solvent peak, which may interfere in the analyte determination. In addition, a large drop is more difficult to handle and may fall off. With ionic liquids higher drop volumes can be used due to the higher viscosity [266].

6. **Sampling temperature**: Rising the temperature enhances the obtained signal up to a certain temperature, and then a decrease in sensitivity is observed. This behavior is observed in the determination of MTBE and alcohols. By increasing the temperature the mass transfer to the HS is favored in these polar compounds, and hence a higher sensitivity. The analyte absorption onto the drop is an exothermic process, so the absorbed amount by the drop decreases upon a further temperature increase [97]. A cooling system for the syringe needle was introduced and used in the MTBE extraction, since the distribution constant between the organic phase and the sample decreases by rising the temperature [267]. The use of ionic liquids allows the use of higher sampling temperature, but the water vapor can become a problem.

7. **Derivatization**: The derivatization can be carried out in the sample matrix and then the derivatives are extracted by SDME or extracted and derivatized in the drop. By means of derivatization, highly volatile, thermolabile, and reactive compounds are transformed into derivatives more adequately for GC analysis. Aldehydes are analyzed in blood by both derivatization and SDME [98,268] and by SDME and in-drop derivatization [269]. Phenols which are high polar compounds, although phenols are not strictly volatile compounds, are derivatized by acylation, silylation, or alkylation because they tend to provide broad and tailing peak increasing the LODs. Phenols are extracted by SDME and derivatized in the syringe [96].

8. **Syringe requirements**: A proper syringe should be used to attain repeatable extraction. The needle should have a minimum dead volume (26s gauge) and a no. 2 point style beveled tip, which allows more than 95% of the drop to be withdrawn [256]. Syringes with a plunger which is a wire inside the glass barrel of the syringe show a higher dead volume than syringe in which
the plunger is a wire inside of the needle. If the first type of syringe is used and the standards are injected directly not being extracted by SDME a dilution factor should be considered in the samples extracted by SDME due to the dilution by the dead volume (a part from the sensitivity loss). Hence, the second type of syringe is recommended [255, 270].

9. Other practical considerations: Washing the microsyringe several times with the solvent used in SDME is recommended to remove the air. Flat-bottom vials allow a set location for the stir bar, so that the water flow pattern is quite similar.

21.5.2.2 SDME Limitations and Advantages

SDME is a fast, inexpensive, and simple LLE technique which uses a negligible volume of solvent. SDME avoids the problems of solvent evaporation as in LLE. SDME offers over SPME additional advantages. Conditioning is not required. The number of solvents for SDME is much higher than the number of sorbent phases currently available for SPME. The cost of a few microliters is negligible when compared with the cost of an SPME fiber [96]. A new drop is used in each sample, avoiding the possibility of carry-over effect. The extraction is carried out in a short time. The GC system does not need any modification [271]. The solvent evaporation is faster than the polymer desorption in the GC injector, which leads to greater tailing peaks. THMs are extracted with 2 μL of hexane and analyzed by GC-ECD, the SDME is compared with SPME [272]. Higher drop volumes and more stability of the drop is accomplished with ionic liquids, however, drop injection in a gas chromatographic system is more problematic [273]. Lab-made [273] or a commercially available [266] interfaces were used to overcome this problem.

However, the extraction is not exhaustive, like SPME or HS, and the technique is not automated. The solvent peak can interfere in overlapping some analyte peaks.

21.5.3 Liquid-Phase Microextraction

Recently, Pedersen-Djergaard and Rasmussen introduced and popularized in the field of drug analysis an alternative liquid–liquid microextraction based on the use of a low cost, disposable porous hollow fiber made from polypropylene [274, 275]. In LPME (the so-called liquid–liquid microextraction), the pores of a hollow fiber are impregnated by an organic solvent, through which the aqueous sample is successively sucked and expelled to reach the analyte enrichment. The theory, main parameters and practical considerations, applications, and different configuration to implement LPME has been reviewed in depth [276]. This technique provides higher enrichment factors than SDME with shorter extraction times [277]. However, LPME has a more limited application field than in vial-LLE, because it only can be used with high and moderate hydrophobic analytes, with distribution coefficients between the solvent and the sample (K_{ow}) higher than 500 [274].

Two sampling modes are distinguished in LPME: two phases and three phases. In the two-phase LPME sampling mode, the analyte is extracted from a water sample (donor phase) through a water-immiscible solvent immobilized in the pores of the hollow fiber into the same organic solvent (acceptor phase) present inside the hollow fiber. While in the three phases the analyte is extracted from the water sample (donor phase) through the solvent which fills the pores in an aqueous phase (acceptor phase). The latter technique is usually combined with HPLC and its applicability can be extended to ionizable analytes, while the former can be combined also with GC [277]. The former mode is better suited for VOCs analysis.

