**Methodical evaluation and improvement of matrix compatible PDMS-overcoated coating for direct immersion solid phase microextraction gas chromatography (DI-SPME-GC)-based applications**

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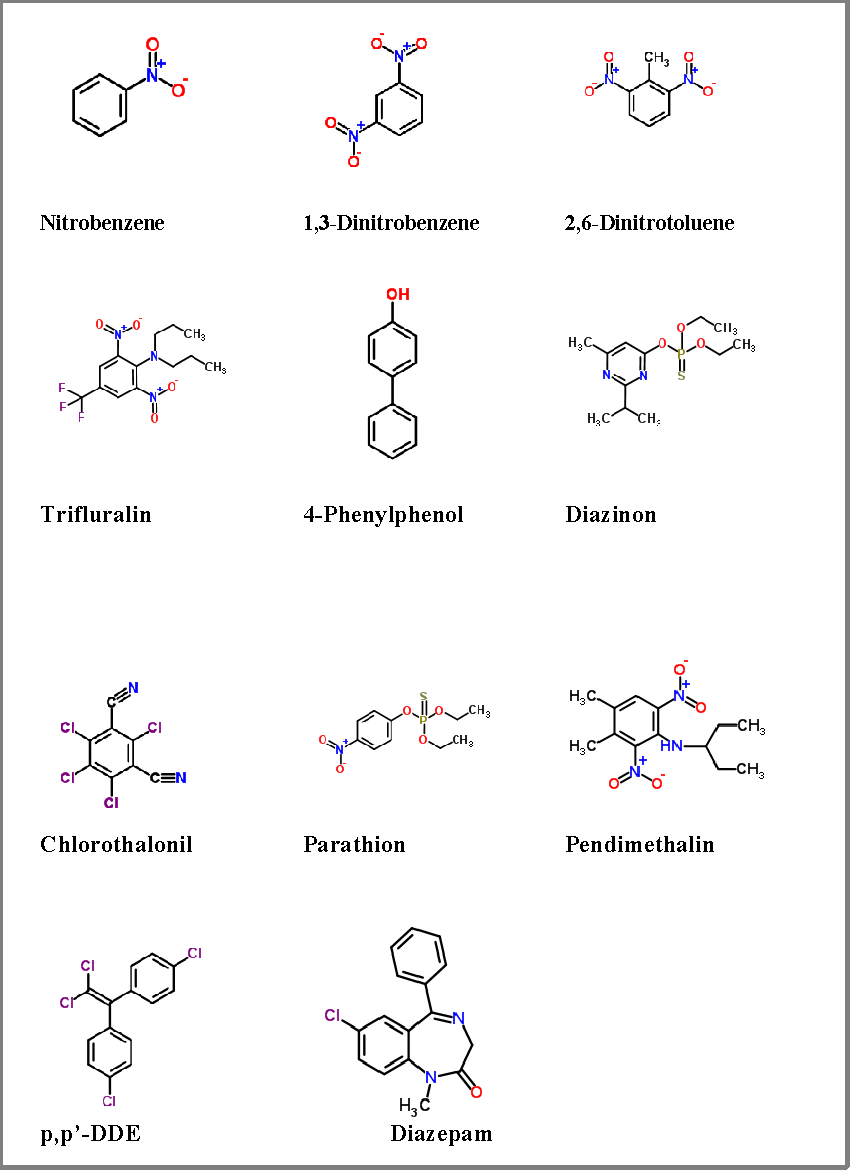
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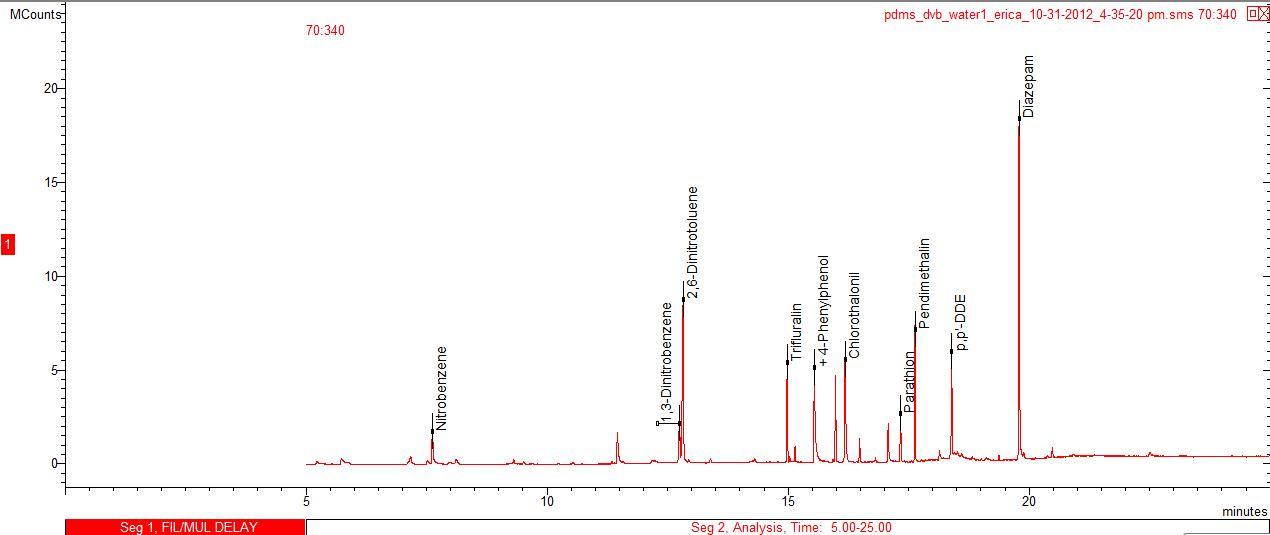
**Supporting Information**

