Rapid LC-MS/MS quantification of Organophosphate non-specific Metabolites in Hair Using Alkaline Extraction Approach

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Table S1: Different simplified procedures to determine DAPs in human hair

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| --- | --- | --- | --- | --- | --- | --- |
| Compound(s) | External decontamination | Extraction procedure | Purification | Derivatization | Instrument analysis | References |
| DMP, DMTP, DEP | Wash with water and then methanol | 5mL of water, sonicate for 1 hour, shake for 12 hour. Get supernatant, add 5g NaCl, 1ml of HCl (6mol/L), 50mg of Na2S2O5 and 5mL of diethyl:acetonitrile (1:1 v/v) (two times). The concentrated extract was subjected to derivatization. | Pass extracts through solid phase of 3g florisil, 1g of bondesil-PSA and 0.5 g of anhydrous sodium sulfate. Wash with 5mL of acetone:n-hexane (2:98, v/v). Elute with 5mL of acetone: n-hexane (15:85, v/v). | PFBBr | GC/MS | Margariti et al[15] |
| DMP, DEP, DETP, DEDTP | Wash twice with water and then methanol |  2mL of methanol for 50mg hair; incubate in an ultrasonic bath for 4hrs, centrifuge. The supernatant was filtered before derivatization step. Derivatized extracts were concentrated and reconstituted in toluene. | No | PFBBr | GC/MS | Tsatsakis et al[18] |
| DMP, DMTP, DMDTP, DEP, DETP, DEDTP, and others | Wash with water and then acetonitrile | 1mL of acetonitrile/water (80:20) and shake overnight at 40C. The mixture was centrifuged. 300µL of supernatant was evaporated, then derivatized. The derivatized solution was concentrated and reconstituted in ethyl acetate.  | The solution was centrifuged to remove particles. Transferred this solution to a vial, repeat concentration step to dryness and reconstitute the solution into 20µL of ethyl acetate. | PFBBr | GC/MS | Hardy et al [16] |
| DMP, DMTP, DMDTP, DEP, DETP, DEDTP | Wash twice with water and then methanol | 1mL of 2% NH4OH in methanol ,; shake overnight at room temperature; sonicate in a water bath at 40°C for 1 hour. Take out 0.6mL of extract. Concentrate the extract to dryness. Reconstitute in 150µL of methanol.  | Centrifuge the solution to remove the solid and particles. Transferred the extract to filter vials.  | no | LC-MS/MSESI(-) | This study |

Table S2: Comparing limit of detection LOD (pg/mg) of different hair analysis methods. Our current method provides satisfactory sensitivity.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | This study | [18] |  [16] | [15] |
| DMP | 0.82 | 6 | 0.5 | 100 |
| DMTP | 0.41 | 5 | 0.5 | 100 |
| DMDTP | 0.3 | 5 | 1.3 | - |
| DEP | 0.24 | 3 | 5.5 | 20 |
| DETP | 0.24 | - | 1.5 | - |
| DEDTP | 0.23 | - | - | - |

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| Figure S1: Extracted ion chromatogram MRM of DAPs their corresponding labeled internal standards |
| Table 2: Method validation data for DAPs |
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| --- | --- | --- | --- | --- | --- | --- | --- |
| Analytes | R2 of calibration curve | LOD (pg/mg)(S/N= 3) | LOQ (pg/mg)(S/N= 10) | Extraction efficiency | Intra-day precision(n=2) | Inter-day precision(n=4) | Accuracy |
|  |  |  |  |  |  |  | 0.1 ng/mg | 0.2 ng/mg |
| DMP | 0.998 | 0.82 | 2.46 | 113 | 5 | 24 | 108 | 111 |
| DMTP | 0.994 | 0.41 | 1.23 | 89 | 7 | 13 | 106 | 111 |
| DMDTP | 0.997 | 0.30 | 0.9 | 152 | 9 | 10 | 111 | 109 |
| DEP | 0.999 | 0.24 | 0.72 | 86 | 6 | 12 | 111 | 115 |
| DETP | 0.999 | 0.24 | 0.72 | 92 | 5 | 11 | 111 | 106 |
| DEDTP | 0.999 | 0.23 | 0.69 | 72 | 0 | 19 | 101 | 108 |

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