**Supporting Information**

**for**

# "A micro-solid phase extraction in glass pipette packed with amino-functionalized silica for rapid analysis of petroleum acids in crude oils"

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**Figure S1.** Photographic image of the glass pipette micro-SPE device.

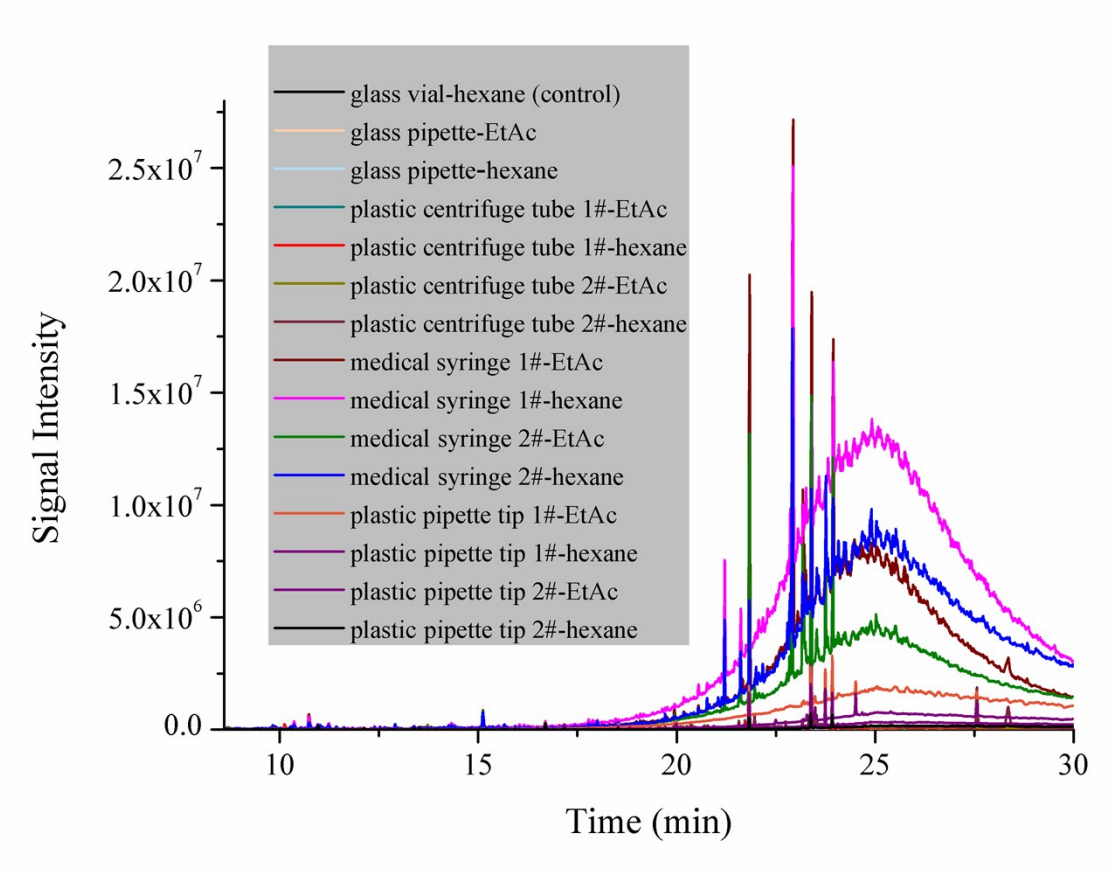



**Figure S2.** Total ion chromatograms of solutions obtained from washing different vessels with ethyl acetate (EtAc) or hexane followed by derivatization with MTBSTFA. The names of different groups were defined as "vessel-solvent". For instance, "glass pipette-EtAc" represents the result produced by washing glass pipette with EtAc. The marks "1#" and "2#" represent different manufacturers.

