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# An Experimental Design Approach for the Determination of Polycyclic Aromatic Hydrocarbons from Highly Contaminated Soil Using Accelerated Solvent Extraction

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**An experimental design approach, based on central composite design, has been used to investigate the dependence of accelerated solvent extraction operating variables (pressure, temperature, extraction time) on the recovery of 16 polycyclic aromatic hydrocarbons (PAHs) from native, contaminated soil. At the 95% confidence interval, no significance in terms of the three operating parameters was found when considering the total PAH recovery. However, when individual PAHs were considered, some compounds were found to be dependent on operating variables. The most significant operating variable was extraction temperature. Low extraction temperature (40 °C) was found to be significant for naphthalene, chrysene, and benzo[*b*]fluoranthene. Using constant operating conditions (100 °C, 14 MPa and an extraction time of 5 min plus 5 min equilibration time), the influence of extraction solvent was evaluated. No dependence on recovery was found when polar organic solvents, i.e., a dipole moment of >1.89, were used.**

Accelerated solvent extraction (ASE) is a new technique for the extraction of a range of organic pollutants from soils and related material.<sup>1</sup> The technique is based on the use of a solvent or combination of solvents to extract organic pollutants at elevated pressure and temperature from a solid matrix.<sup>2–4</sup> The range of organic pollutants for which the technique is proposed includes semivolatile compounds, organochlorine pesticides, organophosphorus pesticides, chlorinated herbicides, and polychlorinated biphenyls.<sup>1</sup> As the semivolatile compounds includes polycyclic aromatic hydrocarbons (PAHs), it was the intention in this paper to investigate the interdependence of selected operating parameters on their recovery from a native, highly contaminated soil.

Table 1. Central Composite Design Used for the Extraction of PAHs from Highly Contaminated Soil

|    | pressure (psi) | temp (°C) | extraction time (min) |
|----|----------------|-----------|-----------------------|
| −α | 1000           | 40        | 2                     |
| −1 | 1300           | 70        | 5                     |
| 0  | 1700           | 120       | 9                     |
| 1  | 2100           | 170       | 13                    |
| +α | 2400           | 200       | 16                    |

Table 2. Results of the Central Composite Design for Accelerated Solvent Extraction of Polycyclic Aromatic Hydrocarbons from Soil

| experiment no. | pressure (psi) | temp (°C) | extraction time (min) | total PAHs (mg kg <sup>−1</sup> ) |
|----------------|----------------|-----------|-----------------------|-----------------------------------|
| 1              | 1300           | 170       | 13                    | 1611.2                            |
| 2              | 2100           | 170       | 5                     | 1788.5                            |
| 3              | 1700           | 120       | 16                    | 1613.4                            |
| 4              | 2100           | 70        | 13                    | 1472.5                            |
| 5              | 1700           | 200       | 9                     | 1557.0                            |
| 6              | 1700           | 120       | 2                     | 1554.9                            |
| 7              | 1300           | 170       | 5                     | 1641.5                            |
| 8              | 1300           | 70        | 5                     | 1517.1                            |
| 9              | 2100           | 170       | 13                    | 1687.5                            |
| 10             | 1700           | 120       | 9                     | 1645.3                            |
| 11             | 2400           | 120       | 9                     | 1558.8                            |
| 12             | 1700           | 120       | 9                     | 1574.6                            |
| 13             | 1000           | 120       | 9                     | 1608.0                            |
| 14             | 2100           | 70        | 5                     | 1592.1                            |
| 15             | 1300           | 70        | 13                    | 1521.0                            |
| 16             | 1700           | 40        | 9                     | 1454.5                            |
| total          |                |           |                       | 1587.4 <sup>a</sup>               |

<sup>a</sup> 5.2% RSD.

