23 **Solvent Selection for Pressurized Liquid Extraction of Polymeric Sorbents Used in Air**

24 **Sampling**

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68 **Abstract**

69    Pressurized liquid extraction (PLE) was evaluated as a method for extracting semivolatile

70 organic compounds (SOCs) from air sampling media; including quartz fiber filter (QFF),

71 polyurethane foam (PUF), and a polystyrene divinyl benzene copolymer (XAD-2). Hansen

72 solubility parameter plots were used to aid in the PLE solvent selection in order to reduce both

73 co-extraction of polyurethane and save time in evaluating solvent compatibility during the initial

74 steps of method development. A PLE solvent composition of 75:25% hexane:acetone was

75 chosen for PUF. The XAD-2 copolymer was not solubilized under the PLE conditions used. The

76 average percent PLE recoveries (and percent relative standard deviations) of 63 SOCs, including

77 polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and

78 organochlorine, amide, triazine, thiocarbamate, and phosphorothioate pesticides, were 76.7 (6.2),

79 79.3 (8.1), and 93.4 (2.9) % for the QFF, PUF, and XAD-2, respectively.

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81 **Keywords**:  Pressurized liquid extraction, Polyurethane foam, Polystyrene divinyl benzene,

82 Quartz fiber filter, Hansen solubility parameter

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91 **Introduction**

92      Pressurized liquid extraction (PLE) is an exhaustive extraction technique that uses less

93 solvent (~100-200 mL) and time (~20 minutes) compared to traditional solvent extraction

94 techniques such as Soxhlet extraction [1]. Extraction efficiencies reported for PLE are similar to

95 those reported for Soxhlet and supercritical fluid extraction [2] and PLE has been shown to be

96 effective for the extraction of semivolatile organic compounds (SOCs) from environmental

97 matrices including: soils, particulate matter, fly ash, and sediments [3-7]. Fitzpatrik et al.

98 previously reported important considerations for the selection of PLE parameters (e.g. cycles,

99 temperature) [7].

100      For more than a decade, the global atmospheric transport of anthropogenic SOCs has been

101 shown to cause surface contamination in remote locations [8] and atmospheric transport is a

102 major environmental transport pathway for SOCs from source regions to remote locations [9].

103 Often, a quartz fiber filter (QFF) is combined with polyurethane foam (PUF) and polystyrene

104 divinyl benzene (XAD-2) in a QFF-PUF-(XAD-2)-PUF sampling train to ensure complete

105 collection of particulate-phase SOCs (QFF), followed by gas-phase SOCs (PUF and XAD-2) [6,

106 10].

107      Because the air sampling media used for trapping gas-phase SOCs are polymers such as PUF

108 and XAD-2, the appropriate selection of PLE extraction solvents is essential in order to minimize

109 matrix interferences due to co-extraction of the polymeric matrix, while simultaneously

110 achieving adequate extraction of the SOCs. The minimization of interferences from PLE

111 extraction cells has been reported [11]; however, the minimization of polymeric matrix

112 interferences from air sampling media has not.

113    Previous research has focused on the intentional extraction of monomers/oligomers and/or

114    polymeric additives from polymers. Lou et al. used PLE to extract monomers and oligomers

115    from nylon-6 and poly(1,4-butyleneterephthalate), showing that the PLE extraction solvent

116    chosen and the extraction temperature were important, but that solvent selection was "largely

117    empirical" [12]. Vandenburg et al. proposed using Hildebrand solubility parameters to select

118    solvents for the extraction of the polymeric additives Irganox 1010 and dioctyl phthalate from

119    ground polypropylene, polyvinyl chloride, and nylon [13].

120    Hildebrand solubility parameters are most effective for substances lacking any significant

121    polar or hydrogen bonding capabilities, thus substances that primarily undergo dispersion type

122    interactions. Hansen solubility parameters divide up the Hildebrand parameter ($\delta$) into three

123    components: dispersion ($\delta_D$), permanent dipole-permanent dipole ($\delta_P$), and hydrogen bonding

124    ($\delta_H$) forces (Equation 1) [14]. These three components take into account the similarities (or

125    dissimilarities) of the polar and hydrogen bonding components of organic compounds to better

126    explain the extent of interaction [14].

