Effects of Extraction Solvents on the Extraction Efficiencies of Polychlorinated Dibenzo-\(p\)-dioxins and Dibenzofurans, and Polychlorinated Biphenyls in Reference Materials

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This study investigated the extraction efficiency of a couple of different extraction solvents for Certified Reference Materials of soil and sediment that include Polychlorinated Dibenzo-\(p\)-dioxins and Dibenzofurans and Coplanar Polychlorinated Biphenyls using Soxhlet and Pressurized Liquid extraction (PLE). \(n\)-Hexane, toluene, acetone, acetone/\(n\)-hexane and acetone/toluene (1:1, v/v) as solvents were examined. Unsatisfactory results for Soxhlet extraction were obtained using \(n\)-hexane alone. For PLE, satisfactory results were obtained using all solvents used for this study. The obtained results for PLE were the same or even higher than those for Soxhlet extraction. We also examined relationship between solubility of 2, 3, 7, 8-Tetrachloro-Dibenzodioxin (TCDD) in the solvent \((X_{\text{env}})\) and the estimated solubility \((X_s)\). The results indicated that a linear relation was found between \(X_{\text{env}}\) and \(X_s\) for Soxhlet extraction, but no linear relation was found in those for PLE. The result suggests that choice of extraction solvent for PLE requires consideration for the analyte solubility in extraction solvent at the temperature and pressure above boiling points of solvents.

Key Words: Extraction Solvent, Extraction Efficiency, Polychlorinated Dibenzo-\(p\)-dioxins and Dibenzofurans, Coplanar Polychlorinated Biphenyls, Certified Reference Material, Solid Environmental Sample.

1. Introduction

In recent years, extraction method of Pressurized liquid extraction (PLE) has been used as an effective extraction technique compared to the conventional ones such as Soxhlet or Ultrasonic extraction [1,2]. This PLE method has use of conventional liquid solvents at elevated pressures (10.3 - 13.8 MPa) and temperatures (50 - 200°C) because it can be possible to extract solid samples quickly with less amount of solvent than those of conventional techniques. The solvents for PLE are commonly used at a temperature above their boiling points to increase the analyte solubilities in solvents. When PLE was used at the higher temperatures, the kinetic processes for the release of analytes from a sample matrix are more accelerated than when solvents are used at room temperature. The higher analyte solubility in the heated solvent resulted in reduction of the amount of solvent for extraction.

Extractions of organic pollutants from solid environmental samples have been performed by PLE [3-6]. Optimization studies of the extraction conditions such as temperatures and solvents have been reported because extraction efficiencies for organic pollutants from environmental samples depend much on the conditions [1-6]. However, the studies of the effect of extraction solvent on the extraction efficiencies of polychlorinated dibenz-\(p\)-dioxins and dibenzofurans (PCDDs/PCDFs) and polychlorinated biphenyls (PCBs) from environmental samples have never been performed sufficiently. For that reason, study on efficiency of extraction solvent should contribute to realize the optimizing the extraction process for those compounds.

This study investigated the extraction efficiency of a couple of different extraction solvents for Certified Reference Materials (CRMs) of soil and sediment that include PCDDs/PCDFs and coplanar PCBs (Co-PCBs) using Soxhlet extraction and PLE. The obtained results have been examined by comparing the analyte solubility in extraction solvent and the estimated solubility to understand extraction efficiency difference between Soxhlet and PLE.

2. Experimental

2.1 Sample

CRMs 0422 (Forest soil) and 0431 (River sediment) containing high ppt levels (ng/kg) of PCDDs/PCDFs and Co-PCBs were purchased from the Japan Society for Analytical Chemistry (Tokyo, Japan). Certified values of PCDDs/PCDFs
and Co-PCBs for CRMs 0422 and 0431 were based on soxhlet extraction with toluene.

