Table 6  List of solvents for separation of morphine

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CAS-NO</th>
<th>Predicted</th>
<th></th>
<th>Experimental</th>
<th></th>
<th>Compound class (RTECS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$T_b$ (K)</td>
<td>$T_m$ (K)</td>
<td>$\delta$ (MPa$^{1/2}$)</td>
<td>$T_b$ (K)</td>
<td>$T_m$ (K)</td>
</tr>
<tr>
<td>Benzene</td>
<td>71-43-2</td>
<td>353.24</td>
<td>278.68</td>
<td>18.73</td>
<td></td>
<td>C,D,M,T,S</td>
</tr>
<tr>
<td>Toluene</td>
<td>108-88-3</td>
<td>383.78</td>
<td>178.18</td>
<td>18.32</td>
<td></td>
<td>C,M,T,S</td>
</tr>
<tr>
<td>CCl₄</td>
<td>56-23-5</td>
<td>349.79</td>
<td>250.33</td>
<td>17.55</td>
<td></td>
<td>C,D,M,T,S</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>110-82-7</td>
<td>353.87</td>
<td>279.69</td>
<td>16.76</td>
<td></td>
<td>M,S</td>
</tr>
<tr>
<td>1,5-Pentanediol</td>
<td>111-29-5</td>
<td>491</td>
<td>253</td>
<td>27.0</td>
<td>512.15</td>
<td>257.15</td>
</tr>
<tr>
<td>Acetol</td>
<td>116-09-6</td>
<td>418</td>
<td>226</td>
<td>27.2</td>
<td>418.65</td>
<td>256.15</td>
</tr>
</tbody>
</table>

D, drug; S, primary irritant; T, reproductive-effector; M, mutagen; C, tumorigen.

However, need to integrate aspects of molecular modelling and computational chemistry before acceptable solutions to problems involving complex solutes and tight environmental regulations can be obtained. Finally, it should be noted that having a good solvent means easier design/operation of the solvent-based separation technique. Therefore, it is important to formulate correctly the solvent selection problem and to find reliable results in the form of optimal solvents.

Further Reading


Steam Distillation

L. Ramos, Free University, Amsterdam, The Netherlands

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Sample preparation is nowadays the limiting step in the trace analysis of organic pollutants in environmental and biological samples. Looking forward to the laboratory of the future, versatile and universal sample enrichment techniques are required, which can produce fast and valid data, with low costs in terms of solvent consumption and operator involvement. A selectivity higher than that of the classical exhaustive extraction methods or the simultaneous elimination of the interference material could be an additional requirement, as it would reduce the amount of solvents and adsorbents used by reducing or eliminating the subsequent clean-up step. Possible additional benefits deriving from a low manual manipulation of the samples would be a reduction in the risk of contamination and loss of the analytes, as well as an easier automation of the process.

Steam distillation extraction—solvent extraction (SDE) has been presented as such a universal sample enrichment technique. SDE allows the simultaneous extraction, clean-up and concentration of the target compounds in a closed system, with short analysis times (1–8 h) and by using small amounts of organic solvents (a few mL). This paper reviews this assumption for the case of the analysis of less volatile organic pollutants in environmental samples. The SDE advantages and shortcomings for such an analysis have been discussed.

Introduction

The monitoring of toxic organic chemicals in environmental and biological samples is a major concern in many different fields. However, the large variety of compounds of interest, the differences existing in
their environmental levels and physico-chemical properties, and the complexity of the matrices typically investigated make the development of universal analytical methods for such an analysis a very difficult goal. This is especially true for the most toxic organic pollutants as their high toxicity makes their reliable detection and accurate quantification at the trace level more relevant.