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

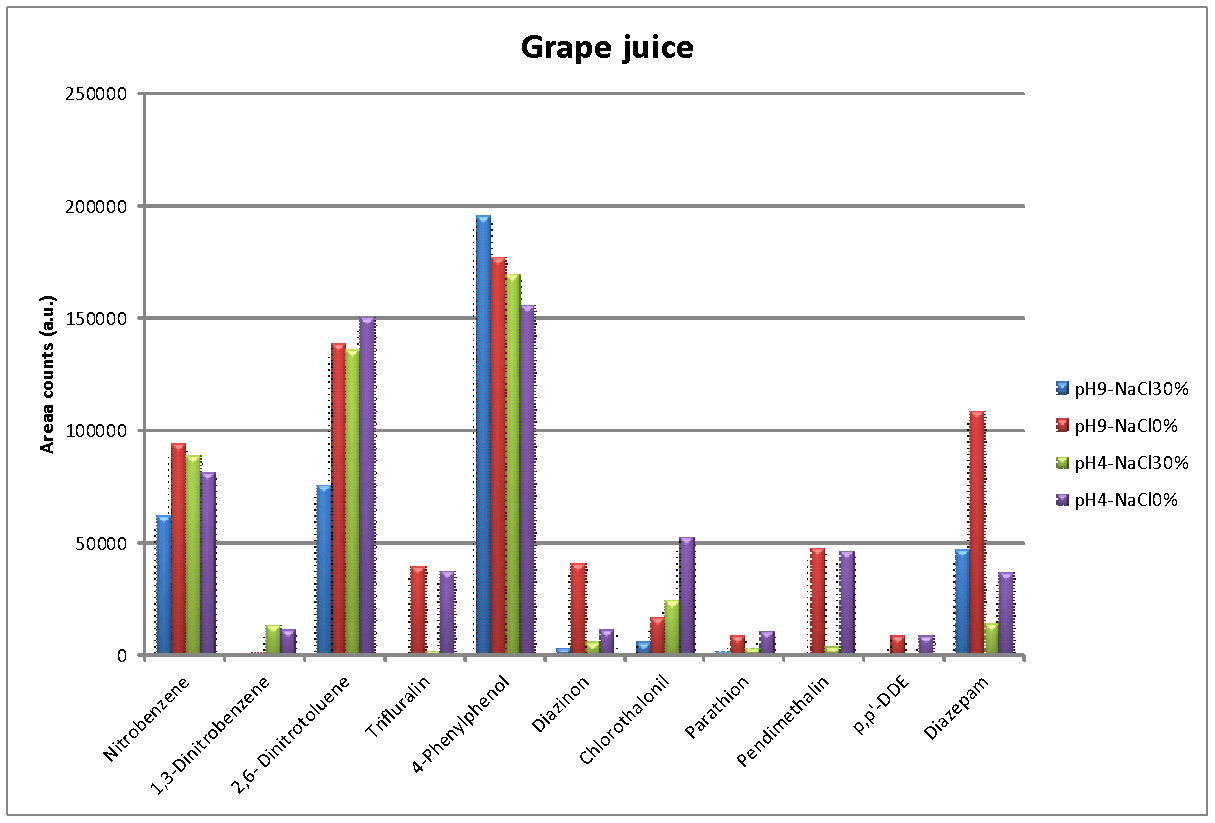
|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **Working Mixture**  **( µg/mL)** | **Log P**  **(pH 7)** | **MW (g/mole)** | **Quant. Ion (*m/z*)** |
| **Nitrobenzene** | 50 | 1.90 | 123 | 77 |
| **1,3-Dinitrobenzene** | 150 | 1.43 | 168 | 168 |
| **2,6-Dinitrotoluene** | 75 | 2.42 | 182 | 165 |
| **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 |