Previous work in this laboratory<sup>4</sup> has confirmed that PAHs can be effectively extracted from soil using the proposed Environmental Protection Agency (EPA) operating conditions of pressure, 14 MPa, temperature, 100 °C, and extraction time 5 min plus a 5 min equilibration time period using a 1 + 1 solvent mixture of acetone and dichloromethane.<sup>1</sup> As the main operating variables identified were pressure, temperature, and extraction time, these operating parameters were chosen to allow the robustness of the proposed EPA method to be considered. The method of optimiza-

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(1) Test Methods for Evaluating Solid Waste, Method 3545, USEPA SW-846, 3rd ed., Update III, U.S. GPO, Washington, DC, January 1995.

(2) Ezzell, J. L.; Richter, B. E.; Felix, W. D.; Black, S. R.; Meikle, J. E. *LC-GC* **1995**, 13, 390.

(3) Richter, B. E.; Jones, B. A.; Ezzell, J. L.; Porter, N. L.; Avdalovic, N.; Pohl, C. *Anal. Chem.* **1996**, 68, 1033.

(4) Dean, J. R. *Anal. Commun.* **1996**, 33, 191.

Table 3. Multilinear Regression Results for Total PAHs Extracted Using ASE

| parameter | variable | coefficient | p value |
|-----------|----------|-------------|---------|
| $b_0$     |          | 1327.89     | 0.063   |
| $b_1$     | $P$      | -0.0147     | 0.978   |
| $b_2$     | $T$      | 1.7389      | 0.639   |
| $b_3$     | $t$      | 22.4592     | 0.596   |
| $b_4$     | $P^2$    | 0.0000(1)   | 0.949   |
| $b_5$     | $T^2$    | -0.0106     | 0.340   |
| $b_6$     | $t^2$    | 0.1041      | 0.943   |
| $b_7$     | $PT$     | 0.0012      | 0.364   |
| $b_8$     | $Pt$     | -0.0151     | 0.374   |
| $b_9$     | $Tt$     | -0.0106     | 0.937   |

tion chosen was a chemometric approach, using a central composite design.<sup>5</sup> The use of a central composite design allows all three operating parameters to be investigated individually, as squared terms, and to consider two-component interaction effects. The results of the central composite design were evaluated using multilinear regression. In addition, the effect of organic solvent on the recovery of PAHs was also investigated. A range of individual or combined solvents were chosen to reflect a dramatic change in solvent polarity.

#### EXPERIMENTAL SECTION

**Soil Preparation.** Contaminated land soil (organic carbon content, 10.2%) was sampled from a known site and then transported to the laboratory where it was air-dried for 24 h prior to sieving through a 2 mm mesh at room temperature. The fine powdered soil was then stored in an air-tight container until required.

**Standards and Solvents.** A standard PAH mixture was supplied by Chem Service, West Chester, PA (PAH mixture 610/525/550). Two internal standards (3,6-dimethylphenanthrene and 6-ethylchrysene) were purchased from Lancaster Chemicals (Lancashire, U.K.). All solvents (acetone, dichloromethane, methanol, hexane, acetonitrile) used were of analytical grade (Merck Ltd., Poole, Dorset, U.K.).

**Accelerated Solvent Extraction Procedure.** Extractions were done using ASE 200 accelerated solvent extractor (Dionex

(UK) Ltd., Camberley, Surrey, U.K.). Samples (7 g) were accurately weighed into the 11 mL cells. The sample cells were then closed to finger tightness and placed into the carousel of the ASE 200 system. Extractions were done using a dichloromethane (DCM) and acetone mixture (1 + 1 v/v). The operating conditions were as imposed by the central composite design. The extracted analytes were purged from the sample cell using pressurized nitrogen (125–150 psi; 1 psi = 6894.76 Pa). The extracts were concentrated to 5 mL using a rotary evaporator and then diluted 2-fold before the addition of internal standards.

