**Supporting Information**

**Insights into the Effect of the PDMS-layer on the Kinetics and Thermodynamics of Analyte Sorption onto the Matrix-Compatible SPME Coating**

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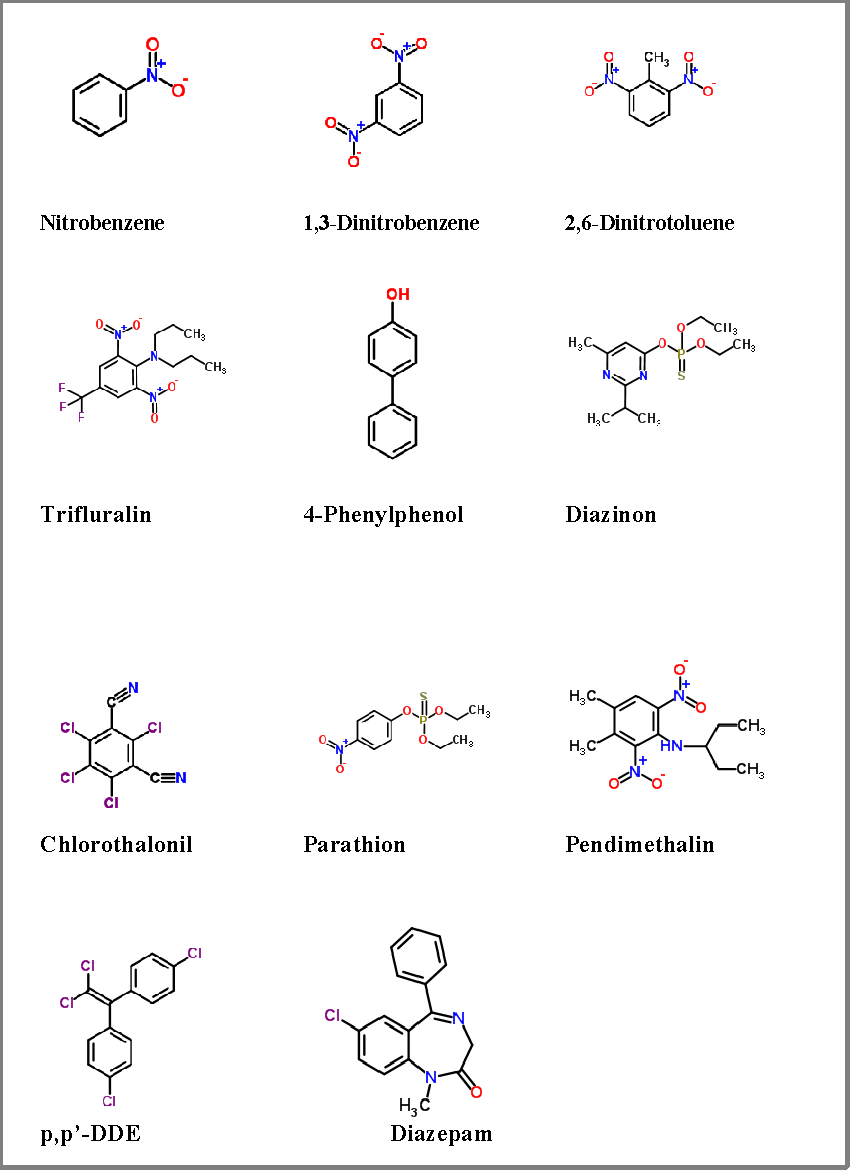
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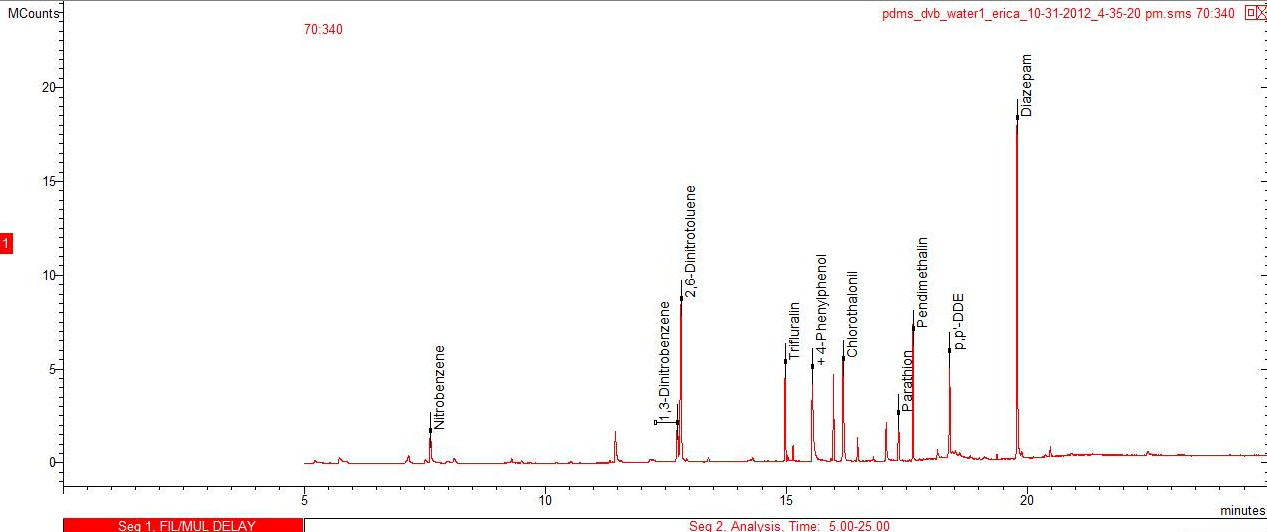
Figure S5 – Concentration profile from the coating inner surface to the bulk of the solution. Infinite volume of sample was considered for the simulation. a) Concentration profile for a polar analyte, 1, 3-dinitrobenzene; b) concentration profile for a non-polar analyte, pendimethalin. Parameters used in the simulation is shown in Table S4 …………………………………………………………………………….S-12