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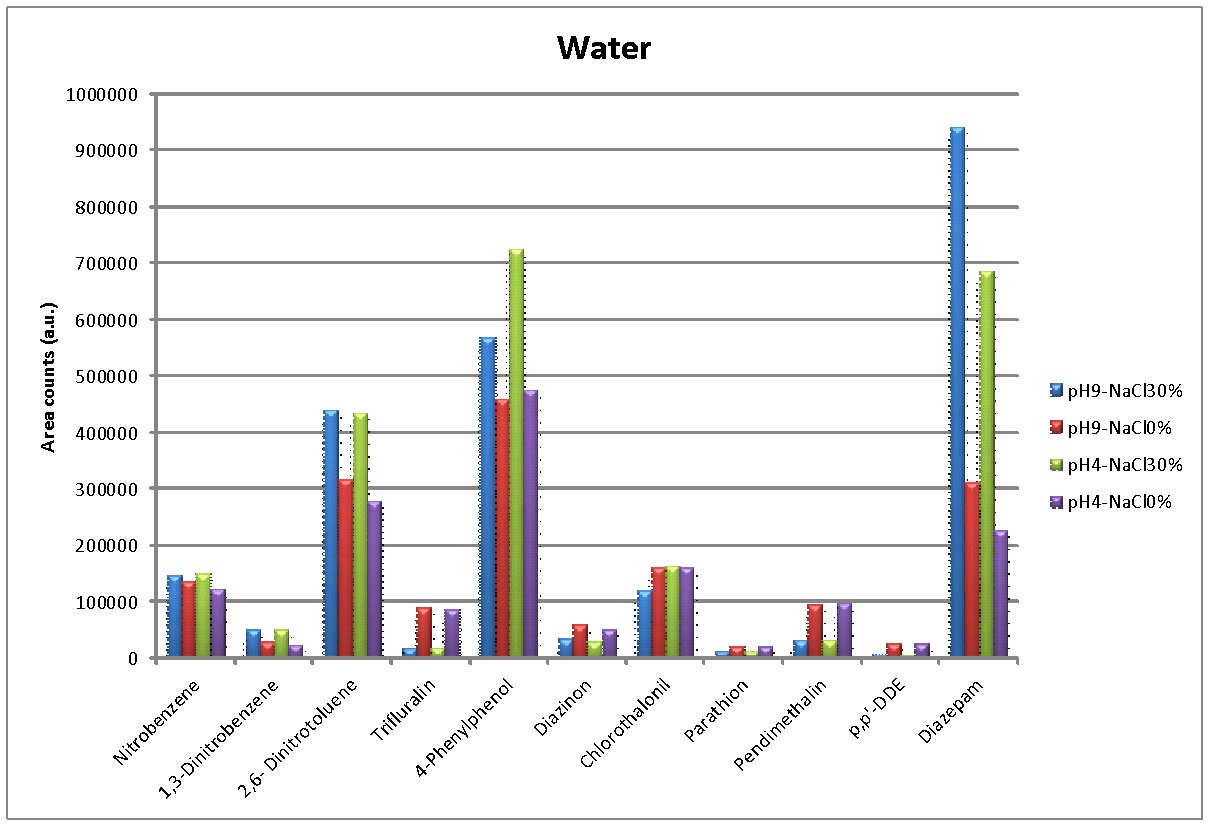
*Figure S1 - Structures of model analytes employed in the current coating evaluation.*



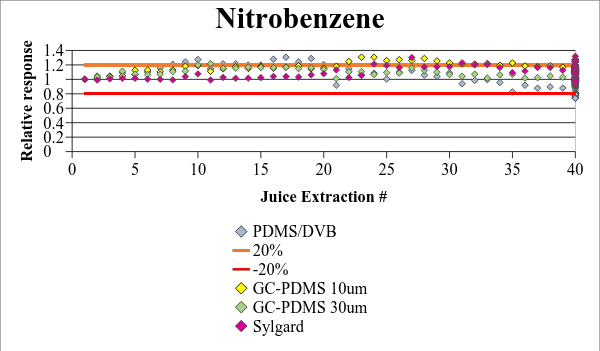
*Figure S2 - Representative chromatogram: analytes from standard mixture extracted from water using commercial PDMS/DVB fiber.*



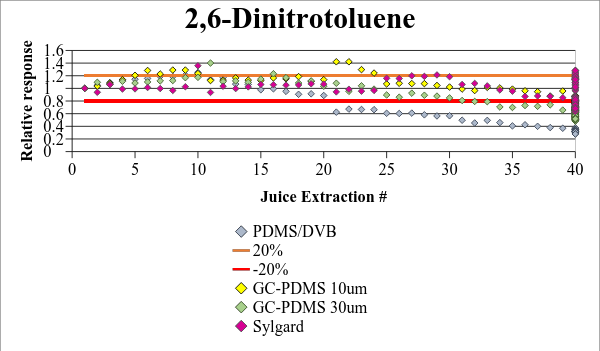
*Figure S3 - pH and salt (%) dependence of the amount extracted by a PDMS/DVB fiber from grape juice samples.*



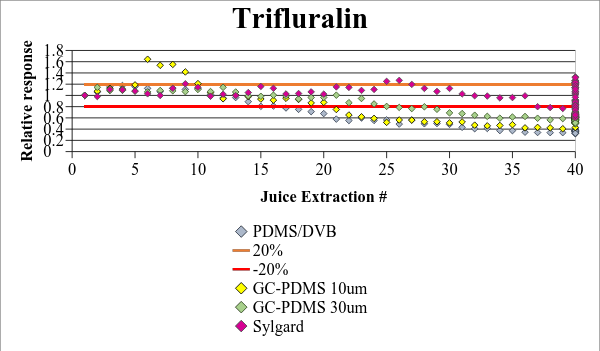
*Figure S4 - pH and salt (%) dependence of the amount extracted by a PDMS/DVB fiber from water samples.*



