Quantification of Persistent Organic Pollutants in Dietary Supplements Using Stir Bar Sorptive Extraction Coupled with GC/MS/MS and Isotope Dilution Mass Spectrometry

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**Supporting Information**

Table S1. Errors (%) of measurements of the spiked analytes in the dietary supplement samples at the four different spiking concentrations. Results showing comparison between IDMS and calibration curves (CC) with and without internal standards (IS) added (n=5).

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | Concentration 1 | | | Concentration 2 | | | Concentration 3 | | | Concentration 4 | | |
| cc | cc w/ IS | IDMS | cc | cc w/ IS | IDMS | cc | cc w/ IS | IDMS | cc | cc w/ IS | IDMS |
| Naphthalene | >100 | 92.8 | 6.83 | 49.6 | 51.0 | 1.68 | 10.3 | 23.5 | 6.67 | 4.52 | 15.8 | 9.87 |
| Acenaphthene | 47.6 | 27.7 | 42.7 | 24.7 | 5.29 | 34.0 | 4.11 | 8.11 | 35.1 | 9.74 | 9.17 | 34.8 |
| Fluorene | 49.0 | 14.5 | 6.22 | 25.6 | 1.75 | 10.1 | 2.84 | 15.4 | 5.74 | 11.6 | 12.2 | 8.30 |
| Phenanthrene | 99.2 | 63.5 | 6.64 | 43.6 | 11.1 | 2.99 | 12.1 | 8.85 | 0.227 | 0.838 | 7.83 | 2.45 |
| Fluoranthene | 65.6 | >100 | 17.8 | 31.8 | 69.0 | 12.3 | 0.239 | 25.4 | 11.1 | 7.39 | 17.4 | 7.77 |
| Pyrene | 49.1 | 28.7 | 7.70 | 14.9 | 0.409 | 2.51 | 7.26 | 10.4 | 9.24 | 9.42 | 10.7 | 8.14 |
| Benz[a]anthracene | 24.6 | 14.6 | 9.99 | 31.3 | 2.73 | 1.12 | 45.1 | 8.18 | 4.96 | 31.5 | 4.76 | 6.51 |
| Chrysene | 8.61 | 14.7 | 19.1 | 2.90 | 3.14 | 5.63 | 21.7 | 14.4 | 4.55 | 14.3 | 12.1 | 4.93 |
| Benzo[b]fluoranthene | 33.3 | 13.5 | 6.01 | 36.5 | 8.25 | 2.11 | 49.3 | 8.72 | 6.18 | 26.4 | 2.04 | 10.6 |
| Benzo[k]fluoranthene | 39.0 | 38.3 | 6.54 | 37.7 | 1.87 | 12.1 | 44.9 | 19.0 | 9.71 | 25.3 | 14.9 | 4.23 |
| Benzo[a]pyrene | 52.0 | 22.7 | 7.22 | 45.5 | 5.91 | 8.75 | 52.5 | 19.5 | 5.03 | 32.8 | 11.4 | 4.38 |
| Indeno[1,2,3-cd]pyrene | 55.4 | 45.8 | 11.7 | 59.1 | 3.23 | 10.4 | 58.6 | 16.7 | 5.61 | 39.5 | 10.8 | 1.17 |
| Benzo[ghi]perylene | 42.9 | 37.0 | 4.61 | 42.1 | 1.57 | 7.53 | 46.5 | 13.8 | 1.67 | 25.0 | 12.4 | 0.183 |
| α-HCH | >100 | 2.04 | 11.2 | 41.1 | 4.60 | 7.95 | 0.232 | 3.95 | 7.83 | 12.6 | 3.29 | 10.0 |
| β-HCH | 93.0 | 22.4 | 4.40 | 30.0 | 0.163 | 9.87 | 2.15 | 7.42 | 7.17 | 10.6 | 2.16 | 3.29 |
| γ-HCH | >100 | 24.7 | 16.1 | 54.2 | 0.320 | 2.54 | 13.6 | 9.39 | 2.28 | 6.34 | 4.93 | 8.29 |
| δ-HCH | 51.0 | 41.7 | 19.4 | 14.1 | 10.2 | 19.6 | 36.5 | 12.4 | 10.6 | 44.4 | 4.17 | 9.72 |
| DDE | 67.6 | 3.24 | 14.9 | 77.2 | 1.83 | 7.75 | 79.2 | 10.7 | 7.63 | 72.7 | 0.754 | 8.63 |
| DDD | 42.9 | 57.6 | 11.6 | 54.4 | 5.92 | 4.37 | 70.0 | 5.06 | 1.17 | 54.3 | 3.78 | 2.69 |
| DDT | 73.9 | >100 | 4.47 | 77.2 | 9.67 | 0.965 | 74.6 | 4.64 | 5.17 | 72.3 | 7.27 | 8.88 |
| CPS | 41.4 | 12.4 | 9.65 | 41.6 | 0.726 | 9.23 | 47.9 | 2.83 | 5.18 | 42.6 | 11.2 | 0.324 |

Fig S1. Relative recovery of the spiked analytes in dietary supplement sample using different extraction solvents (n=5, 95% CI). The relative recovery of each analyte was normalized to a 0-100% scale.

Fig S2. Relative recovery of the spiked analytes in dietary supplement sample using different extraction time (n=5). The relative recovery of each analyte was normalized to a 0-100% scale.

Table S2. Measurements of the analytes in the 12 commercially available dietary supplement samples using SBSE-GC-MS/MS-IDMS (n=5, 95% CI). Units are in ng/g. Results below limit of quantification are shown as N/A.