**Analysis of Extracts by GC/MS.** The extracts were analyzed using a HP 5890 Series II+ GC fitted with a HP 5972A mass spectrometer and 7673 autosampler (Hewlett-Packard Ltd., Bracknell, Berkshire, U.K.). A 30 m × 0.25 mm i.d. × 0.25 μm film thickness DB-5 capillary column (J&W Scientific, supplied by Phase Separations Ltd., Clwyd, U.K.), was used with GC temperature programmed from an initial temperature held at 85 °C for 2 min before commencing at 6 °C min<sup>-1</sup> to 300 °C, with a final time of 7 min. The split/splitless injector was held at 300 °C and operated in splitless mode with the split valve closed for 1 min following sample injection. The split flow was set at 40 mL min<sup>-1</sup>, and the mass spectrometer transfer line was maintained at 270 °C. Electron impact (EI) ionization at 70 eV with an electron multiplier voltage set at 1500 V was used while operating in single ion monitoring (SIM) mode. PAH quantitation was carried out using a five-point calibration plot containing 50, 20, 10, 5, and 2 μg L<sup>-1</sup> PAH standard mixtures and 20 μg mL<sup>-1</sup> internal standards (3,6-dimethylphenanthrene and 6-ethylchrysene).

**Analysis of Extracts by GC-FID.** Gas chromatographic separation and identification of the PAHs was performed on a Carlo Erba HRGC 5300 Mega Series (Fisons Ltd., Crawley, Surrey, U.K.) with on-column injection and flame ionization detection. A 30 m × 0.32 mm id × 0.1 μm film thickness DB-5 HT capillary column (J&W Scientific) was used to achieve separation with the following temperature program: initial column temperature, 50 °C; hold for 2 min; increase at 15 °C min<sup>-1</sup> to 90 °C; hold for 2 min; increase at 6 °C min<sup>-1</sup> to 300 °C; hold for 8 min. The detector temperature was set at 290 °C. PAH quantitation was carried out using a five-point calibration plot containing 50, 40, 30, and 20

Table 4. Accelerated Solvent Extraction of Polycyclic Aromatic Hydrocarbons from Contaminated Soil: Central Composite Design Results (mg kg<sup>-1</sup>)