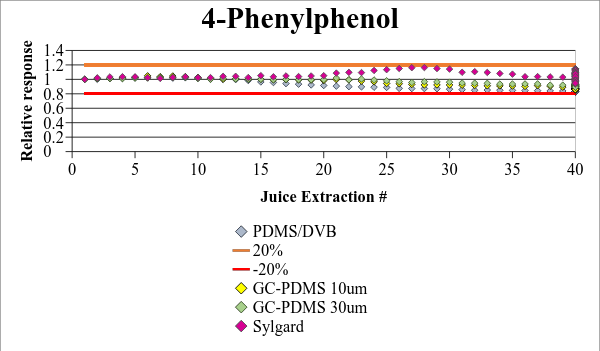
*Figure S5 - Nitrobenzene: reusability profile of coatings subjected to 40 DI-SPME in Concord grape juice.*



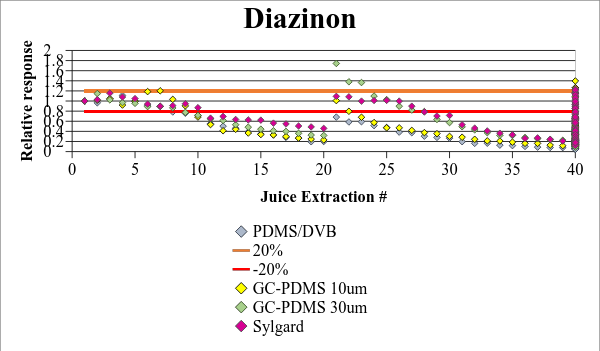
*Figure S6 - 2,6-Dinitrotoluene: reusability profile of coatings subjected to 40 DI-SPME in Concord grape juice.*



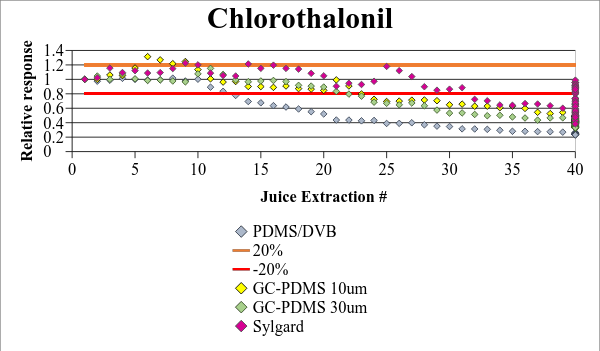
*Figure S7 - Trifluralin: reusability profile of coatings subjected to 40 DI-SPME in Concord grape juice.*



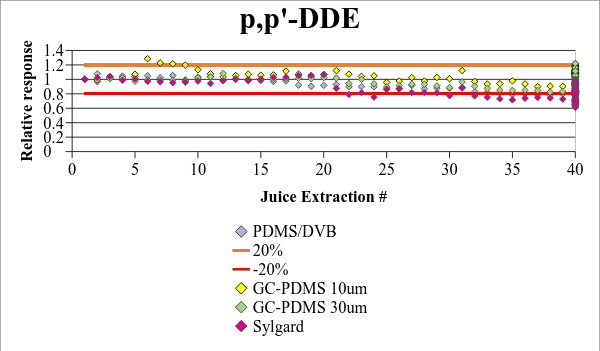
*Figure S8 - 4-Phenylphenol: reusability profile of coatings subjected to 40 DI-SPME in Concord grape juice.*



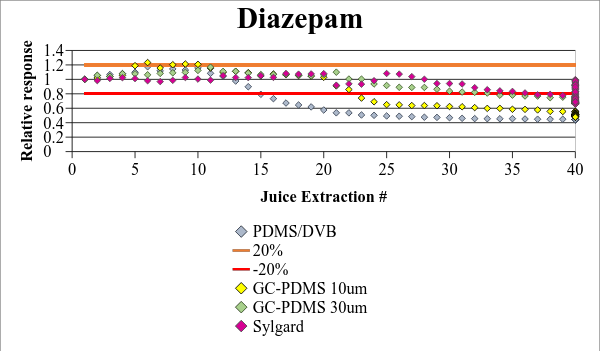
*Figure S9 - Diazinon: reusability profile of coatings subjected to 40 DI-SPME in Concord grape juice.*



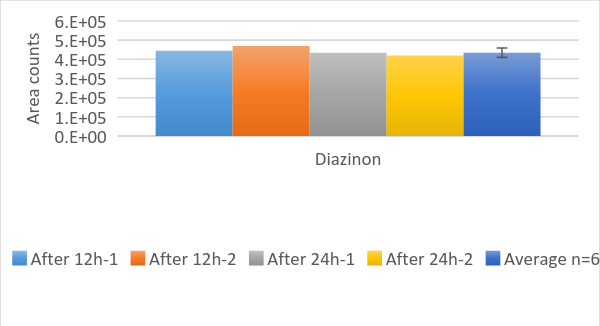
*Figure S10 - Chlorothalonil: reusability profile of coatings subjected to 40 DI-SPME in Concord grape juice.*