Most of the procedures described in the literature for the analysis of less volatile organic pollutants are time-consuming, laborious and specific for the determination of an analyte (or family of compounds) in a selected matrix. Examples of selective extraction of the target compounds, allowing their determination without any additional clean-up, can be found in the literature. However, most of these procedures involve sophisticated and expensive analytical techniques, such as supercritical fluid extraction or gel permeation chromatography. On the other hand, the efficiency of these methods has been recognized to be highly matrix-dependent. Because of these unresolved shortcomings, classical exhaustive extraction techniques, i.e. liquid-liquid extraction, LLE, solid-liquid extraction or Soxhlet extraction, are still widely used in official methods and routine applications. Due to the low selectivity of these methods, subsequent elimination of the co-extracted material is recommended. Such a clean-up step is mandatory for reliable trace level determination of lipophilic and bio-accumulative pollutants in biological and complex environmental samples.

Steam distillation-solvent extraction (SDE) has been used mainly for the extraction and concentration of fragrance and flavour compounds. However, a variety of SDE methods reporting sample preparation for the analysis of pollutants in environmental samples can be found in the literature. Most of these methods allow the simultaneous extraction, clean up and concentration of the target compounds. The investigated compounds range from volatile polar and non-polar pollutants to non-ionic surfactants. This article reviews the suitability and the limitations of SDE for the determination of less volatile trace organic pollutants, such as pesticides, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs), or surfactants, in environmental and biological matrices. The most relevant variables affecting the efficiency of the SDE of these compounds are discussed and the results of some selected applications reviewed.

**General Considerations**

According to the theoretical model developed by Rijks et al., in 1983, the efficiency of the SDE process increased with the extraction time and with the liquid and vapour flows. The process also depends on analyte-specific parameters related to the activity coefficient (calculated from the water solubility of the analyte at 100°C) and the gas-liquid distribution coefficient of the compound in water at the process temperature (i.e., 100°C for water steam). Not unexpectedly, the recoveries increased with the affinity of the target compounds for the extracting solvent. This theoretical model is applicable only under ideal conditions, which are achieved when all volumes and flow rates remain constant and there is ideal mixing and equilibrium at every stage. In spite of these limitations, the model reflects the effect of several experimental factors on the SDE process. In fact, the different modifications carried out on the SDE devices originally described by Likens and Nickerson in 1964 and by Flath and Forrey in 1977 reveal the influence of several parameters on the recoveries of the target compounds. The modifications were mainly focused on increasing the size of the vapour chamber and/or the condensing surface to allow a more complete mixing of the solvent and steam vapours, as well as on the miniaturization of the system. As a consequence of the changes in design (Figure 1), the efficiency of the extraction was increased, the analysis time reduced and the field of SDE expanded through the analysis of residue levels of less volatile pollutants in environmental samples.

Due to the characteristics of the technique, the feasibility of SDE for the analysis of less volatile compounds depends on their (i) potential for forming azeotropes with water and (ii) relative solubility in water and in the extraction solvent. However, the SDE of the target compounds from complex samples can be expected to occur only after destruction or degradation of the main matrix components, which usually entrap the analytes (see below). Therefore, as stated by Nash in 1984, the applicability of the SDE technique to the analysis of this kind of environmental matrices would be limited by the resistance of the investigated compounds to the selected degradation procedure. Alternatively, in some cases, co-distillation solvents have been used to improve the SDE efficiency by reducing the surface tension of the water and by increasing the extraction power (polarity) of the organic solvent. Finally, rather different results have been published about the suitability of adding anti-foam agents in applications involving fatty samples (see Table 3).

**Application of SDE to the Analysis of Aqueous Samples**

Water was one of the first environmental samples selected to evaluate the feasibility of the SDE
technique for the determination of less volatile organic contaminants levels. Table 1 summarizes relevant data concerning some reported methods for the analysis of this matrix.

Quantitative recoveries of spiked organochlorinated pesticides, OCPs (globally, in the range 90–106 ppb), and PCBs (globally, in the range 70–104 ppb) in aqueous samples have been reported using the SDE technique. The reported methods allowed the simultaneous extraction and concentration of the analytes in 1–1.3 h in a relatively small amount of a non-polar solvent (1–15 mL). Usually, no additional treatment of the sample or the organic extract was required. The SDE technique was favourably compared with other widely used extraction procedures, such as LLE or solid-phase extraction (SPE) by Ramos et al. in 1995, e.g. similar recoveries have been published for the analysis of PCBs in water at the ppb (ng mL$^{-1}$) level by using SDE, LLE or SPE. However, the higher repeatability of the SDE procedure (relative standard deviations, RSD, lower than 10%) and the small amount of organic solvent involved, as well as the short sample preparation times, makes SDE a valuable alternative technique for such an extraction, especially when a large number of analyses have to be carried out.