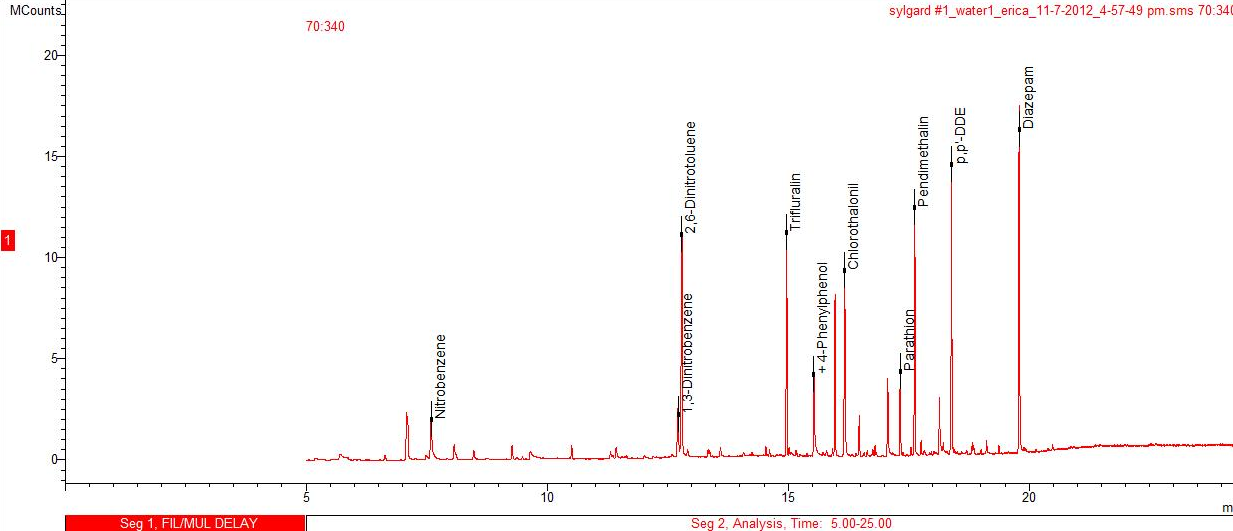
*Table S1 - Model analytes in standard mixture for coating evaluation.*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **Working Mixture**  **( µg/mL)** | **Log P**  **(pH 7)** | **MW (g/mole)** | **Quant. Ion (*m/z*)** |
| **Nitrobenzene** | 50 | 1.90 | 123 | 77 |
| **1,3-Dinitrobenzene** | 150 | 1.43 | 168 | 168 |
| **2,6-Dinitrotoluene** | 75 | 2.42 | 182 | 165 |
| **Trifluralin** | 5 | 5.07 | 325 | 306 |
| **4-Phenylphenol** | 20 | 3.20 | 170 | 170 |
| **Diazinon** | 7.5 | 3.40 | 304 | 304 |
| **Chlorothalonil** | 15 | 2.94 | 266 | 266 |
| **Parathion** | 5 | 3.83 | 291 | 291 |
| **Pendimethalin** | 5 | 5.18 | 281 | 252 |
| **p,p'-DDE** | 2.5 | 6.00 | 318 | 318 |
| **Diazepam** | 100 | 2.80 | 284 | 256 |