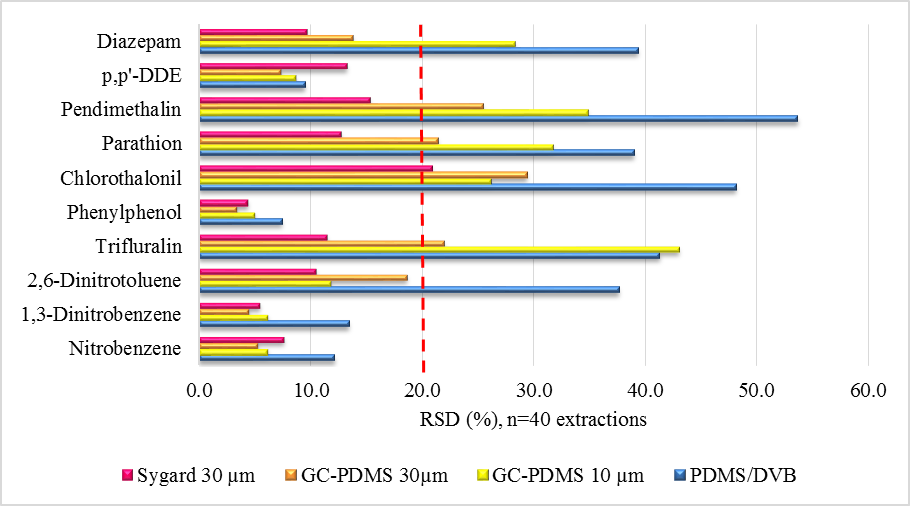
*Figure S11 - p,p'-DDE: reusability profile of coatings subjected to 40 DI-SPME in Concord grape juice.*



*Figure S12 - Diazepam: reusability profile of coatings subjected to 40 DI-SPME in Concord grape juice.*

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*Figure S13 - Diazinon stability test in water matrix.*



*Figure S14 - Comparison of RSDs throughout 40 extractions in grape juice sample.*

*Table S2 - Intra-fiber: paired two samples for means (for each fiber, comparing the first 20 and last 20 extractions).*

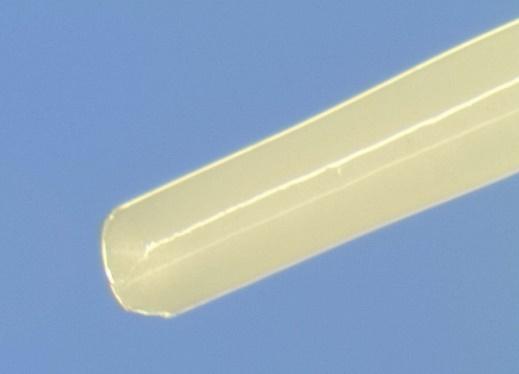
|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Paired t-test for means** | | | | |
|  | ***PDMS/DVB*** | ***GC-PDMS 30µm*** | ***GC-PDMS***  ***10 µm*** | ***Sylgard 30 µm*** |
| **Nitrobenzene** | No | No | Yes | Yes |
| **1,3-Dinitrobenzene** | No | No | No | Yes |
| **2,6-Dinitrotoluene** | No | No | No | Yes |
| **Trifluralin** | No | No | No | Yes |
| **4-Phenylphenol** | No | No | No | Yes |
| **Chlorothalonil** | No | No | No | No |
| **Parathion** | No | No | No | No |
| **Pendimethalin** | No | No | No | No |
| **p,p’-DDE** | No | Yes | Yes | No |
| **Diazepam** | No | No | No | No |

*Table S3 - Inter-fiber: two-sample assuming unequal or equal variances (n=100, except PDMS/DVB n=60)).*

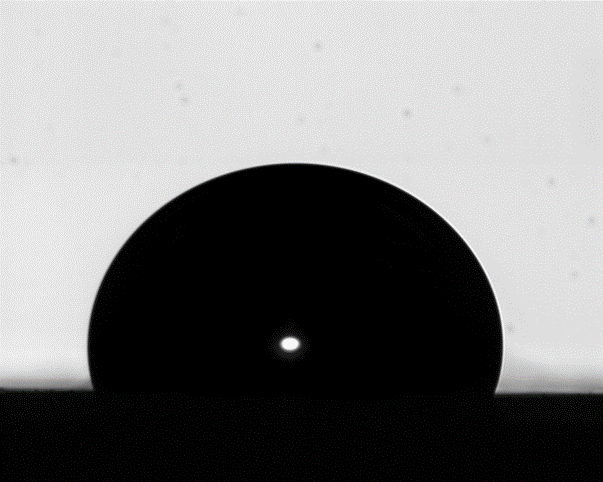
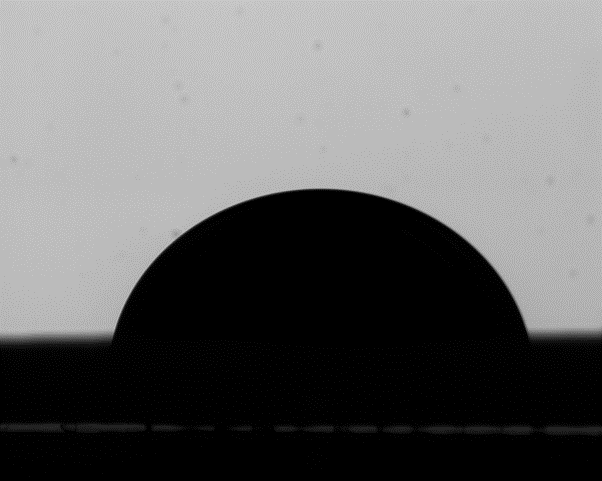
|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Two sample t-test** | | | | | | |
|  | ***Syl/***  ***GC30µm*** | ***Syl/***  ***GC10µm*** | ***Syl/***  ***PDMS/DVB*** | ***GC30µm/***  ***PDMS/DVB*** | ***GC10µm/***  ***PDMS/DVB*** | ***GC30µm/***  ***GC10µm*** |
| **Nitrobenzene** | No | No | No | No | No | Yes |
| **1,3-Dinitrobenzene** | No | No | No | No | No | No |
| **2,6-Dinitrotoluene** | No | No | No | Yes | Yes | Yes |
| **Trifluralin** | No | No | No | No | No | Yes |
| **4-Phenylphenol** | No | No | No | Yes | Yes | Yes |
| **Chlorothalonil** | No | No | No | No | No | Yes |
| **Parathion** | No | No | No | No | No | No |
| **Pendimethalin** | No | No | No | No | No | Yes |
| **p,p’-DDE** | No | No | No | No | No | No |
| **Diazepam** | Yes | No | No | No | Yes | No |