Nevertheless, some limitations of SDE have also been reported for less volatile pollutants in water samples. Nash et al. in 1984 studied different parameters affecting the efficiency of the steam distillation process. They concluded that this technique is probably limited to compounds with a vapour pressure of about 1 kPa at 100°C. Their results also showed that the performance of SDE depends on the concentration investigated and that recoveries tend to increase with the spiking level.

Similar tendencies have been observed by Ramos et al. in 1995 when using the SDE technique for the extraction of water spiked with the 2,3,7,8-substituted-CDD/Fs at different levels of concentration (0.25–2 ng mL$^{-1}$, 0.025–0.2 ng mL$^{-1}$ and 0.0025–0.02 ng mL$^{-1}$). The recoveries obtained for the lower and higher boiling point congeners (tetra- and octa-CDD/Fs, respectively) are consistently lower than those found for the rest of the investigated congeners: respectively 40–76% and 73–137% at the highest level of concentration investigated, 39–60% and 62–92% at the intermediate, and 37–55% and 25–72% at the lowest spiking level. These results also show that the SDE recoveries for a given compound decrease with the concentration level when using n-pentane as the extraction solvent. The simple substitution of n-pentane for a solvent more selective for the PCDD/Fs (dichloromethane) increases recoveries from 25–73% to 71–139% for tetra- to hepta-CDD/Fs at the 0.0025–0.02 ng mL$^{-1}$ level. However, no additional improvement is obtained for the octa-CDD/F recoveries (38–56%). In spite of the low recoveries obtained for OCDD/F, the proposed SDE procedure compares favourably with results previously published by using LLE or SPE in terms of repeatability, analysis time and solvent consumption.

Good recoveries (in the range 84–100%) have been reported by Meissner et al. for the analysis of surfactants such as fatty alcohol sulfates and alkyl polyglycosides in water (Table 1). SDE of the fatty alcohols yielded by hydrolysis and subsequent LLE of the original compounds is an attractive technique for the effective clean-up and concentration of these complex mixtures of compounds at the trace level. On the other hand, the application of SDE to the extraction of fatty alcohol ethoxylates with more than three ethoxy units in the molecule cannot be accomplished due to their high solubility in water.
Table 1  SDE methods for the analysis of less volatile organic pollutants in aqueous samples