**

*Figure S1 - Structures of model analytes employed in the current coating evaluation.*



** 

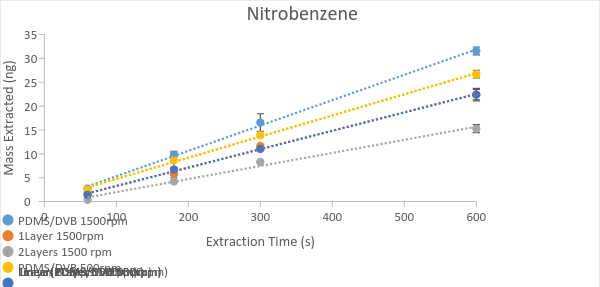
*Figure S2 - Representative chromatogram: analytes from standard mixture extracted from water using commercial PDMS/DVB fiber (A), and PDMS-overcoated (B).*

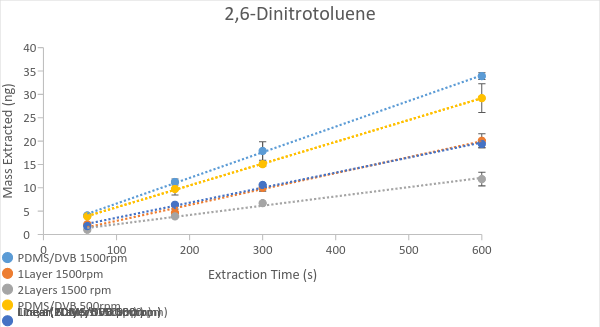
*Table S2 Calculated values of diffusion in water (Dw) at 30 ºC.*

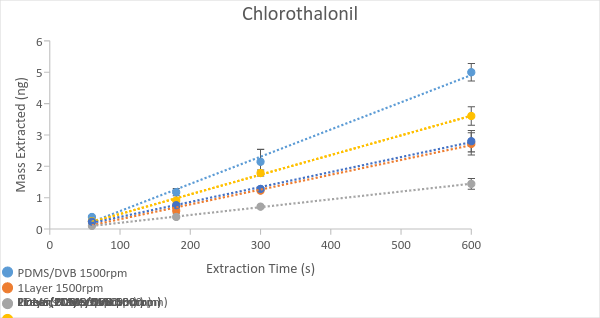
|  |  |
| --- | --- |
| **Dw** | |
| **Nitrobenzene** | 1.01E-05 |
| **1,3-Dinitrobenzene** | 8.99E-06 |
| **2,6-Dinitrotoluene** | 8.29E-06 |
| **Trifluralin** | 5.51E-06 |
| **4-Phenylphenol** | 7.76E-06 |
| **Diazinon** | 5.75E-06 |
| **Chlorothalonil** | 6.92E-06 |
| **Parathion** | 6.38E-06 |
| **Pendimethalin** | 5.77E-06 |
| **4,4'-DDE** | 5.90E-06 |
| **Diazepam** | 5.87E-06 |

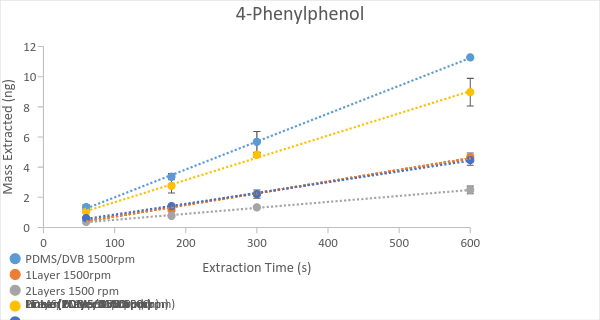
*Table S3 Calculated values of aqueous boundary layer thicknesses (in µm) for different sample agitation speed (in rpm)*