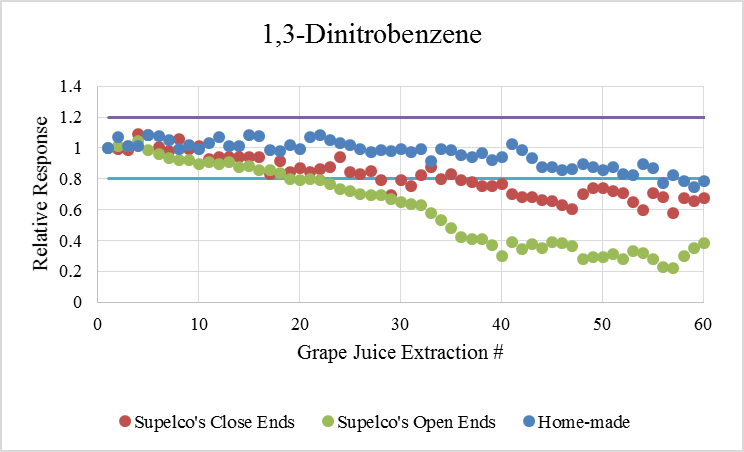
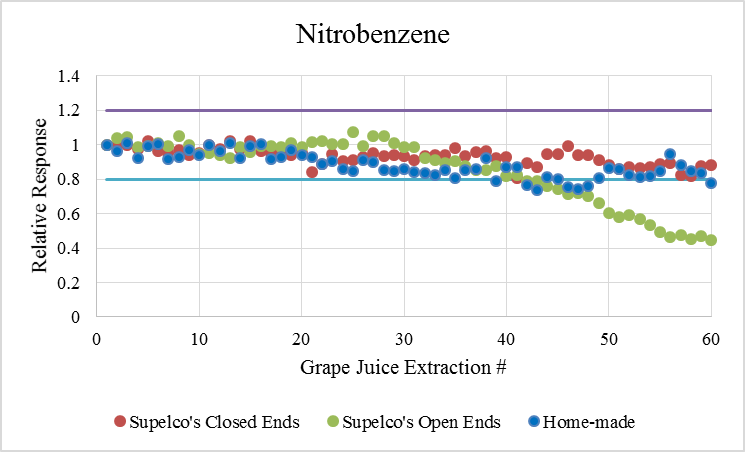
*Figure S15 - Microscopic pictures of coatings after 60 extractions in grape juice.*

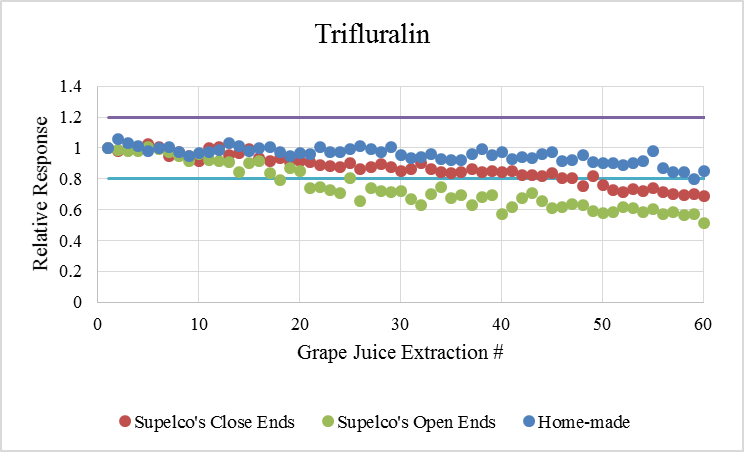
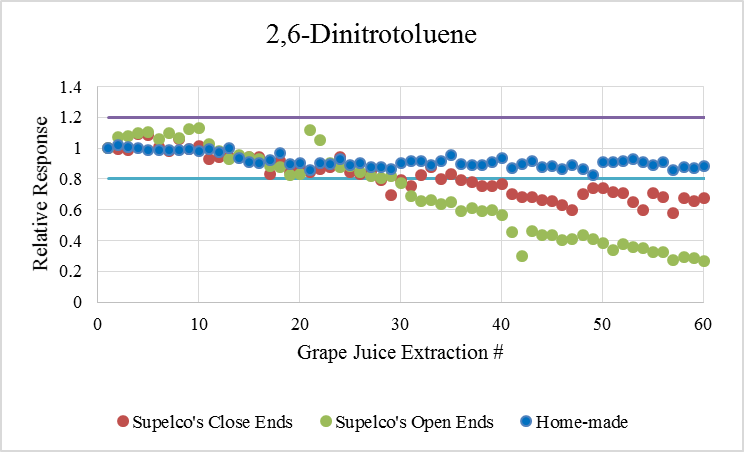
 