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| Naphthalene | 1.90 ± 0.414 | 2.03 ± 0.395 | 2.28 ± 0.253 | 1.90 ± 0.428 | 3.53 ± 0.607 | 2.42 ± 0.410 | 2.61± 0.179 | 3.89 ± 0.713 | 6.45 ± 1.71 | 0.917 ± 0.194 | 3.53 ± 0.335 | 4.25 ± 0.646 |
| Acenaphthene | 0.852 ± 0.0464 | 0.879 ± 0.164 | 0.519 ± 0.0807 | 1.01 ± 0.130 | 23.3 ± 4.18 | 0.265 ± 0.0421 | 5.65 ± 0.590 | 6.46 ± 0.470 | 0.743 ± 0.0739 | 0.175 ± 0.0298 | 0.819 ± 0.0925 | 2.97 ± 0.542 |
| Fluorene | 0.459 ± 0.158 | 0.549 ± 0.111 | 0.759 ± 0.128 | 1.74 ± 0.352 | 0.772 ± 0.136 | 0.388 ± 0.0564 | 0.803 ± 0.0403 | 1.94 ± 0.298 | 1.71 ± 0.354 | 0.609 ± 0.107 | 1.91 ± 0.191 | 7.14 ± 1.26 |
| Phenanthrene | 2.31 ± 0.321 | 1.24 ± 0.154 | 1.65 ± 0.193 | 1.60 ± 0.184 | 2.66 ± 0.352 | 1.15 ± 0.166 | 1.83 ± 0.204 | 3.25 ± 0.204 | 5.55 ± 0.733 | 11.1 ± 0.253 | 12.1 ± 1.48 | 26.0 ± 1.72 |
| Fluoranthene | 1.87 ± 0.132 | 0.725 ± 0.0719 | 0.928 ± 0.0621 | 0.589 ± 0.101 | 2.10 ± 0.254 | 0.626 ± 0.108 | 1.92 ± 0.181 | 1.22 ± 0.238 | 2.12 ± 0.340 | 4.35 ± 0.152 | 5.71 ± 0.820 | 10.5 ± 0.706 |
| Pyrene | 1.91 ± 0.258 | 0.494 ± 0.0902 | 0.616 ± 0.0971 | 0.265 ± 0.0243 | 2.79 ± 0.470 | 0.496 ± 0.0690 | 2.23 ± 0.313 | 2.42 ± 0.348 | N/A | 5.42 ± 0.350 | 6.72 ± 1.36 | 6.72 ± 1.06 |
| Benz[a]anthracene | 0.539 ± 0.0922 | 0.212 ± 0.0340 | 0.124 ± 0.0186 | 0.584 ± 0.111 | 0.453 ± 0.0635 | 0.126 ± 0.0219 | 0.383 ± 0.0692 | 1.05 ± 0.183 | 1.37 ± 0.240 | 0.507 ± 0.109 | 0.838 ± 0.0976 | 1.82 ± 0.259 |
| Chrysene | 0.779 ± 0.151 | 0.101 ± 0.0169 | 0.182 ± 0.0354 | 1.67 ± 0.332 | 0.726 ± 0.141 | 0.255 ± 0.0410 | 0.725 ± 0.0461 | 2.10 ± 0.282 | 1.64 ± 0.338 | 1.39 ± 0.202 | 0.787 ± 0.140 | 2.00 ± 0.217 |
| Benzo[b]fluoranthene | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A |
| Benzo[k]fluoranthene | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A |
| Benzo[a]pyrene | N/A | N/A | N/A | N/A | 1.49 ± 0.242 | 0.691 ± 0.120 | N/A | 17.3 ± 2.79 | 2.43 ± 0.560 | N/A | N/A | N/A |
| Indeno[1,2,3-cd]pyrene | 0.887 ± 0.192 | 0.111 ± 0.0273 | N/A | N/A | 0.415 ± 0.0944 | N/A | 0.207 ± 0.0337 | N/A | 1.43 ± 0.236 | N/A | 0.674 ± 0.0546 | N/A |
| Benzo[ghi]perylene | 1.03 ± 0.164 | 0.167 ± 0.0329 | 0.625 ± 0.0112 | N/A | 0.501 ± 0.0718 | N/A | 0.272 ± 0.0511 | N/A | 1.79 ± 0.329 | N/A | 1.49 ± 0.268 | 2.68 ± 0.355 |
| α-HCH | N/A | N/A | N/A | N/A | N/A | 0.105 ± 0.0197 | 0.252 ± 0.0413 | N/A | N/A | 1.01 ± 0.105 | N/A | N/A |
| β-HCH | N/A | N/A | N/A | N/A | 1.61 ± 0.169 | N/A | N/A | 1.96 ± 0.232 | N/A | N/A | N/A | N/A |
| γ-HCH | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | 6.80 ± 0.992 | N/A | N/A |
| δ-HCH | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A |
| DDE | N/A | N/A | N/A | N/A | 0.382 ± 0.0782 | N/A | 0.239 ± 0.0433 | N/A | N/A | 0.618 ± 0.133 | 0.768 ± 0.140 | N/A |
| DDD | N/A | N/A | N/A | N/A | 0.132 ± 0.246 | 0.187 ± 0.0392 | 0.228 ± 0.0657 | N/A | N/A | 0.622 ± 0.0950 | 1.16 ± 0.105 | N/A |
| DDT | N/A | 0.747 ± 0.143 | 0.446 ± 0.0956 | N/A | 0.298 ± 0.0265 | 0.157 ± 0.0145 | N/A | 0.539 ± 0.106 | N/A | 1.62 ± 0.314 | 0.687 ± 0.142 | 1.59 ± 0.222 |
| Chlorpyrifos | 0.436 ± 0.0740 | N/A | N/A | N/A | 1.24 ± 0.102 | N/A | 0.371 ± 0.0767 | N/A | N/A | 1.34 ± 0.105 | 16.2 ± 1.88 | 1.51 ± 0.229 |