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | **PDMS/DVB** | | **1 Layer PDMS overcoat** | | **2 Layers PDMS overcoat** | |
|  | **δ500 rpm** | **δ1500 rpm** | **δ500 rpm** | **δ1500 rpm** | **δ500 rpm** | **δ1500 rpm** |
| **Nitrobenzene** | **10.98** | **5.55** | **11.28** | **5.71** | **11.85** | **5.99** |
| **1,3-Dinitrobenzene** | **10.5** | **5.31** | **10.79** | **5.46** | **11.33** | **5.74** |
| **2,6-Dinitrotoluene** | **10.18** | **5.15** | **10.46** | **5.29** | **10.99** | **5.56** |
| **Trifluralin** | **8.72** | **4.41** | **8.96** | **4.53** | **9.41** | **4.76** |
| **4-Phenylphenol** | **9.93** | **5.03** | **10.2** | **5.16** | **10.72** | **5.42** |
| **Diazinon** | **8.86** | **4.48** | **9.11** | **4.61** | **9.56** | **4.84** |
| **Chlorothalonil** | **9.51** | **4.81** | **9.77** | **4.94** | **10.26** | **5.19** |
| **Parathion** | **9.22** | **4.66** | **9.47** | **4.79** | **9.95** | **5.03** |
| **Pendimethalin** | **8.87** | **4.49** | **9.12** | **4.61** | **9.58** | **4.85** |
| **4,4'-DDE** | **8.95** | **4.53** | **9.19** | **4.65** | **9.66** | **4.89** |
| **Diazepam** | **8.93** | **4.52** | **9.18** | **4.64** | **9.64** | **4.88** |

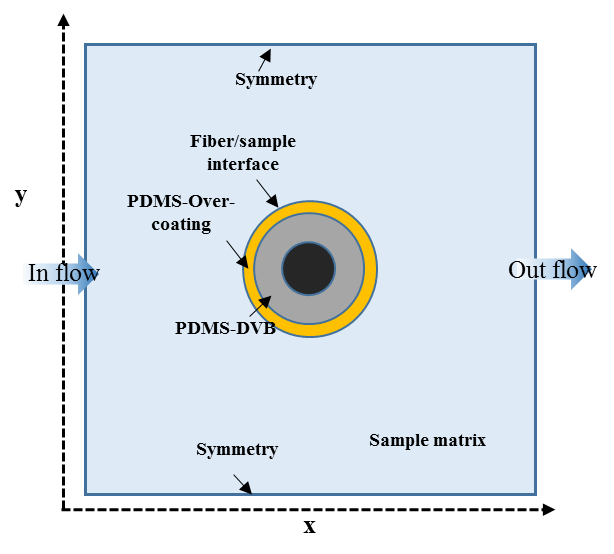








*Figure S3 - Mass uptake profiles of most polar target analytes obtained from aqueous solutions at 30 ºC.*



*Figure S4 - Schematic representation of the model domains used in the Comsol modeling and simulations.*

*Table S4 Parameters used in the modeling and simulations.*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Parameters | Unit | 1,3-Dinitrobenzene | Diazinon | Pendamethalin |
| Partition coefficient PDMS-DVB/Water |  | 886 | 18916 | 114295 |
| Partition coefficient PDMS/Water |  | 25 | 2500 | 151356 |
| Partition coefficient PDMS/PDMS-DVB |  | 33 | 7.51 | 5 |
| Diffusion coefficient in water | cm2/s | 8.99E-06 | 5.75E-06 | 7.37E-06 |
| Diffusion coefficient in coating and overcoating | cm2/s | 1.50E-06 | 9.58E-07 | 1.23E-06 |
| Fluid linear velocity (for 1500 rpm) | cm/s | 3.5 | 3.5 | 3.5 |
| Fluid linear velocity (for 500 rpm) | cm/s | 2.5 | 2.5 | 2.5 |
| Temperature | C | 35 | 35 | 35 |
| Volume of PDMS-DVB | mL | 4.40E-04 | 4.40E-04 | 4.40E-04 |
| Volume of over coating | µl | 8.80E-02 | 8.80E-02 | 8.80E-02 |
| Diameter of the fiber core | mm | 1.30E-01 | 1.30E-01 | 1.30E-01 |
| Total diameter of the over coated fiber (1 Layer) | mm | 2.70E-01 | 2.70E-01 | 2.70E-01 |
| Total diameter of the over coated fiber (2 Layers) | mm | 2.90E-01 | 2.90E-01 | 2.90E-01 |
| Initial concentration | ng/mL | 150 | 7.5 | 5 |

|  |
| --- |
| Figure S 5. Concentration profile from the coating inner surface to the bulk of the solution. Infinite volume of sample was considered for the simulation. a) Concentration profile for a polar analyte, 1, 3-dinitrobenzene; b) concentration profile for a non-polar analyte, pendimethalin. Parameters used in the simulation is shown in Table S4. |