|                        | experiment no. |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |
|------------------------|----------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
|                        | 1              | 2      | 3      | 4      | 5      | 6      | 7      | 8      | 9      | 10     | 11     | 12     | 13     | 14     | 15     | 16     |
| naphthalene            | 192.0          | 196.3  | 158.0  | 117.2  | 167.5  | 148.5  | 158.3  | 128.4  | 184.6  | 160.1  | 148.8  | 167.7  | 166.8  | 137.3  | 138.3  | 94.3   |
| acenaphthylene         | 38.1           | 39.7   | 31.4   | 28.8   | 36.1   | 33.5   | 36.1   | 31.2   | 38.1   | 37.2   | 31.7   | 32.8   | 34.0   | 29.7   | 30.2   | 30.3   |
| acenaphthene           | 54.3           | 59.5   | 56.1   | 51.4   | 56.0   | 50.0   | 54.2   | 56.2   | 56.4   | 58.1   | 52.7   | 52.5   | 54.2   | 54.8   | 52.5   | 53.5   |
| fluorene               | 93.4           | 107.5  | 100.0  | 87.3   | 100.7  | 88.5   | 99.0   | 92.0   | 99.8   | 97.6   | 88.4   | 91.5   | 96.0   | 90.2   | 87.2   | 91.0   |
| phenanthrene           | 344.2          | 408.2  | 369.8  | 338.0  | 372.2  | 334.4  | 372.5  | 332.1  | 366.4  | 371.9  | 337.4  | 345.9  | 363.7  | 362.9  | 344.8  | 355.6  |
| anthracene             | 87.6           | 91.5   | 92.0   | 85.7   | 93.9   | 85.9   | 89.4   | 88.6   | 95.8   | 88.3   | 90.9   | 71.7   | 82.5   | 78.4   | 79.3   | 83.1   |
| fluoranthene           | 250.6          | 277.1  | 252.6  | 239.0  | 255.4  | 249.6  | 267.7  | 260.6  | 272.8  | 262.4  | 249.4  | 246.9  | 252.1  | 262.4  | 247.6  | 258.6  |
| pyrene                 | 183.2          | 203.9  | 182.8  | 169.3  | 183.6  | 179.4  | 193.9  | 189.1  | 192.6  | 197.9  | 182.2  | 182.9  | 188.6  | 197.4  | 186.3  | 188.7  |
| benz[a]anthracene      | 63.4           | 68.2   | 60.2   | 56.7   | 59.2   | 61.2   | 62.8   | 62.3   | 61.6   | 67.4   | 61.2   | 62.6   | 62.9   | 63.1   | 61.5   | 59.2   |
| chrysene               | 64.3           | 65.2   | 62.1   | 55.9   | 61.3   | 62.6   | 58.3   | 52.6   | 62.3   | 66.5   | 63.7   | 61.3   | 54.1   | 60.3   | 56.1   | 30.8   |
| benzo[b]fluoranthene   | 80.5           | 85.2   | 79.7   | 75.5   | 32.5   | 82.4   | 77.6   | 78.1   | 79.3   | 86.8   | 79.4   | 82.4   | 78.5   | 78.7   | 73.5   | 39.5   |
| benzo[k]fluoranthene   | 31.2           | 31.0   | 27.7   | 28.2   | 28.7   | 29.0   | 27.7   | 28.8   | 28.5   | 31.9   | 27.4   | 30.7   | 28.0   | 31.1   | 27.9   | 27.8   |
| benzo[a]pyrene         | 54.6           | 56.8   | 51.3   | 52.9   | 25.4   | 55.0   | 52.1   | 24.6   | 55     | 17.2   | 51.4   | 50.7   | 52.6   | 53.6   | 49.6   | 50.2   |
| indeno[123-cd]pyrene   | 46.2           | 46.2   | 41.6   | 40.6   | 41.2   | 45.5   | 42.6   | 42.9   | 43.3   | 47.4   | 43.8   | 43.1   | 43.5   | 43.5   | 39.9   | 42.8   |
| dibenzo[a,h]anthracene | 9.6            | 9.7    | 9.3    | 8.9    | 8.3    | 9.3    | 9.4    | 9.7    | 9.6    | 10.4   | 9.2    | 9.3    | 9.5    | 9.2    | 8.6    | 8.8    |
| benzo[ghi]perylene     | 18.0           | 42.5   | 38.8   | 37.1   | 35.0   | 40.1   | 39.9   | 39.9   | 41.4   | 44.2   | 41.2   | 42.6   | 41.0   | 39.5   | 37.7   | 40.3   |
| total                  | 1611.2         | 1788.5 | 1613.4 | 1472.5 | 1557.0 | 1554.9 | 1641.5 | 1517.1 | 1687.5 | 1645.3 | 1558.8 | 1574.6 | 1608.0 | 1592.1 | 1521.0 | 1454.5 |

Table 5. Statistical Treatment of Individual PAH Data Using Multilinear Regression

