Implementation of new Fast-GC-MS and UHPLC-MS/MS data in a conventional GC-MS database for heroin profiling

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Introduction: Classical databases used to profile heroin samples are actually fed with GC-MS data. Despite its ability to obtain suitable results for the classification of heroin samples and the establishment of chemical similarity [1], this chromatographic technique could be time-consuming and not available in all laboratories.

Objectives: The aims of the study were, firstly, to optimize the separation and detection of the relevant components for classification of heroin samples. Secondly, to shorten the GC-MS analysis time thanks to design of experiment methodology (Fast-GC). Thirdly, to use alternative fast chromatographic techniques, such as UHPLC, for the analysis of heroin samples after optimisation with dedicated modelling software (Osiris). Moreover, three ionisation modes (ESI, APCI and APPI) were tested to maximize sensitivity. In this work, a particular attention was paid to the development of generic chemometric strategies (mathematical models) to convert data afforded by any other analytical technique to compare with the results obtained with the classical GC-MS.

Method: The selected variables are the normalized area of specific fragments of six alkaloids co-extracted from opium with heroin. These alkaloids are meconin, acetylcodeine, acetylthebaol, 6-monoacetylmorphine, papaverin and noscapin. In GC and Fast-GC, the street seized heroin samples were derivatized with MSTFA. In UHPLC, the samples were just dissolved into hydro-organic mixture. Seven multi-linear regressions (MLR) were evaluated and used for comparison purpose.

Results: Using the chemometric strategy of experimental design, the original GC-MS method of 30 min was shortened to less than 5 min in fast-GC-MS. While correlations between the variables (peak area) coming from Fast-GC and GC were acceptable, a conversion factor (MLR) was mandatory to implement the original database with Fast-GC-MS values. The quadratic transfer models were able to transfer 95% of the heroin samples, recorded in Fast-GC, in the GC database. Concerning UHPLC, electrospray ionisation (ESI) was found to be the most adapted for a sensitive detection of the above mentioned compounds. The optimal conditions (gradient of 4.8 min of methanol from 5 to 95% with ammonium formate 10mM pH9 buffer on a BEH Shield RP18) allowed a separation in less than 4 min. and can also provide results which can be added to the original database after data correction using multi linear regression. With UHPLC, the simplified full model (the terms of the mathematical model are selected with a Pareto analysis) was the most adequate model for transfer and offers a predictive ability of 82%.

Conclusions: Using those strategies, analysis times were reduced down to 5 min and the time devoted to derivatization (mandatory for GC-MS and Fast-GC) could be avoided with the help of liquid based separation techniques. The respective mathematical models give a predictive ability of 95% and 82% for Fast-GC and UHPLC, respectively. Finally, the time needed to establish the chemical similarity between heroin samples is now shorter and give the opportunity to the forensic scientist to play a deeper role with the investigators.

References:

[1] Guéniat O. and Esseiva P., Heroin and cocain profiling, 1st Edition, 2005, Lausanne.