2.2 Soxhlet Extraction

Five gram of samples were extracted using ca. 400 ml of extraction solvent for 16 h with a 30 min reflux cycle time. Each of n-hexane, toluene, acetone, acetone/n-hexane (1:1, v/v), and acetone/toluene (1:1, v/v) as the extraction solvents were used. Experiments with each solvent were made in triplicate. The solvent extraction and cleanup procedures were accomplished according to a Japanese official test method for PCDDs/PCDFs and Co-PCBs in soil and sediment [7,8]. To remove the water from the samples, a Dean-Stark Water Separator was attached to the soxhlet extractor.

2.3 Pressurized Liquid Extraction (PLE)

PLE was carried out using an ASE 200 Accelerated Solvent Extraction system (Dionex Corporation, Sunnyvale, CA) equipped with 33 ml stainless-steel extraction cells. PLE was also carried out using the same sample amounts and solvents as described for soxhlet extraction. The PLE conditions were as follows: system pressure of 13.8 MPa, an oven heat-up time of 7 min, two 10 min-static periods, and oven temperature of 150°C [9]. Periodic extractions were respectively performed four times under these conditions until no more analytes were almost found in the extracts (Total extraction time: ca. 4 h). Experiments with each solvent were made in triplicate. The cleanup procedures were accomplished according to the official test methods.

2.4 HRGC/HRMS analysis

GC/MS analysis was performed using a HRGC/HRMS (JMS-700D; JEOL, Tokyo, Japan). The HRGC/HRMS were performed using conditions as described previous reports [10].

2.5 Analyte Solubility in Extraction Solvent and the Estimated Solubility

The following equations were used to assess the relationship between analyte solubility in extraction solvent and the estimated solubility.

Analyte solubility in a single solvent \( X_{\text{solv}} \) was given by

\[
X_{\text{solv}} = n_{\text{sol}} / (n_{\text{tot}} + n_{\text{sol}}),
\]

where, \( n_{\text{sol}} \) is the analyte mole number, \( n_{\text{tot}} \) is the total mole number, \( W_{\text{sol}} \) is the analytic extraction amount (pg), \( W_{\text{tot}} \) is the solvent weight (1000g), \( M_{\text{sol}} \) is the analyte molecular weight, \( M_{\text{sol}} \) is the solvent molecular weight.

Solubility of a solid \( X_{s} \) can be estimated using the following equation [11]:

\[
\ln X_{s} = -V_{s} \phi f^{2} (\delta i - \delta s)^{2}/RT + \ln P_{s}/P_{s}^{*},
\]

where \( \phi \) is the predicted solubility of a solute in solvent (mole fraction), \( V_{s} \) is the molar volume of solute (cm³/mol), \( \delta s \) and \( \delta i \) represent the solubility parameters of solute and solvent (cal/cm³)²/2, respectively.

The equation (4) was changed the formula as follows:

\[
X_{s} = \exp (-V_{s} \phi f^{2} (\delta i - \delta s)^{2}/RT + \ln P_{s}/P_{s}^{*}), \tag{5}
\]

where \( \phi \) is the predicted solubility of a solute in solvent (mole fraction), \( V_{s} \) is the molar volume of solute (cm³/mol), \( \delta s \) and \( \delta i \) represent the solubility parameters of solute and solvent (cal/cm³)²/2, respectively.

R is the universal gas constant (1.987 cal/(mol·K)), and \( T \) represents temperature (K). \( P_{s}^{*} \) is the solid vapor pressure of solute (Pa), \( P_{s}^{*} \) is the subcooled liquid vapor pressure of solute (Pa). For dilute solutions, \( \phi \) approaches unity. Therefore, this term is deleted from Eq. (5).

The solubility parameters of solute \( (\delta s) \) and solvent \( (\delta i) \) may be estimated using the following equation:

\[
\delta s = (\Delta H_{s} - RT)/V_{s}, \tag{6}
\]

\[
\delta i = (\Delta H_{i} - RT)/V_{i}, \tag{7}
\]

where \( \Delta H_{s} \) and \( \Delta H_{i} \) are the enthalpy of vaporization (cal/mol), and \( V_{s} \) and \( V_{i} \) are the molar volume (cm³/mol).