<table>
<thead>
<tr>
<th>Compound</th>
<th>Spiking level (ng mL⁻¹)</th>
<th>Solvent (mL)</th>
<th>Extraction time (h)</th>
<th>Cc. factorᵃ (water:solvent, v/v)</th>
<th>Post-treatmentᵇ</th>
<th>Recovery (%)</th>
<th>RSD (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCP</td>
<td>0.004–0.016</td>
<td>Isooctane/toluene (15)</td>
<td>1</td>
<td>167:1</td>
<td>NR</td>
<td>90–104</td>
<td>?</td>
<td>Hemmerling et al. (1991)</td>
</tr>
<tr>
<td>Arochlor 1016, 1242, 1248, 1254</td>
<td>0.016</td>
<td>Isooctane/toluene (15)</td>
<td>1</td>
<td>167:1</td>
<td>NR</td>
<td>98–100</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>OCP</td>
<td>0.4–4.0</td>
<td>n-pentane (1)</td>
<td>1.3</td>
<td>50:1</td>
<td>NR</td>
<td>97–106</td>
<td>?</td>
<td>Godefroot et al. (1982)</td>
</tr>
<tr>
<td>Arochlor 1260</td>
<td>10</td>
<td>n-pentane (1)</td>
<td>1.3</td>
<td>50:1</td>
<td>NR</td>
<td>81–104ᵇ</td>
<td>?</td>
<td>Ramos et al. (1995)</td>
</tr>
<tr>
<td>Toxic PCBs</td>
<td>0.01–1.0</td>
<td>n-pentane (2)</td>
<td>1</td>
<td>50:1</td>
<td>Concentration</td>
<td>70–115</td>
<td>&lt;10</td>
<td></td>
</tr>
<tr>
<td>PCDD/Fs</td>
<td>0.025–2.0</td>
<td>n-pentane (2)</td>
<td>1</td>
<td>50:1</td>
<td>Concentration</td>
<td>49–139</td>
<td>&lt;10</td>
<td>Ramos et al. (1995)</td>
</tr>
<tr>
<td>PCDD/Fs</td>
<td>0.0025–0.02</td>
<td>Dichloromethane (2)</td>
<td>1</td>
<td>50:1</td>
<td>Change of solvent</td>
<td>49–139</td>
<td>&lt;10</td>
<td></td>
</tr>
<tr>
<td>Fatty alcohol sulfates</td>
<td>500 nM</td>
<td>Ethyl acetate (2)</td>
<td>3ᵇ</td>
<td>100:1</td>
<td>Derivatization</td>
<td>87–100</td>
<td>5.6–7.0</td>
<td>Meissner et al. (1999)</td>
</tr>
<tr>
<td>Alkyl polyglycosides</td>
<td>2 μM</td>
<td>Ethyl acetate (2)</td>
<td>4ᵇ</td>
<td>25:2</td>
<td>Derivatization</td>
<td>84</td>
<td>?</td>
<td></td>
</tr>
</tbody>
</table>

ᵃConcentration factor. ᵇPost-SDE treatment required. ᶜNR, not required. ᵈRecoveries for some selected peaks.  ᵇThe SDE was conducted after hydrolysis with 4 M H₂SO₄ plus liquid–liquid extraction with diethyl ether of the hydrolysate and concentration.

Application of SDE to the Analysis of Non-Fatty Environmental Samples

Table 2 summarizes relevant data related to some reported SDE methods for the analysis of less volatile organic pollutants in non-fatty environmental samples. Most of the reported SDE applications referred to the analysis of OCPs and toxic aromatic compounds, e.g. PCBs, polychlorinated naphthalenes (PCNs), or polynuclear aromatic hydrocarbons (PNAs), in soils and sediments. Contrary to what might be expected from the high complexity of these samples, most of the methods did not include any further pre-treatment of the matrix but blending with the selected volume of water. Only a few procedures involving drastic treatments (e.g. blending of the sample with H₂SO₄ and K₂Cr₂O₇) during the SDE to guarantee the destruction of the soil or sediment components in which the target compounds could be entrapped, can be found in the literature.

The efficiency (or need) of such a drastic treatment is difficult to evaluate from the data published. In general, high (quantitative) recoveries have been reported for freshly spiked analytes (globally in the range 78–102% for PCBs and OCPs at the 20–90 μg g⁻¹ level) with all the procedures (Table 2). However, the efficiency of the proposed SDE methods for the extraction of endogenous pollutants from weathered samples has been scarcely evaluated. In these studies, Seidel et al. (1993) and Cooke et al. (1980) found concentrations very close or below the limit of detection have usually been reported for the endogenous contaminants, but the lack of comparison of the SDE results with those obtained by standard or more exhaustive methods, i.e. Soxhlet extraction, do not allow any discussion about the methods used.

Dunnivant et al. in 1988 reported recoveries ranging from 47 to 99% for SDE of certified sediments with PCBs at the 2.34–24.6 μg g⁻¹. However, as quoted above, this SDE method involved a digestion of the sample under drastic conditions.