| param | variable | naphthalene |         | acenaphthylene |         | acenaphthene |         | fluorene    |         |
|-------|----------|-------------|---------|----------------|---------|--------------|---------|-------------|---------|
|       |          | coeff       | p value | coeff          | p value | coeff        | p value | coeff       | p value |
| $b_0$ |          | 27.6917     | 0.7703  | 20.3362        | 0.3429  | 51.6661      | 0.0713  | 88.6147     | 0.1162  |
| $b_1$ | $P$      | 0.0156      | 0.8388  | 0.0067         | 0.6948  | 0.0054       | 0.8057  | 0.0063      | 0.8861  |
| $b_2$ | $T$      | 0.8163      | 0.1313  | 0.0304         | 0.7931  | -0.1238      | 0.4102  | -0.1102     | 0.7110  |
| $b_3$ | $t$      | 9.5065      | 0.1246  | 0.8960         | 0.5020  | 1.1197       | 0.5127  | 0.5285      | 0.8759  |
| $b_4$ | $P^2$    | 0.0000(008) | 0.9695  | -0.0000(03)    | 0.5788  | -0.0000(03)  | 0.6331  | -0.0000(06) | 0.6209  |
| $b_5$ | $T^2$    | -0.0040     | 0.0184  | -0.0002        | 0.6101  | 0.0000(4)    | 0.9344  | 0.0002      | 0.8336  |
| $b_6$ | $t^2$    | -0.0840     | 0.6831  | -0.0357        | 0.4394  | -0.0383      | 0.5166  | -0.0071     | 0.9515  |
| $b_7$ | $PT$     | 0.0003      | 0.1677  | 0.0000(4)      | 0.3785  | 0.0000(7)    | 0.2140  | 0.0001      | 0.3043  |
| $b_8$ | $Pt$     | -0.0059     | 0.0232  | -0.0003        | 0.5542  | -0.0004      | 0.5641  | 0.000000    | 1.0000  |
| $b_9$ | $Tt$     | 0.0206      | 0.2834  | 0.0013         | 0.7664  | 0.0019       | 0.7283  | -0.0038     | 0.7279  |

  

| phenanthrene |         | anthracene |         | fluoranthene |         | pyrene      |         |
|--------------|---------|------------|---------|--------------|---------|-------------|---------|
| coeff        | p value | coeff      | p value | coeff        | p value | coeff       | p value |
| 234.0108     | 0.2780  | 179.3032   | 0.0019  | 328.6399     | 0.0065  | 183.8259    | 0.0611  |
| 0.0647       | 0.7060  | -0.0664    | 0.1060  | -0.0283      | 0.7421  | 0.0088      | 0.9064  |
| -0.0670      | 0.9539  | -0.3917    | 0.1552  | -0.6885      | 0.2472  | -0.3070     | 0.5473  |
| 12.8142      | 0.3413  | -6.2197    | 0.0551  | -2.8089      | 0.6734  | 4.1823      | 0.4742  |
| -0.0000(1)   | 0.7601  | 0.0000(1)  | 0.2431  | 0.0000(0001) | 0.9996  | -0.0000(04) | 0.8464  |
| 0.0011       | 0.7524  | 0.0012     | 0.1496  | 0.0011       | 0.5149  | -0.0000(6)  | 0.9697  |
| -0.1094      | 0.8113  | 0.1663     | 0.1281  | 0.0205       | 0.9287  | -0.1306     | 0.5168  |
| 0.0002       | 0.6253  | 0.0000(9)  | 0.3387  | 0.0002       | 0.2580  | 0.0002      | 0.3318  |
| -0.0040      | 0.4529  | 0.0018     | 0.1505  | 0.0002       | 0.9291  | -0.0020     | 0.4009  |
| -0.0369      | 0.3867  | 0.0031     | 0.7464  | 0.0094       | 0.6575  | 0.0056      | 0.7599  |

  

| benz[a]anthracene |         | chrysene    |         | benzo[b]fluoranthene |         | benzo[k]fluoranthene |         |
|-------------------|---------|-------------|---------|----------------------|---------|----------------------|---------|
| coeff             | p value | coeff       | p value | coeff                | p value | coeff                | p value |
| 37.1120           | 0.1190  | -22.9479    | 0.6726  | 29.0437              | 0.7940  | -2.4849              | 0.8217  |
| 0.0131            | 0.4819  | 0.0344      | 0.4378  | -0.0226              | 0.8019  | 0.0281               | 0.0059  |
| 0.0978            | 0.4395  | 0.6674      | 0.0374  | 1.3433               | 0.0407  | 0.0669               | 0.2786  |
| 2.4987            | 0.0962  | 1.4110      | 0.6787  | -1.6997              | 0.8075  | 1.2793               | 0.0794  |
| -0.0000(03)       | 0.5053  | -0.0000(05) | 0.6821  | 0.0000(08)           | 0.7316  | -0.0000(06)          | 0.0139  |
| -0.0007           | 0.0787  | -0.0023     | 0.0164  | -0.0058              | 0.0054  | -0.0003              | 0.0861  |
| -0.0638           | 0.2091  | 0.0232      | 0.8430  | 0.1235               | 0.6093  | -0.0449              | 0.0749  |
| 0.0000(5)         | 0.2805  | -0.0000(1)  | 0.9077  | 0.0000(1)            | 0.9549  | -0.0000(06)          | 0.7760  |
| -0.0009           | 0.1138  | -0.0013     | 0.3602  | -0.0006              | 0.8212  | -0.0006              | 0.0606  |
| 0.000000          | 1.0000  | 0.0025      | 0.8167  | 0.0025               | 0.9100  | 0.0031               | 0.1679  |