The value of \( \Delta H \) and \( V \) at each temperature (K) may be expressed as [12]

\[
\Delta H_{298.15} = -2950 + 23.7T_{m} + 0.027T_{m}^{2}, \tag{8}
\]

\[
\Delta H(T) = \Delta H_{298.15} - 13 (T - 298.15), \tag{9}
\]

\[
V(T) = V_{298.15} [1 + 0.001237 (T - 298.15)], \tag{10}
\]

The value of \( \ln (P_{s}^{*}/P_{s}^{*}) \) may be expressed as [13]

\[
\ln (P_{s}^{*}/P_{s}^{*}) = -6.8 (T_{m} - T)/T, \tag{11}
\]

where \( T_{m} \) is the melting point (K). \( \Delta H_{m,15} \) is the enthalpy of vaporization at 298.15 K. \( V_{298.15} \) is the molar volume at 298.15 K.

Eqs. (4) – (11), where the parameters of each equation, such as \( V_{298.15}, T_{m}, T_{m} \) were values from the literature [13-18].

3. Results and Discussion

3.1 Soxhlet Extraction

We examined CRMs 0422 and 0431 using Soxhlet extraction to assess the effects of different solvents on analyte extraction efficiency. Table 1 shows those obtained results. The extraction efficiencies for PCDDs/PCDFs and Co-PCBs were calculated by the factor \( f = (\text{analyte concentrations with each of n-hexane, toluene, acetone, acetone/n-hexane, acetone/toluene}) / \text{certified concentrations} \).

Among the single solvents, satisfactory results for average factor \( f \) of PCDDs/PCDFs and Co-PCBs were obtained using toluene and acetone \( (f = 0.87 - 1.08 \text{ for PCDDs, } 0.85 - 1.15 \text{ for PCDFs, and } 0.94 - 1.13 \text{ for Co-PCBs}) \). Unsatisfactory results for those factors were obtained using n-hexane alone \( (f = 0.46 - 0.82 \text{ for PCDDs, } 0.54 - 0.76 \text{ for PCDFs, and } 0.64 - 0.85 \text{ for Co-PCBs}) \). For mixed solvents, satisfactory results for those factors were obtained those using both n-hexane and toluene mixed with acetone \( (f = 0.84 - 1.10 \text{ for PCDDs, } 0.90 - 1.04 \text{ for PCDFs, and } 0.93 - 1.12 \text{ for Co-PCBs}) \). Particularly, the results for n-hexane mixed with acetone produced good extraction efficiencies compared to those for Soxhlet extraction with n-hexane. This result indicates that addition of acetone contribute to the effective extraction of the analyte from the sample matrix. In contrast, the results obtained using toluene mixed with acetone was the same or slightly lower than those for toluene. This lack of effects might results from the difference in the composition in the Soxhlet chamber during Soxhlet extraction because the difference of boiling points were quite large compared to the case of n-hexane mixed with acetone.

3.2 Pressurized Liquid Extraction (PLE)

PLE was carried out using the same extraction solvents as Soxhlet extraction. The extraction efficiencies of PCDDs/PCDFs and Co-PCBs were also calculated in the same manner as described.
Table 1: Extraction Efficiencies for Soxhlet Extraction of Polychlorinated Dibenzo"p"Dioxins (PCDDs) and Dibenzofurans (PCDFs), and Polybrominated Biphenyl Esters (PBDEs) in Soil and Sediment Samples

<table>
<thead>
<tr>
<th>Compound</th>
<th>Soil (CRM 0422)</th>
<th>Sediment (CRM 0422)</th>
</tr>
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<tbody>
<tr>
<td>PCDDs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2,3,4-TCDD</td>
<td>0.98</td>
<td>0.95</td>
</tr>
<tr>
<td>1,2,3,4,6-PentaCDD</td>
<td>0.99</td>
<td>0.97</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-HeptaCDD</td>
<td>0.99</td>
<td>0.97</td>
</tr>
<tr>
<td>PCDFs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2,3,4-TetraCDF</td>
<td>0.98</td>
<td>0.95</td>
</tr>
<tr>
<td>1,2,3,4,5-PentaCDF</td>
<td>0.99</td>
<td>0.97</td>
</tr>
<tr>
<td>PBDEs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9973/9974</td>
<td>0.98</td>
<td>0.95</td>
</tr>
<tr>
<td>9975/9976</td>
<td>0.99</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Table 2: Extraction Efficiency for Presumed Liquid Extraction of Polybrominated Dibenzo-p-Dioxins (PCDDs) and Polybrominated Biphenyl Esters (PBDEs) in Certified Reference Materials (CRMs) of Soil and Sediment