In a closely related study, Nash et al. compared the efficiency of steam distillation with subsequent organic solvent extraction to that of Soxhlet extraction for the analysis of pesticides in soil, plant tissues and air (polyurethane foam filters). Both procedures provided similar recoveries for the spiked samples (in the ranges 80–90%, 80–90% and 90–100%, respectively). However, the SDE levels determined for weathered soils blended with water were 40–50% lower than the concentrations found by the Soxhlet procedure. The study also showed that the efficiency
Table 2  SDE methods for the analysis of less volatile organic pollutants in non-fatty environmental samples (symbols as in Table 1)

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Compound</th>
<th>Spiking level (μg g⁻¹)</th>
<th>Pre-treatment</th>
<th>Solvent</th>
<th>Extraction time (h)</th>
<th>Post-treatment Recovery (%)</th>
<th>RSD (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment</td>
<td>Arochlor 1016</td>
<td>50</td>
<td>Blended with 2.5 L water</td>
<td>Isooct/toluene (15)</td>
<td>1</td>
<td>Elimination S 78</td>
<td>?</td>
<td>Veith et al. (1977)</td>
</tr>
<tr>
<td>Weathered sediment</td>
<td>PCBs, PCNs, PNA s</td>
<td>–</td>
<td>Blended with 0.8–1.1 L water</td>
<td>n-Hexane (10)</td>
<td>2.2</td>
<td>Concentration –</td>
<td>1.1–23</td>
<td>Cooke et al. (1979)</td>
</tr>
<tr>
<td>Sediment</td>
<td>Chlorinated benzenes</td>
<td>100–1000</td>
<td>Blended with 0.25 L water</td>
<td>n-Hexane (10)</td>
<td>3</td>
<td>Elimination S 76–91</td>
<td>0.5–21</td>
<td>Onuska et al. (1985)</td>
</tr>
<tr>
<td>Sediment</td>
<td>Chlorinated benzenes</td>
<td>10–100</td>
<td>Blended with 0.25 L water</td>
<td>n-Hexane (10)</td>
<td>3</td>
<td>Elimination S 71–88</td>
<td>1.4–33</td>
<td></td>
</tr>
<tr>
<td>Sediment</td>
<td>Chlorinated benzenes</td>
<td>1–10</td>
<td>Blended with 0.25 L water</td>
<td>n-Hexane (10)</td>
<td>3</td>
<td>Elimination S 66–89</td>
<td>1.4–17</td>
<td></td>
</tr>
<tr>
<td>Certif. Sediment</td>
<td>PCBs</td>
<td>2.34–24.6</td>
<td>200 mL H₂SO₄ + K₂Cr₂O₇, 200 mL H₂SO₄ + K₂Cr₂O₇</td>
<td>n-Hexane (15)</td>
<td>8</td>
<td>Alumina 47–99</td>
<td>0.3–5.4</td>
<td>Dunnivant et al. (1988)</td>
</tr>
<tr>
<td>Sediment</td>
<td>PCBs</td>
<td>33.6–90.0</td>
<td>100 g soil + 20 mL water + 10 mL ethanol + ultrasonic, 1 min</td>
<td>Alumina (15)</td>
<td>8</td>
<td>Alumina 102</td>
<td>4.7–9.3</td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>HCB</td>
<td>20.0</td>
<td>100 g soil + 20 mL water + 10 mL ethanol + ultrasonic, 1 min</td>
<td>Petrobenzine (?)</td>
<td>1</td>
<td>NR 100</td>
<td>2.7</td>
<td>Seidel et al. (1993)</td>
</tr>
<tr>
<td>Weathered soil</td>
<td>Endogenous OCP</td>
<td>–</td>
<td>100 g soil + 20 mL water + 10 mL ethanol + ultrasonic, 1 min</td>
<td>Petrobenzine (?)</td>
<td>1</td>
<td>NR –</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Particulate</td>
<td>PCDD (homologues)</td>
<td>0.045–8.56</td>
<td>150 g (sample + water) + HCl + sonication</td>
<td>n-Hexane (10)</td>
<td>3</td>
<td>Basic alumina 85–116</td>
<td>?</td>
<td>Townsend et al. (1989)</td>
</tr>
<tr>
<td>Fruits, vegetables</td>
<td>OCCs, OCPs</td>
<td>0.01–1.0</td>
<td>5–10 g sample blended with 0.25 L water</td>
<td>n-Hexane (5)</td>
<td>1.5</td>
<td>NR 66–108</td>
<td>?</td>
<td>Hemmerling et al. (1991)</td>
</tr>
<tr>
<td>Fruits, vegetables</td>
<td>PCBs</td>
<td>0.1</td>
<td>5–10 g sample blended with 0.25 L water</td>
<td>n-Hexane (5)</td>
<td>1.5</td>
<td>NR 68–89</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Sediments</td>
<td>Chiral PCBs</td>
<td>–</td>
<td>5 g sample blended with 4 g Cu + 50 mL water</td>
<td>n-Pentane (2)</td>
<td>1</td>
<td>NR –</td>
<td>–</td>
<td>Glausch et al. (1996)</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>Nonylphenol polyethoxylates</td>
<td>100</td>
<td>1 g sample blended with 0.1 L water</td>
<td>Cyclohexane (1–2)</td>
<td>3</td>
<td>NR (HPLC) 30</td>
<td>?</td>
<td>Lee et al. (1997)</td>
</tr>
<tr>
<td>Toothpaste</td>
<td>Fatty alcohol sulfates</td>
<td>–</td>
<td>30 g sample + 50 mL 4M H₂SO₄ + LLE (diethyl ether, 10 mL) + concentrat.</td>
<td>Ethyl acetate (2)</td>
<td>3</td>
<td>Derivatization –</td>
<td>–</td>
<td>Meissner et al. (1999)</td>
</tr>
</tbody>
</table>