  

| benzo[a]pyrene |         | indeno[123-cd]pyrene |         | dibenzo[a,h]anthracene |         | benzo[ghi]perylene |         |
|----------------|---------|----------------------|---------|------------------------|---------|--------------------|---------|
| coeff          | p value | coeff                | p value | coeff                  | p value | coeff              | p value |
| 96.1985        | 0.4726  | 25.7046              | 0.1706  | 14.1204                | 0.0478  | 42.6488            | 0.3360  |
| -0.0881        | 0.4178  | 0.0127               | 0.3934  | -0.0041                | 0.4501  | -0.0039            | 0.9121  |
| 0.2100         | 0.7737  | 0.1084               | 0.2863  | -0.0090                | 0.8060  | 0.0633             | 0.7918  |
| -1.4080        | 0.8658  | 0.4676               | 0.6822  | -0.0883                | 0.8329  | 0.2469             | 0.9281  |
| 0.0000(4)      | 0.1776  | -0.0000(02)          | 0.6217  | 0.0000(01)             | 0.6400  | -0.0000(07)        | 0.4362  |
| 0.0008         | 0.6964  | -0.0005              | 0.1321  | -0.0001                | 0.3827  | -0.0012            | 0.1195  |
| 0.4205         | 0.1578  | -0.0195              | 0.6217  | -0.0034                | 0.8123  | -0.1050            | 0.2765  |
| -0.0002        | 0.5258  | -0.0000(1)           | 0.7299  | 0.0000(1)              | 0.3529  | 0.0002             | 0.0668  |
| -0.0024        | 0.4674  | -0.0005              | 0.3080  | -0.0000(00)            | 1.0000  | 0.0015             | 0.1846  |
| -0.0144        | 0.5882  | 0.0038               | 0.3080  | 0.0013                 | 0.3529  | -0.0119            | 0.1846  |

mg mL<sup>-1</sup> PAH standard mixtures and 25 mg mL<sup>-1</sup> internal standards (3,6-dimethylphenanthrene and 6-ethylchrysene). Correlation coefficients between 0.9997 and 0.9888 were obtained.

**Experimental Design Approach.** To fully understand the way in which ASE operating variables affect extraction, individual operating variables must be considered along with nonlinear effects and interaction terms. The operating variables, pressure, temperature and extraction time, were studied using a full second-order central composite design (CSS Statistica/W, Release 5.0 with

Industrial units, Statsoft UK, Letchworth, U.K.). Each of the variables had levels set at five coded levels:  $-\alpha$ ,  $-1$ ,  $0$ ,  $+1$ , and  $+\alpha$ , requiring 16 experiments in total. The results from the central composite design can be assessed using multilinear regression (Microsoft Excel, version 6.0, Microsoft Corp.), using an equation of the form

$$Y = b_0 + b_1P + b_2T + b_3t + b_4P^2 + b_5T^2 + b_6t^2 + b_7PT + b_8Pt + b_9Tt \quad (1)$$

where  $Y$  is the extraction recovery and  $b_0$  the intercept.