<table>
<thead>
<tr>
<th>Compound</th>
<th>Soil (CRM 0422)</th>
<th>Sediment (CRM 0422)</th>
</tr>
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<tr>
<td>1,2,3,4,6,7,8-HeptaCDD</td>
<td>0.99</td>
<td>0.97</td>
</tr>
<tr>
<td>PCDFs</td>
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</tr>
<tr>
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<td>1,2,3,4,5-PentaCDF</td>
<td>0.99</td>
<td>0.97</td>
</tr>
<tr>
<td>PBDEs</td>
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<tr>
<td>9973/9974</td>
<td>0.98</td>
<td>0.95</td>
</tr>
<tr>
<td>9975/9976</td>
<td>0.99</td>
<td>0.97</td>
</tr>
</tbody>
</table>
in section 3.1. The extraction efficiencies were sum of four separate extractions with two static extractions.

Table 2 shows those obtained results. The factors $f$ of PLE using single and mixed solvents produced good extraction efficiencies of analyte (Single solvents: average $f = 0.97 - 1.29$ for PCDDs, 0.93 - 1.40 for PCDFs, and 0.92 - 1.28 for Co-PCBs, mixed solvents: average $f = 1.30 - 1.35$ for PCDDs, 1.11 - 1.59 for PCDFs, and 1.01 - 1.32 for Co-PCBs). The extraction efficiencies for PLE were the same or even higher than those for Soxhlet extraction. The effects of addition of acetone on the extraction efficiencies of analyte could be also confirmed PLE with mixed solvents. This may be caused by the effect that acetone which is highly capable of building hydrogen bonding, can effectively disrupts the strong analyte-matrix interaction caused by hydrogen bonding of the analyte molecules and active sites on a sample matrix [1]. These results indicate that less-polar solvent mixed with acetone for PLE are effective extraction solvents to produce the good extraction efficiencies of those compounds.

3.3 Relationship between Analyte Solubility in Extraction Solvent and the Estimated Solubility

To understand the differences between Soxhlet extraction and PLE, we focused the relationship between solubility of those compounds in extraction solvent ($X_{\text{ex}}$) and their estimated solubility ($X_s$) because of their solubility might be one of the most important physical-chemical parameters in the extraction process. In addition, $X_s$ values were estimated using physical-chemistry relationship as described in section 2.4 because of the experimental solubility in various solvents have never been reported.

Figure 1 shows relationship between $X_{\text{ex}}$ of the 2,3,7,8-TetraCDD/CDF and their estimated $X_s$. Linear relation was found between $X_{\text{ex}}$ and $X_s$ for those of Soxhlet extraction. The results indicate that extraction efficiencies of Soxhlet extraction might be strongly depend on their analyte solubility in extraction solvent. Therefore, it is likely that only the choice of extraction solvent that has the higher analyte solubility in extraction solvent at the temperature under boiling point and air pressure is necessary. In contrast, no linear relation was found between $X_{\text{ex}}$ and $X_s$ for PLE. The result indicates that extraction efficiencies of PLE might be due to the effects of the analyte solubility in extraction solvent at the temperature or pressure above boiling points of solvents. Therefore, it is likely that choice of extraction for PLE requires consideration for the analyte solubility in extraction solvent at the temperature and pressure above boiling points of solvents.

References


Figure 1 Relationship between analyte solubility in extraction solvent ($X_{\text{ex}}$) and the estimated solubility ($X_s$): (a) 2,3,7,8-TetraCDD, (b) 2,3,7,8-TetraCDF.