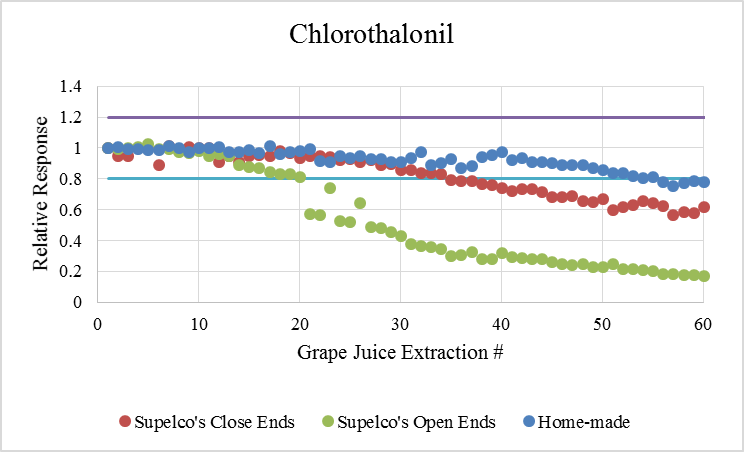
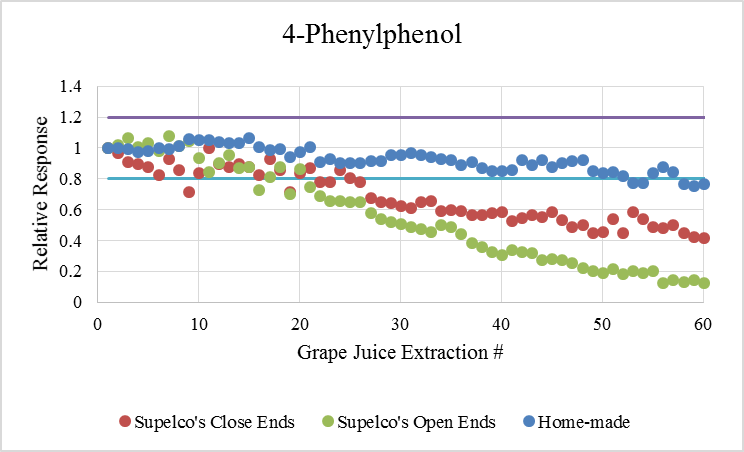
*Figure S16 - Overcoated fiber tips.*

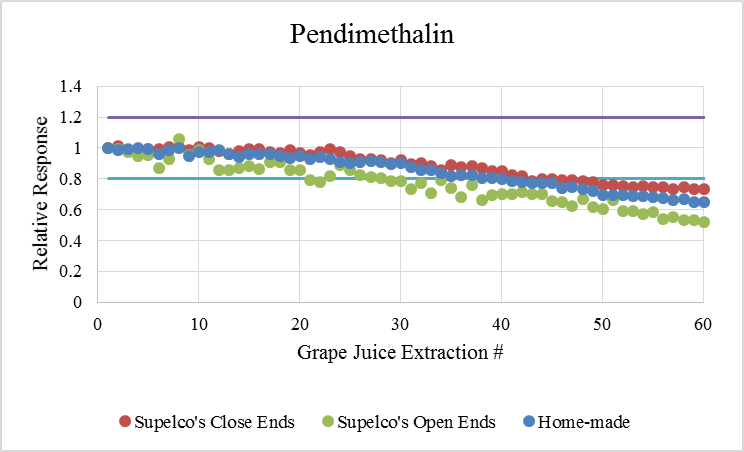
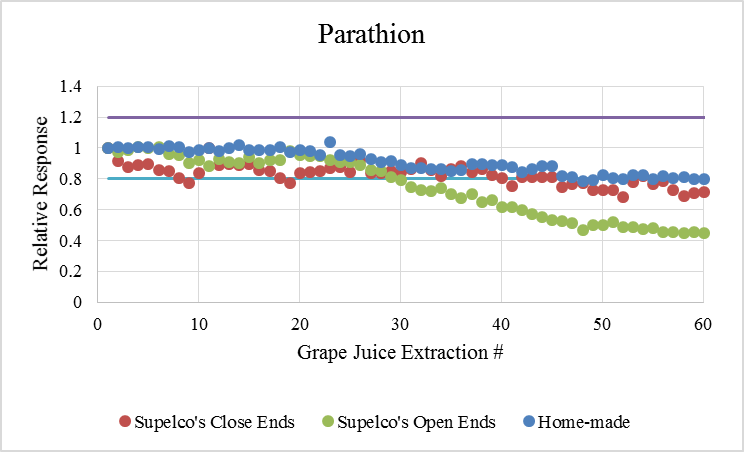
 