*Isooctane/toluene.
*Replace hexane layer after 1, 2, 4 and 8 h intervals.
*Range for different homologues.
*Mass balance calculations for the whole SDE system by comparison with the initial amount.
*Total concentration for all NPₙEO (n = 1–17).
*By comparison with SFE, except for NP₁EO.
of the SDE depends on the soil type and, in agreement with that mentioned for aqueous samples, on the volatility of the selected compounds. The less volatile the compound, the lower the recovery: SDE recoveries for DDT were only 21–60% of those found by Soxhlet extraction.

Onuska and Terry observed a similar trend when comparing the SDE and the Soxhlet efficiencies for the extraction of spiked chlorinated benzenes from a sediment. The concentrations found using SDE were 14–36% lower than those using the Soxhlet method, except for pentachlorobenzene and 1,3-dichlorobenzene, which were not determined by the latter procedure. The authors also reported a decrease in the SDE recoveries of the target compounds as the investigated concentration level decreased (Table 2). The recoveries of the studied chlorinated benzenes decreased from 76–91% to 66–89% as the spiking level decreases from 100–1000 µg g\(^{-1}\) to 1–10 µg g\(^{-1}\).

In a recent study, Meissner et al. used SDE for the determination of fatty alcohol sulfates in cosmetics (toothpaste) by combining this technique with a hydrolysis treatment. However, the application of SDE to the analysis of nonylphenol polyethoxylates in sewage sludge by Lee et al. failed when compared with the more efficient supercritical fluid extraction technique.

In general, the published SDE methods for the analysis of non-fatty environmental samples involve longer extraction times (1–8 h) than those reported for aqueous samples (1–1.3 h). In addition, and contrary to that proposed by the theoretical model of Rijks et al., the recoveries of less volatile compounds from non-fatty complex samples have been found to be independent of the vapour flow rates. However, it is important to note that in this study by Seidel ethanol was added to the water flask to improve the OCP recoveries, and that the possible effect of a co-distillation solvent was not included in the theoretical model.