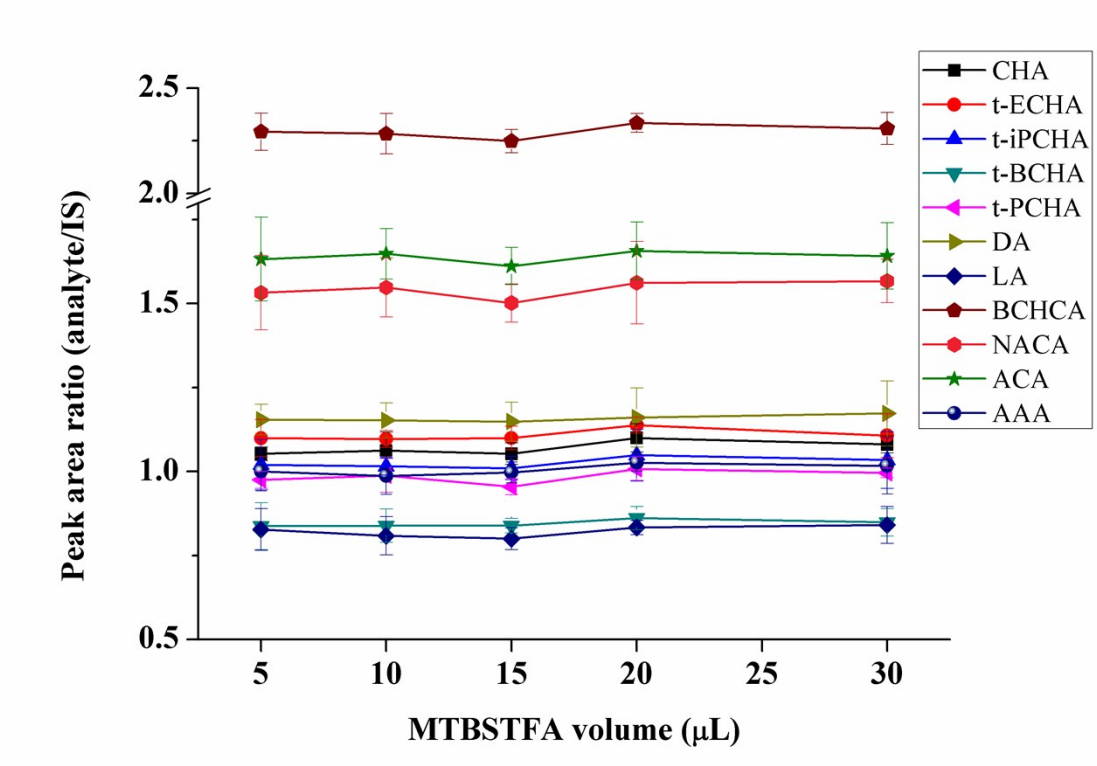



**Figure S3.** Effect of volume of MTBSTFA on derivatization efficiency in TFA/EtAc (1/99, v/v).

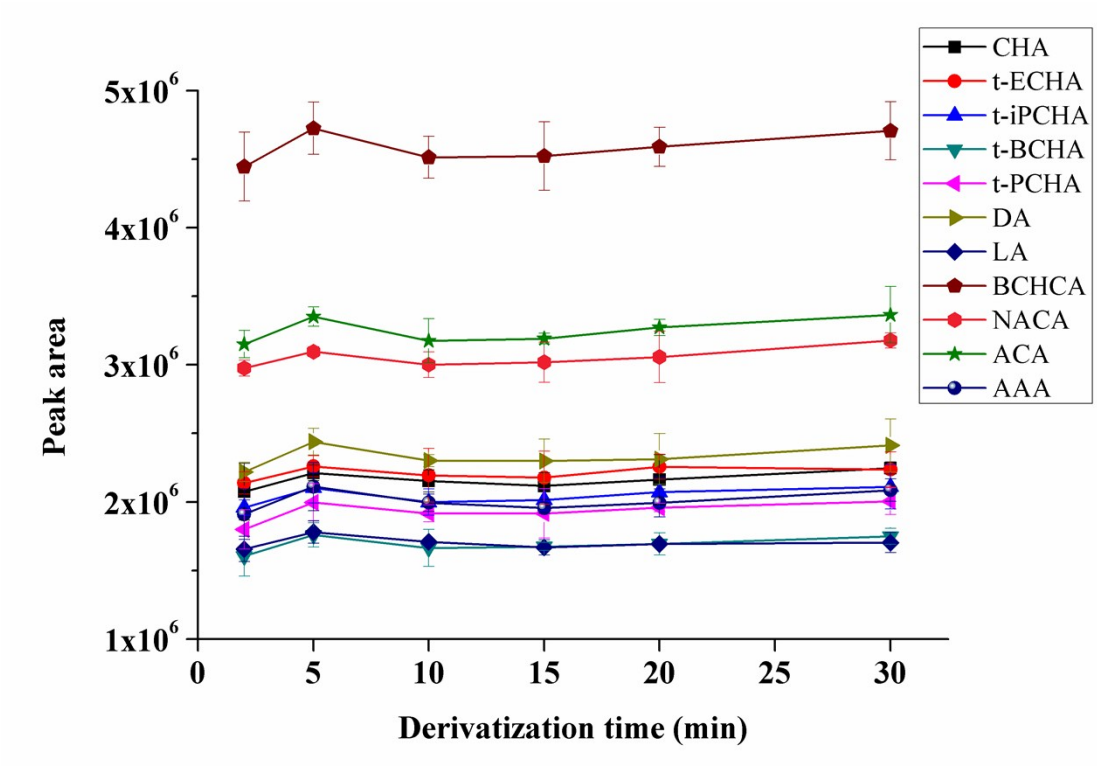



**Figure S4.** Effect of reaction time on derivatization efficiency.

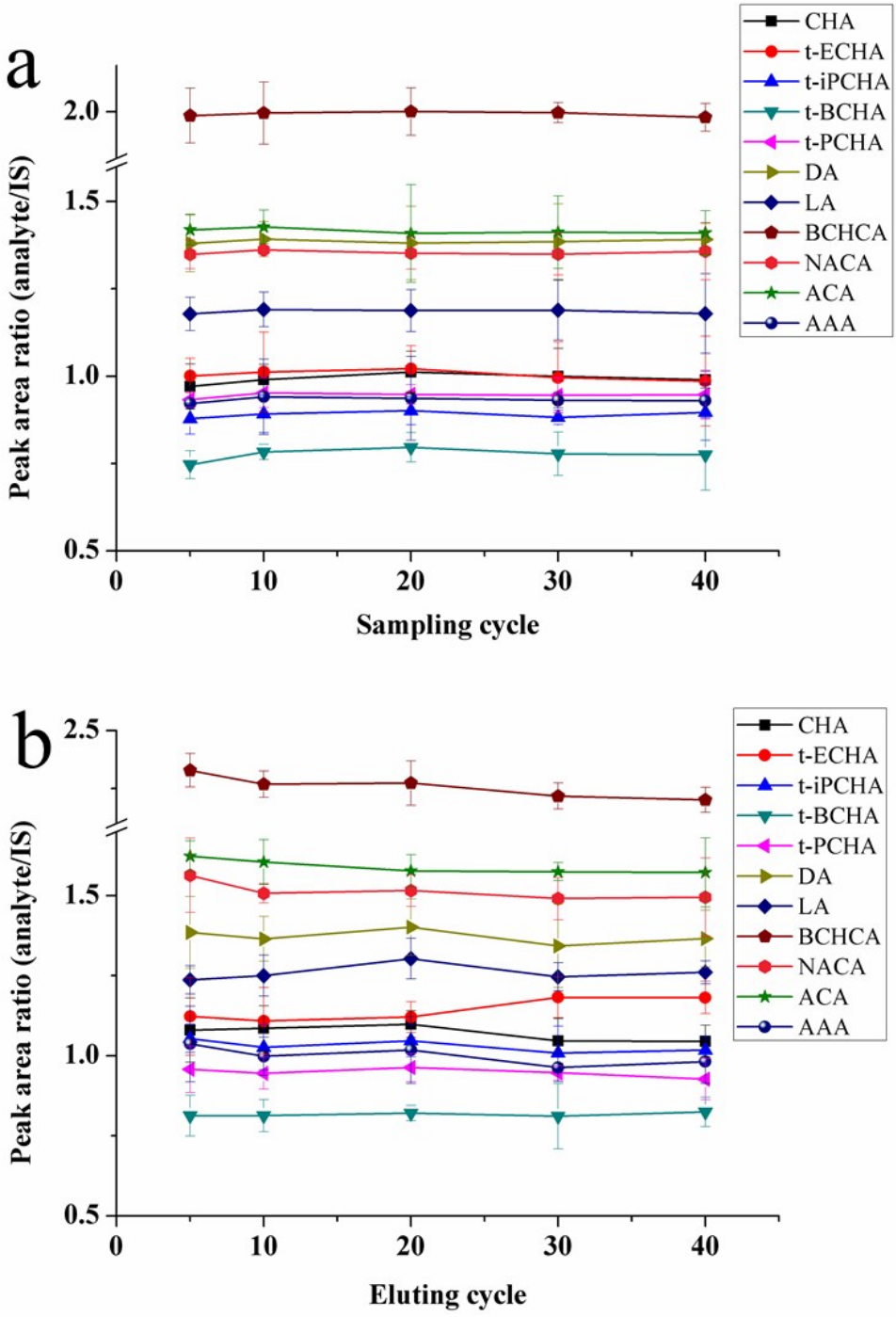



**Figure S5.** Effect of sampling cycle (a) and eluting cycle (b) on extraction efficiency.

**Table S1.** Chemical structures, molecular weights (Mw), retention times ($t_R$) and target ions for the GC-MS analysis of the petroleum acids after derivatization.