21.5.3.1 Parameters Affecting the Technique

1. The hollow fiber: The porous hollow fiber should be hydrophobic and compatible with the solvent. The most commonly used are made from polypropylene (with i.d. of ~600, 0.2, and 0.64 μm of nominal and maximum porous size, respectively).

2. Organic solvent: For analytes without ionizable groups, the partition coefficient is determined by the organic solvent selected. The solvent should be water immiscible, highly immobilized in
the pores of the hollow fiber, and have an excellent GC behavior. It should provide an adequate selectivity and high extraction recoveries. A variety of solvents with different polarity and water solubility should be tested. For highly hydrophilic analytes (in their neutral form) LPME is not the extraction technique of choice.

3. **Sample agitation**: In LPME, the solvent is soaked in the pores, so the technique can tolerate high agitation speeds. However, high speed can lead the formation of air bubbles that tend to adhere to the hollow fiber, favoring the solvent evaporation. The sample vibration is advantageous, since it avoids the contamination from the stirrers [275] and affects all the liquid phases [274]. An alternative is the use of dynamic LPME, in which the mass transfer is improved.

4. **Salt addition and pH adjustment**: Increasing the ionic strength leads to different effects depending on the analyte nature. Changes in pH of the water sample favor the extraction of analyte when an acid–base equilibrium is attained.

5. **Sample and solvent volumes**: The instrumental response is increased by raising the ratio of the sample–solvent volumes, taking into account the volume injected in the chromatograph.

6. **Extraction time**: Extraction-time profiles of the analytes are a good approach to choose the extraction time. The extraction time should be shorter than the chromatographic cycle time to allow high sample throughput, although the equilibrium is not reached whenever the required sensitivity is attained.

7. **Sample viscosity**: The sample viscosity reduces the extraction speed.

### 21.5.3.2 LPME Limitations and Advantages

LPME is proved to be an extremely simple, low-cost, and virtually solvent-free sample-preparation technique, which provided a high degree of selectivity and enrichment by additionally eliminating the possibility of carry-over between runs [278–280]. LPME overcomes the drawback of the droplet fall. An alternative LPME was performed in a hollow fiber of 2 cm, which is sealed and immersed in the sample to extract the analytes. With this approach higher enrichment factors are obtained for penta- and hexachlorobenzene and can be used for slurry, real environmental, and biological samples [281].

The analyte extraction is limited to highly or moderate hydrophobic compounds with large $K_{ow}$.

### 21.5.4 Dispersive Liquid–Liquid Microextraction

In the last lustrum, dispersive liquid–liquid microextraction, a revolution in liquid-phase extraction, was introduced by Assadi and coworkers in 2006 [282]. This technique is based on a few microliters of an organic solvent (chlorobenzene, chloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene, etc.) with high density and a disperser solvent (methanol, acetonitrile, or acetone) with high miscibility in both extractant and aqueous phases. The mixture of both solvents is added to an aqueous sample forming a cloudy solution of fine droplets. The tertiary mixture is centrifuged and the sedimeted drop is recovered with a syringe for the injection on the chromatographic system. The reader is directed to a good review by the pioneering of the technique [283].

Some variations were developed using ultrasound (ultrasound-assisted liquid–liquid microextraction, USLLME) [284,285] in order to produce the cloudy solution or a vortex-assisted agitation (vortex-assisted liquid–liquid microextraction) [286,287] instead of the disperser solvent. Low-density solvents have been used and recovering the drop from the upper surface of the solution after centrifugation is done with the help of a syringe [286,287] or the solidification of the drop decreasing the temperature of the solution, and taking the drop with a micro spatula [288,289] in dispersive liquid–liquid microextraction method based on the solidification of floating organic drop (dLLME-SFOD). Another strategy consists of mixing a few microliters of ionic liquids with the aqueous sample and changing the temperature to achieve the separation of the two phases [290] is called the temperature-controlled ionic liquid-dispersive liquid-phase microextraction (TCIL-DLPME).
21.6 Conclusions

Several extraction techniques are treated and their applications to VOCs are referenced in the respective tables. As a general remark, the extraction of VOCs from the HS usually affords shorter extraction times. The extraction of polar compounds is more difficult, and several extraction techniques poorly extract these compounds. Water involves some problems in techniques like P&T. The sample matrix should be considered in order to choose the adequate extraction technique. Recently, miniaturized and polymer-based extractions are interesting for the analytical chemist achieving lower quantitation limits, higher sensitivity, higher reproducibility and sample throughput and lower analysis costs for a lot of compounds.

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Determination of Volatile Organic Compounds in Water


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