127    $$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \qquad \textbf{(1)}$$

128    The human and environmental safety of the organic solvents used is also an important

129    consideration in PLE solvent selection. For example, if dichloromethane, a probable human

130    carcinogen (http://www.atsdr.cdc.gov/tfacts14.pdf), is used as a PLE solvent to clean air

131    sampling media and any residual dichloromethane remains after cleaning, it may be released

132    during sample collection and result in human exposure [15].

133    To date, the use of PLE has focused on the extraction of SOCs from various solid matrices

134    and the intentional extraction of monomers/oligomers and additives from polymers. There were

135    two major goals in the selection of solvents for the PLE of SOCs from polymeric air sampling

136    media. The first goal was to efficiently extract the SOCs from the media and the second goal was

137    to avoid co-extraction of the polymeric matrix. Using Hansen solubility parameters, PLE

138    solvents were selected which minimized co-extraction of polymeric matrix interferences, but

139    resulted in good recoveries of 63 commonly measured SOCs. The SOCs selected for extraction

140    and analysis were from nine chemical classes and their physical chemical properties (octanol-

141    water partition coefficient, water solubility, and vapor pressure) spanned 7 to 10 orders of

142    magnitude [16].

143    **Materials and Methods**

144       Semivolatile organic compounds (SOCs) evaluated for PLE recoveries covered several

145    chemical classes (**Table 1**). A complete list of the isotopically labeled surrogates and internal

146    standards that were used for quantitation has been previously reported [16].  The SOC standards

147    were obtained from the U.S. Environmental Protection Agency repository, Chemical Services

148    (West Chester, PA, USA), Restek (Bellefonte, PA, USA), Sigma-Aldrich (St. Louis, MO, USA),

149    and AccuStandard (New Haven, CT, USA).  Isotopically labeled standards were obtained from

150    CDN Isotopes (Pointe-Claire, QC, Canada) or Cambridge Isotopes Laboratories (Andover, MA,

151    USA).  The standards were stored at 4° C until use. All solvents (hexane, dichloromethane, and

152    acetone) were from Fisher Scientific (Fairlawn, NJ, USA) and were optima grade.

153    *Pressurized liquid extraction solvent evaluation*

154       The initial selection of solvents was based on Hansen solubility parameter plots for the

155    polymeric media and solvents. Following this initial selection, two experiments were conducted

156    to evaluate the suitability of the solvents for PLE. First, the polymeric media was cleaned by

157    PLE with the solvents to evaluate co-extraction of the polymer. After selecting PLE solvent

158    systems that did not significantly co-extract the polymeric media, the PLE recoveries of 63 SOCs

159    from the sampling media were measured.

160    *Evaluation of background interferences.*

161    In order to evaluate the potential polymeric interferences due to PLE of PUF (Tisch

162    Environmental, Cleves, OH, USA), three 7.6 cm x 7.6 cm PUF plugs were cleaned with an

163    accelerated solvent extractor (ASE®) 300 (Dionex, Sunnyvale, CA, USA) in 66 ml ASE

164    extraction cells. Sequential extractions of 100% dichloromethane, 100% acetone, 75:25%

165    hexane:acetone, and 100% hexane were used. The ASE parameters for the four extractions were:

166    cell temperature 100°C, static time 5 min., solvent flush 50% of cell volume, one static cycle,

167    and a $N_2$ purge time of 240 s.  After cleaning, one PUF plug was extracted with 100%

168    dichloromethane, the second with 100% hexane, and the third with 75:25% hexane:acetone using

169    the same ASE parameters described above, except two static cycles were used instead of one.

170    Copolymers such as XAD-2 are considered non-soluble in organic solvents due to their cross

171    linking [17]. To evaluate the potential interferences from XAD-2 (Supelco, St. Louis, MO,

172    USA), approximately 50 g of XAD-2 were cleaned by PLE (**Table 2**) in a 100 ml ASE extraction

173    cell. After cleaning, the XAD-2 was extracted with 50:50% hexane:acetone using the ASE

174    parameters described in Table 2. The 50:50% hexane:acetone solvent system has been previously

175    reported being used with XAD-2 and PLE (http://www1.dionex.com/en-us/webdocs/

176    4522_AN347_V16.pdf) . The PUF and XAD-2 extracts were concentrated using a Turbovap® II

177    (Caliper Life Sciences, MA, USA) at 37 °C to approximately 600 μl and further concentrated to

178    a final volume of approximately 300 μl using a micro $N_2$ stream concentrator.