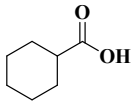
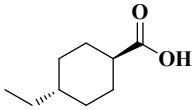
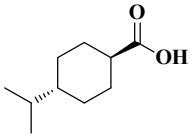
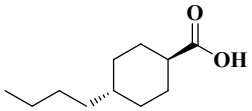
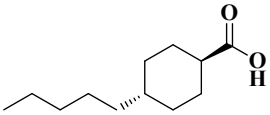
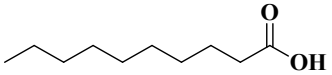
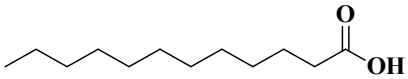
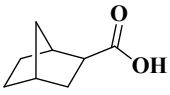
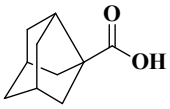
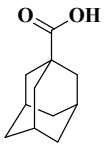
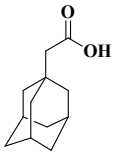
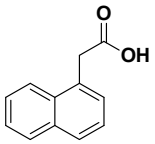
| Analytes | Chemical structure | Mw | $t_R$ | Quantifier (m/z) |
|---|---|---|---|---|
| CHA |  | 128 | 9.39 | 185 |
| t-ECHA |  | 156 | 12.70 | 213 |
| t-iPCHA |  | 170 | 14.48 | 227 |
| t-BCHA |  | 184 | 16.34 | 241 |
| t-PCHA |  | 198 | 18.00 | 255 |
| DA |  | 172 | 13.99 | 229 |
| LA |  | 200 | 17.46 | 257 |
| BCHCA |  | 140 | 10.89 | 197 |
| NACA |  | 166 | 14.13 | 223 |
| ACA |  | 180 | 16.62 | 237 |
| AAA |  | 194 | 18.19 | 251 |
| NAA (IS) |  | 186 | 19.05 | 243 |

**Table S2.** Peak areas of detected hexadecanoic acid and octadecanoic acid after derivatization.

| | Peak Area ($10^6$) | |
|---|---|---|
| | Hexadecanoic Acid | Octadecanoic Acid |
| glass vial-hexane (control) | 0.56 | 0.28 |
| glass pipette-EtAc | 0.75 | 0.33 |
| glass pipette-hexane | 0.49 | 0.24 |
| plastic centrifuge tube 1#-EtAc | 269.23 | 292.63 |
| plastic centrifuge tube 1#-hexane | 238.21 | 268.43 |
| plastic centrifuge tube 2#-EtAc | 1032.18 | 787.38 |
| plastic centrifuge tube 2#-hexane | 911.45 | 766.48 |
| medical syringe 1#-EtAc | 1379.70 | 1085.12 |
| medical syringe 1#-hexane | 289.35 | 374.50 |
| medical syringe 2#-EtAc | 805.72 | 788.52 |
| medical syringe 2#-hexane | 223.04 | 328.70 |
| plastic pipette tip 1#-EtAc | 72.04 | 88.50 |
| plastic pipette tip 1#-hexane | 78.69 | 88.07 |
| plastic pipette tip 2#-EtAc | 57.83 | 52.44 |
| plastic pipette tip 2#-hexane | 27.45 | 32.97 |

The names of different groups were defined as “vessel-solvent”. For instance, “glass pipette-EtAc” represents the result produced by washing glass pipette with ethyl acetate. The marks “1#” and “2#” represent different manufacturers.

**Table S3.** Recoveries of petroleum acids in crude oil with the micro-SPE method.

| | CHA | t-ECHA | t-iPCHA | t-BCHA | t-PCHA | DA | LA | BCHCA | NACA | ACA | AAA |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Recovery | 76 | 83 | 84 | 91 | 89 | 74 | 89 | 76 | 79 | 83 | 92 |
| (RSD, %; n=5) | (5.4) | (3.8) | (6.3) | (5.9) | (4.2) | (4.8) | (6.1) | (3.4) | (2.9) | (5.7) | (5.6) |

**Table S4.** Calibration curves, LODs and LOQs of petroleum acids.

| Analytes | Linear dynamic range (ng/g) | Regression line | | | LODs (ng/g) | LOQs (ng/g) |
|---|---|---|---|---|---|---|
| | | Slope | Intercept | *R* value | | |
| CHA | 20-5000 | 0.0010 | -0.0063 | 0.9998 | 6 | 20 |
| t-ECHA | 10-5000 | 0.0011 | -0.0033 | 0.9993 | 3 | 9 |
| t-iPCHA | 10-5000 | 0.0010 | -0.0051 | 0.9994 | 3 | 10 |
| t-BCHA | 10-5000 | 0.0009 | -0.0038 | 0.9997 | 2 | 7 |
| t-PCHA | 10-5000 | 0.0011 | -0.0046 | 0.9986 | 3 | 10 |
| DA | 10-5000 | 0.0012 | 0.0038 | 0.9996 | 2 | 7 |
| LA | 10-5000 | 0.0010 | 0.0014 | 0.9991 | 2 | 6 |
| BCHCA | 10-5000 | 0.0020 | 0.0062 | 0.9984 | 3 | 9 |
| NACA | 10-5000 | 0.0014 | 0.0176 | 0.9983 | 3 | 9 |
| ACA | 10-5000 | 0.0015 | 0.0132 | 0.9997 | 3 | 10 |
| AAA | 10-5000 | 0.0010 | 0.0006 | 0.9993 | 3 | 10 |