(5) Brereton, R. G. *Chemometrics: Applications of Mathematics and Statistics to Laboratory Systems*; Ellis Horwood: Chichester, Sussex, U.K., 1990; Chapter 2.

Table 6. Statistical Significance at the 95% Confidence Interval of Individual PAHs

| compound     | variable of significance | compound                        | variable of significance |
|--------------|--------------------------|---------------------------------|--------------------------|
| naphthalene  | $T^2$ and $Pt$           | benzo[ <i>b</i> ]fluoranthene   | $T$ and $T^2$            |
| anthracene   | intercept                | benzo[ <i>k</i> ]fluoranthene   | $P$ and $P^2$            |
| fluoranthene | intercept                | dibenzo[ <i>a,h</i> ]anthracene | intercept                |
| chrysene     | $T$ and $T^2$            |                                 |                          |

Table 7. Effect of Solvent on the Recovery of Polycyclic Aromatic Hydrocarbons from Contaminated Soil<sup>a</sup> (mg kg<sup>-1</sup>). Analysis by GC-FID

|   | acetone         | DCM/acetone | DCM    | methanol | ACN    | hexane/acetone | hexane |
|---|-----------------|-------------|--------|----------|--------|----------------|--------|
| naphthalene   | 154.5           | 193.9       | 212.6  | 215.3    | 144.9  | 215.0          | 69.6   |
| acenaphthylene  | 27.4            | 28.5        | 30.8   | 29.1     | 29.3   | 32.3           | 24.5   |
| acenaphthene  | 47.1            | 52.9        | 56.6   | 55.5     | 55.5   | 57.5           | 50.6   |
| fluorene  | 91.3            | 92.6        | 95.2   | 101.8    | 99.9   | 103.1          | 89.8   |
| phenanthrene  | 246.0           | 260.2       | 284.1  | 283.1    | 272.5  | 295.4          | 260.0  |
| anthracene  | 89.4            | 87.0        | 92.0   | 83.2     | 89.9   | 89.1           | 78.1   |
| fluoranthene  | 193.4           | 198.4       | 209.1  | 200.1    | 201.8  | 213.4          | 197.5  |
| pyrene  | 172.1           | 176.0       | 174.8  | 172.2    | 173.5  | 179.2          | 160.4  |
| benz[ <i>a</i> ]anthracene                                    | 93.8            | 96.7        | 109.3  | 87.9     | 98.7   | 118.1          | 94.4   |
| chrysene  | 60.6            | 58.7        | 53.7   | 56.0     | 44.2   | 59.5           | 42.0   |
| benzo[ <i>b</i> ]fluoranthene + benzo[ <i>k</i> ]fluoranthene | 134.5           | 130.2       | 121.7  | 107.5    | 109.6  | 138.8          | 97.3   |
| benzo[ <i>a</i> ]pyrene                                       | 33.1            | 41.3        | 45.1   | 24.2     | 32.9   | 40.7           | 34.3   |
| indeno[123- <i>cd</i> ]pyrene                                 | 62.1            | 65.5        | 69.6   | 56.1     | 58.6   | 72.2           | 47.2   |
| dibenzo[ <i>a,h</i> ]anthracene                               | nd <sup>b</sup> | nd          | nd     | nd       | nd     | nd             | nd     |
| benzo[ <i>ghi</i> ]perylene                                   | 46.7            | 49.7        | 48.0   | 39.7     | 47.3   | 46.5           | 38.0   |
| total   | 1452.2          | 1531.6      | 1602.7 | 1511.7   | 1458.5 | 1660.8         | 1283.8 |

<sup>a</sup> Based on duplicate extraction/analyses. <sup>b</sup> nd, not detected, i.e., <15 mg kg<sup>-1</sup>.

Each operating variable was assigned limits, dependent upon instrumental constraints, and these are shown in Table 1. The total number of experiments (16) were randomized to prevent operator intervention.