179    *PLE recoveries.*

180  After the selection of PLE solvents was made using Hansen solubility parameter plots and

181 the resulting polymeric interferences were evaluated, the PLE recoveries of 63 SOCs were

182 measured in triplicate. The QFFs (Whatman, Kent, UK) were cleaned by baking at 350 °C for 12

183 h [6, 10] and the PUF and XAD-2 were cleaned using the ASE conditions described in Table 2.

184 For PUF and XAD-2 cleaning, the extraction solvents were used in order of polarity (from more

185 to less polar). After cleaning, the air sampling media was fortified with 15 µl of 10 ng/µl

186 solutions of the target SOCs using a syringe and immediately extracted using the PLE solvents

187 and parameters listed in Table 2. The resulting PLE extracts were fortified with 15 µl of 10 ng/µl

188 solutions of the 24 isotopically labeled surrogates to assess SOC recoveries from the PLE step

189 only. The extracts were concentrated to approximately 300 µl and fortified with 15 µl of 10 ng/µl

190 solutions that contained the four isotopically labeled internal standards to track recoveries of the

191 surrogates (i.e. recoveries from the remaining steps of the method).

192 ***Instrumental analysis***

193  Qualitative analysis of monomeric and oligomeric interferences was conducted using gas

194 chromatography (GC) on an Agilent 6890 gas chomatograph (Santa Clara, CA, USA) coupled

195 with mass spectrometry (MS) (Agilent 5973N, mass selective detector). A 30 m x 0.25 mm inner

196 diameter x 0.25 µm film thickness, DB-5 column (J&W Scientific, Palo Alto, CA, USA) was

197 used. The GC oven temperature program was: 60 °C held for 1 min., followed by 6.0 °C/min to

198 300 °C and then held for 3 min, finishing with 20.0 °C/min. to 320 °C and held for 9 min. The

199 mass spectrometer was operated in electron impact ionization mode and scanned from 35 to 500

200 *m/z*.

201  Quantitative analysis of SOC recoveries was conducted using the same GC/MS system in

202 selective ion monitoring mode, using either negative chemical ionization or electron impact

203  ionization modes, depending on which form of ionization gave the lowest instrumental detection

204  limit. Details of the instruments, ions monitored, instrument limit of detections, and GC oven

205  temperature program have been provided elsewhere [6, 16].

206  **Results and Discussion**

207  *Pressurized liquid extraction solvent selection*

208      Hansen solubility parameter plots are used to graphically display the Hansen solubility

209  parameters for various solvents and polymers. The *x*-axis of these plots represents the dipole-

210  dipole and the *y*-axis represents the hydrogen bonding components [14]. The *z*-axis (dispersion)

211  is often not displayed for organic compounds because there is usually little difference between

212  them [14].

213      Hansen solubility parameters were used to identify solvents which were compatible with

214  polyurethane. **Figure 1** shows the Hansen solubility parameter plot of polyurethane with various

215  organic solvents [14]. The solubility circle (Figure 1) represents the region where a solvent is

216  likely to dissolve polyurethane [14]. The closer a solvent is to the center of the circle, the more

217  likely it is to solubilize polyurethane [17]. Of the organic solvents shown in Figure 1,

218  dichloromethane and 50:50% hexane:acetone are closest to polyurethane and hexane is the

219  furthest. It should be noted that at higher temperatures, Hansen solubility parameters tend to

220  decrease, while the solubilization circle tends to increase [14]. However, Hansen notes that the

221  parameters at higher temperatures are similar to the established values at 25°C [14]. The data

222  shown in Figure 1 is for 25 °C, which is lower than typical PLE temperatures (~100 °C).

223      The use of PLE to extract SOCs from polymeric air sampling media with organic solvents

224  can lead to matrix interferences. The GC/mass spectrometer chromatograms of the PLE of PUF

225  using 100% dichloromethane, 100% hexane, and 75:25% hexane:acetone are overlaid in **Figure**

226   **2**A for comparison in order to evaluate the resulting matrix interferences. Figure 2A also shows a

227   solvent injection of 100% dichloromethane. The chromatographic base-line signal was elevated

228   when 100% dichloromethane was used as the PLE extraction solvent as compared to 75:25%

229   hexane:acetone and 100% hexane. This result is consistent with the Hansen solubility parameter

230   plot for polyurethane (Fig. 1).