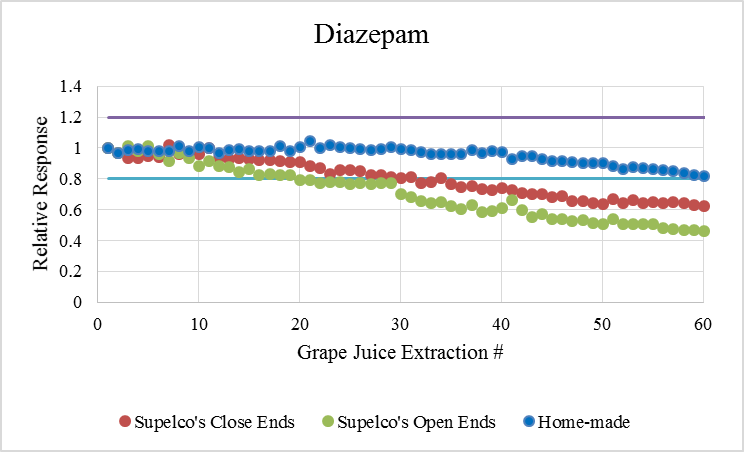
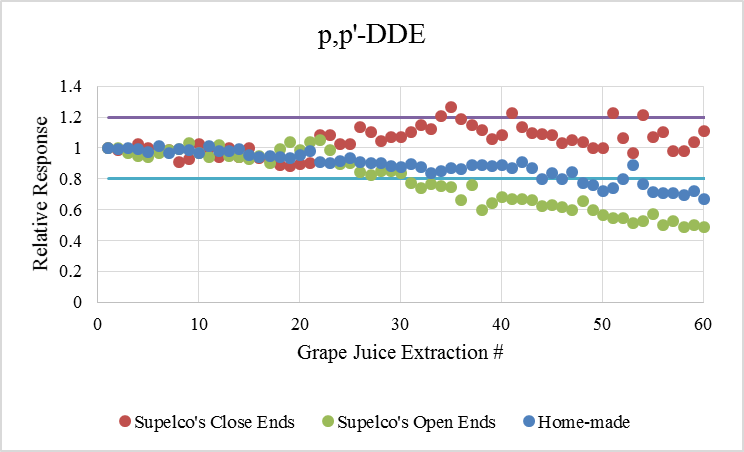
*Figure S17 – Water contact angle images for both types of PDMS obtained by measuring the contact angle of 30 µL water drops according to the sessile drop method. Images were acquired every 2 s over a 10 min period, and repeated three times. Contact angle measurements were collected using Axisymmetric Drop Shape Analysis (ADSA).*



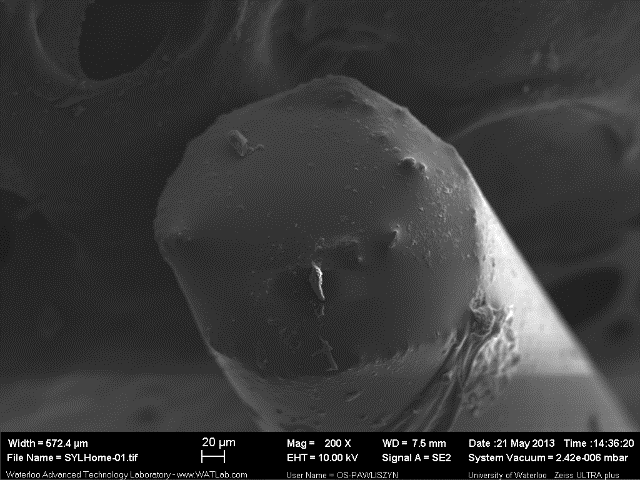
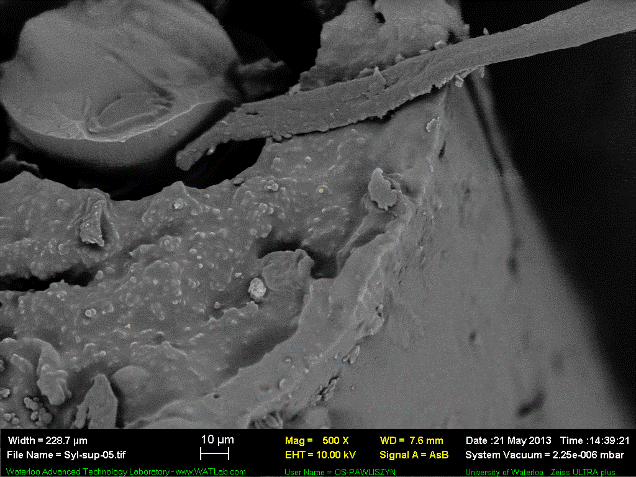




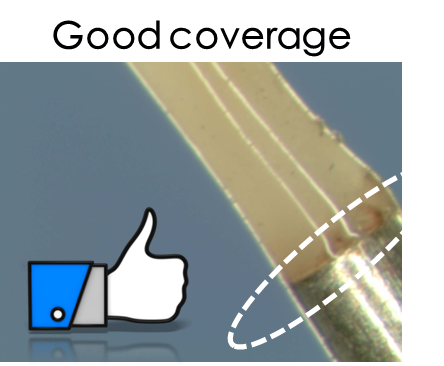




*Figure S18 - Reusability profile of coatings subjected to 60 DI-SPME in Concord grape juice.*

*Figure S19 - SEM images of the PDMS-modified coatings: (A) Sylgard sealed end 200x magnification; (B) Partially sealed GC-PDMS end using 500x magnification.*



*Figure S20 - Pictures depicting an effective PDMS overcoating of coating/metal junction.*