**Application of the SDE to the Analysis of Fatty Biological Samples and Food**

Due to the high lipophilicity of some of the most toxic pollutants, such as OCPs, PCBs and PCDD/Fs, the classical procedures for the analysis of these pollutants in fatty samples were based on an exhaustive extraction of the lipids from the matrix. Subsequent removal of the co-extracted lipids has been widely recognized as the main problem with these kinds of methods, especially when analysing samples with high fat contents such as dairy products. Because of the characteristics of the SDE technique, the disruption of the strongly bound pollutant-matrix in these samples can be accomplished before SDE by degradation of the matrix components entrapping the target compounds. Treatment with 1–2 M sulfuric acid followed by ultrasonication in a bath and heating of the sample during the SDE process has been found to be one of the most efficient procedures for breaking down the matrix structure allowing steam distillation of the analytes. Furthermore, this acid treatment allowed a simultaneous clean up of the final extract as the matrix components form more polar products, which can then be easily separated from the non-polar analytes. According to the published results, most samples submitted to this kind of treatment did not require any additional clean up. Filek et al. report good recoveries for the SDE of OCPs from dairy products when using this type of acid pre-treatment: in the range 83–126% for powdered milk and human milk spiked at the 20.0–51.3 ng g\(^{-1}\) level, and in the range of 73–111% for a certified dairy product (OCP levels ranging from 1.5 to 6.6 ng g\(^{-1}\)). However, the SDE method failed when it was used for the extraction of the endogenous PCBs from dairy products with different fat contents. According to the reference method, the PCBs detected by Ramos et al., in 1998 ranged from 2 to 0.01 ng g\(^{-1}\) in the investigated matrices. Nevertheless, most of the PCB congeners were found to be non-detectable with the SDE procedure and, when found at quantifiable levels, the reported concentrations were less than 26% of those determined by the reference method.

Rather similar results were reported by Seidel and Lindner in 1993 for the analysis of the OCPs in dairy products and human milk as none of the investigated compounds were found to be at a quantifiable level. However, no additional comparison with a reference method was included in this study, in which 10 g of sample was blended with water and ethanol. In this case, the alcohol, added as a co-distillation solvent, would also be able to disrupt the fat globule thereby allowing the SDE of the analytes. An important shortcoming of this kind of approach is the formation of large oil drops during the extraction, which increase the diffusion layer and hinder the SDE process. Filek et al. proposed blending of the sample with surfactants has been proposed as a possible solution for the case of fatty matrices without natural emulsifiers.

When no pre-treatment of the fatty sample was carried out, a co-distillation (total, according to Yoon et al., or partial, according to Ramos et al.) of the lipids with the less volatile compounds occurred. Then, a post-treatment for isolation of the target compounds from the co-extracted matrix components was required. Following the implication of these results, it is rather surprising that neither pre- nor post-treatment of the sample was included.
Table 3  SDE methods for the analysis of less volatile organic pollutants in fatty environmental samples (symbols as in Table 1)