## RESULTS AND DISCUSSION

All extracts were analyzed using both GC-FID and GC-MSD. A comparison of the concentrations obtained between the GC-FID and GC-MSD was made. For direct comparison, compounds benzo[*b*]fluoranthene and benzo[*k*]fluoranthene were taken as a single combined concentration, as in the case of the GC-FID complete resolution was not possible. In addition, dibenzo[*a,h*]anthracene was also excluded as its level was below the limit of sensitivity obtainable using GC-FID, i.e., <15 mg kg<sup>-1</sup>. All other data were included for each individual PAH. As no notable differences were observed between the data (correlation coefficient,  $r = 0.9240$ ,  $r^2 = 0.8537$ ,  $n = 224$  determinations), the results for the GC-MSD only are reported in this paper, with the exception of the extraction solvent experiment (see later). This was done as it was not possible to separate all 16 PAHs using the column in the GC-FID; i.e., benzo[*b*]fluoranthene and benzo[*k*]fluoranthene were not totally separated. Also, the enhanced sensitivity of the GC-MSD operated in SIM mode allowed dibenzo[*a,h*]anthracene to be determined.

Multilinear regression was applied to the results of the central composite design. The results based on the total of the 16 PAHs recovered are shown in Table 2. Statistical treatment of the data is shown in Table 3. It is seen that at the 95% confidence level ( $p$  value <0.05) no terms are significant. The same statistical approach was then applied to the 16 individual PAHs. The results of the 16 individual experiments, as determined in the central

composite design, are shown in Table 4. Statistical treatment of these data is shown in Table 5. It is apparent that some individual PAHs do have statistical significance at the 95% confidence level ( $p$  value <0.05), and this is summarized in Table 6. As the intercept is significant for three individual PAHs, i.e., for anthracene, fluoranthene, and dibenzo[*a,h*]anthracene, this indicates that the operating parameters of ASE are insensitive to changes. This noncorrelation is highlighted by the good precision ( $n = 16$ ) obtained for the compounds, i.e., anthracene (mean recovery 86.5 mg kg<sup>-1</sup>; 7.3% RSD), fluoranthene (mean recovery, 256.6 mg kg<sup>-1</sup>; 4.0% RSD), and dibenzo[*a,h*]anthracene (mean recovery 9.3 mg kg<sup>-1</sup>; 5.3% RSD). As a consequence of this good precision, a large directional influence is given by the intercept term, leading to its significance. For naphthalene, chrysene, and benzo[*b*]fluoranthene, the significance of temperature is highlighted by the poorer recoveries obtained in the central composite design when the temperature was at its lowest, i.e., 40 °C in Table 4, experiment 16. The significance of pressure for benzo[*k*]fluoranthene is not obvious to explain.

**Effect of Extraction Solvent.** A selection of organic solvents, singly or in combination, were chosen to investigate their influence on the recovery of PAHs. The individual solvents selected were (in solvent polarity order, i.e., dielectric constant, as determined at 20 °C, nonpolar first) as follows: hexane (1.89), dichloromethane (9.08), acetone (20.7 at 25 °C), methanol (33.62), and acetonitrile (37.5). In addition, two solvent combinations were also chosen, i.e., dichloromethane + acetone and hexane + acetone, both as 1 + 1 combinations (vol %). The results (Table 7) obtained under standard operating conditions, as recommended in EPA method 3545,<sup>1</sup> i.e., temperature of 100 °C, pressure of 14

MPa, and an extraction time of 5 min with 5 min equilibration time, indicate that the solvent, singly or in combination, has no effect on the recovery of PAHs, except hexane. The poor recoveries obtained for hexane are attributable to its lower polarity.

#### CONCLUSIONS

The robustness of accelerated solvent extraction for the extraction of polycyclic aromatic hydrocarbons from contaminated soil is demonstrated. Within the operating limits of the technique, the technique was found to provide good recoveries. No influence was found between the use of polar solvents and the extraction of polycyclic aromatic hydrocarbons.

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