231       A copolymer of polystyrene divinyl benzene (i.e. XAD-2), was not solubilized under the PLE

232   conditions used. Figure 2B shows the chromatogram of a 50:50% hexane:acetone XAD-2 extract

233   compared to a solvent injection of hexane. Because XAD-2 contains cross linking, a low signal

234   base-line was expected [17]. Solubility parameters have not been developed for XAD-2 because

235   it is considered non-soluble in organic solvents (B. Vogler, Supelco, St. Louis, MO, USA,

236   personal communication). Figure 2B confirms the lack of XAD-2 solubilization during PLE. A

237   Dionex technical report has noted the formation of naphthalene during extraction of XAD-2 at

238   elevated temperatures, thus a PLE temperature of 75°C was chosen (Table 2)

239   (http://www1.dionex.com/en-us/ webdocs / 4522_AN347_V16.pdf). For the PUF, the PLE

240   temperature was 100°C, a typical temperature for PLE.  Lower temperatures were not

241   investigated because 100°C was found to be effective and did not damage the PUF.

242   ***Pressurized liquid extraction recovery of semivolatile organic compounds***

243       Pressurized liquid extraction has been reported to have similar extraction efficiencies

244   compared to Soxhlet [5], supercritical fluid extraction, and microwave assisted extraction [2].

245   For the PUF recovery study, the 75:25% hexane:acetone solvent system was chosen over hexane

246   to ensure the extraction of polar, current-use pesticides. For example, atrazine recoveries were

247   only 12% and atrazine desethyl was not detected using hexane ($n$=1). For more non-polar SOCs

248   (e.g. organochlorines and polycyclic aromatic hydrocarbons), hexane was as effective as the

249   75:25% hexane-acetone solvent system. For QFF, PUF, and XAD-2 the average percent

250   recoveries (and percent relative standard deviation) were 76.7 (6.2), 79.3 (8.1), and 93.4 (2.9) %,

251   respectively (Table 1). For the PUF, the chlordane and nonachlor PLE recoveries were lower

252   (~50%).  If needed, an additional extraction cycle could be used to increase recoveries of these

253   SOCs.

254        The average absolute percent SOC recovery (and percent relative standard deviation) over

255   the entire analytical method for the QFF, PUF, and XAD-2 were 66.3 (4.8), 76.0 (5.5), and 77.1

256   (3.3) %, respectively. These recoveries included the solvent evaporation steps and resulted in

257   SOC recoveries that were lower than the PLE step alone.  Estimated method detection limits,

258   calculated using U.S. Environmental Protection Agency method 8280A [18] and assuming an

259   average air volume of 644 $m^3$, ranged from 0.0001 to 100, 0.001 to 114, and 0.0003 to 108 $pg/m^3$

260   for the QFF, PUF, and XAD-2, respectively.

261        Polymers (i.e. PUF and XAD-2) are effective sorbents for sampling gas-phase SOCs from

262   the atmosphere and PLE is a rapid and effective cleaning and extraction method for the

263   extraction of SOCs with a wide range of physical and chemical properties. Care should be taken

264   in PLE solvent selection when extracting SOCs from polymeric sampling materials and Hansen

265   solubility parameters can provide useful guidance to save time in evaluating solvent

266   compatibility during the initial steps of method development.

267   **Acknowledgement**

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**Figure 1:** Hansen solubility parameter plot of polyurethane at 25°C [14]. Various solvents including, 100% acetone, 100% hexane, 100% ethyl acetate, 50:50% hexane: acetone, 75:25% hexane: acetone, and dichloromethane, are shown in the figure with respect to polyurethane. The circle represents the solubility circle for polyurethane (see discussion).

**Figure 2: (A)** Total ion chromatogram of interferences due to co-extraction of monomers and oligomers from polyurethane foam (response versus time). The figure shows the effects of three pressurized liquid extraction solvents on polyurethane foam: dichloromethane (DCM), 100% hexane (Hex), and 75:25% hexane:acetone (Hex:Ace). Also shown for reference is a solvent injection of DCM. **(B)** Total ion chromatogram comparing polystyrene divinyl benzene (i.e. XAD-2) interferences using the pressurized liquid extraction solvent mixture of 50:50% Hex:Ace compared to a solvent injection of Hex.