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Compound</th>
<th>Spiking level (ng g⁻¹)</th>
<th>Pre-treatment</th>
<th>Solvent</th>
<th>Extraction time (h)</th>
<th>Post-treatment Recovery (%)</th>
<th>Recovery (%)</th>
<th>RSD (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fish tissue</td>
<td>PCBs</td>
<td>1700</td>
<td>Blended with 2.5 L water</td>
<td>Isooct/tol. (15)</td>
<td>7–14</td>
<td>NR</td>
<td>82–85</td>
<td>?</td>
<td>Veith et al. (1977)</td>
</tr>
<tr>
<td>Muscle, liver, kidney</td>
<td>PCBs, PCNs, ΣDDT</td>
<td>5000</td>
<td>Blended with 0.1 L water</td>
<td>n-Heptane (10)</td>
<td>2</td>
<td>Concentration</td>
<td>67–100</td>
<td>1.0–20</td>
<td>Dunnivant et al. (1988)</td>
</tr>
<tr>
<td>Muscle, liver, kidney</td>
<td>PCBs, PCNs, ΣDDT</td>
<td>1000</td>
<td>Blended with 0.1 L water</td>
<td>n-Heptane (10)</td>
<td>2</td>
<td>Concentration</td>
<td>65–85</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Dairy products,</td>
<td>Endogenous</td>
<td>–</td>
<td>10 g sample + water + ethanol</td>
<td>Petrobenzine (?)</td>
<td>1</td>
<td>NR</td>
<td>–</td>
<td>?</td>
<td>Seidel et al. (1993)</td>
</tr>
<tr>
<td>Human milk</td>
<td>OCPs</td>
<td>100</td>
<td>10 g sample + water + ethanol + surfactant</td>
<td>Petrobenzine (?)</td>
<td>1</td>
<td>NR</td>
<td>65–89</td>
<td>6–12</td>
<td></td>
</tr>
<tr>
<td>Pumpkin seed</td>
<td>OCPs</td>
<td>1.5–6.6</td>
<td>5 g sample + 80 mL 2 M H₂SO₴ + ultrasonic, 1 min + 1 mL ethanol + surfactant</td>
<td>Petrobenzine (20)</td>
<td>1.5</td>
<td>Concentration</td>
<td>73–111</td>
<td>?</td>
<td>Filek et al. (1995)</td>
</tr>
<tr>
<td>Certif. dairy product</td>
<td>OCPs</td>
<td>1.5</td>
<td>5 g sample + 80 mL 2 M H₂SO₴ + surfactant</td>
<td>Petrobenzine (20)</td>
<td>1.5</td>
<td>Concentration</td>
<td>83–126</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Powdered milk,</td>
<td>OCPs</td>
<td>20.0–51.3</td>
<td>5 g sample + 80 mL 2 M H₂SO₄ + ultrasonic, 1 min + 1 mL ethanol + surfactant</td>
<td>Petrobenzine (20)</td>
<td>1.5</td>
<td>Concentration</td>
<td>83–126</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Human milk</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Powdered milk</td>
<td>Endogenous</td>
<td>–</td>
<td>15 g sample + 60 mL 1 M H₂SO₄ + surfactant, 1 min</td>
<td>Dichlorometane (2)</td>
<td>60–90</td>
<td>SiO₂·HSO₄</td>
<td>&lt; 26</td>
<td>?</td>
<td>Ramos et al. (1998)</td>
</tr>
<tr>
<td>Dairy products</td>
<td>PCBs</td>
<td>0.5</td>
<td>15 g sample + 60 mL 1 M H₂SO₄ + ultrasonic, 1 min</td>
<td>Dichlorometane (2)</td>
<td>60</td>
<td>SiO₂·HSO₄</td>
<td>&lt; 10</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Herbal essential</td>
<td>OCPs</td>
<td>500–10 000</td>
<td>Blended with 0.05 L water</td>
<td>?</td>
<td>?</td>
<td>LLE (hexane : ethyl ether) + H₂SO₄</td>
<td>83–105</td>
<td>2.4–10</td>
<td>Rajendran et al. (1991)</td>
</tr>
<tr>
<td>OPs</td>
<td></td>
<td>500–10 000</td>
<td>Blended with 0.05 L water</td>
<td>?</td>
<td>?</td>
<td>LLE (hexane : ethyl ether) + H₂SO₄</td>
<td>72–116</td>
<td>0.5–10</td>
<td></td>
</tr>
</tbody>
</table>

*a DDT + DDE + TDE.
in some of the first reported applications of SDE for the analysis of toxic aromatic compounds in biological matrices. The investigated samples included fish tissues, muscle, liver and kidney and, although satisfactory recoveries (67–100%) were reported for the spiked PCBs, PCNs and ΣDDT (i.e. DDT + DDE + TDE), it is important to note that the spiking level in these experiments ranged from 1000–5000 ng g⁻¹ (Table 3). Even at such a high level of concentration, the authors reported an evident dependence of SDE recoveries on the analyte concentration. In fact, Cooke et al. found that the PCB, PCN and ΣDDT recoveries from animal tissues decreased from 67–100% to 65–85% when the spiking level decreased from 5000 to 1000 ng g⁻¹. According to this trend, it can be concluded that the very low levels of the endogenous pollutants in environmental samples together with the typical complexity of the matrix would be the main reasons for the disappointing results reported for some SDE applications involving non-spiked fatty samples.

See also: II/Extraction: Analytical Extractions; Solid-Phase Extraction; Solid-Phase Microextraction; Supercritical Fluid Extraction. Distillation: Extractive Distillation.

Further Reading


