Recent Advances in the Analytical Chemistry of Cadaveric Decomposition

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In forensic sciences, cadaveric decomposition has been and still is a topic of high interest as the study of the volatilome related to death can be supportive to various types of investigations [1]. Indeed, the volatile profile of decaying bodies is so wide that subtle differences can be expected based on the context of the death [2]. To highlight such differences in the volatile organic compound (VOC) fingerprints, there is a need for powerful separation science tools supported by integrated solutions allowing to robustly screen samples [3]. Comprehensive two-dimensional gas chromatography coupled to high resolution time-of-flight mass spectrometry (GCxGC-HRTOFMS) is one of the most potent tool in that area [4]. However, because of the overall resolution power of the technique relying on enhanced peak capacity of GCxGC, deconvolution of MS signals, and high mass accuracy, very large and complex data sets are routinely produced and require the development of computing tools for automated data processing prior to any relevant usage.

In that context, in order to ensure the production of reliable results for decision making, it is of prime importance to optimize and apply stringent QA/QC criteria to each step of the analytical process. The use of central composite design is, for example, a method of choice to establish optimal analytical conditions for solid-phase microextration (SPME) and thermal desorption (TD), where peak intensities can be used as a quality metric versus the fiber/adsorbent type, incubation/loading time, flows, and temperatures as variable parameters. For the GC×GC-TOFMS, there is no properly defined quality metrics. Peak dispersion and chromatographic space occupation can be used versus the temperature ramp and the carrier gas flow. Different mass spectra screening scripts can also be developed in order to automatically remove contaminants, such as plasticizers and siloxanes emitted by the sorbents and columns to provide clean data sets for feature selection.

As part of data processing, and because untargeted screening relies on the relative quantification, a proper normalization is required prior to any data mining. Z-score and probabilistic quotient normalization are often the two best performing approaches for GC×GC-TOFMS, depending on the level of control on sampling methods. Pearson and Spearman correlation, as well as unsupervised principal component analysis, can be used to evaluate the normalization efficiency.

Finally, different approaches can be compared for feature selection and information extraction. A widely used approach in the field is based on Fisher Ratio calculation. This univariate method relieson the ratio between variances, as for an ANOVA. Another approach uses machine learning like Random Forest. At the end, sample clustering is used to evaluate the efficiency of the different approaches.

Globally, all these steps allow the proper data handling of complex GC×GC-TOFMS forensic data. This will be illustrated over selected examples where the volatilome of tissue decomposition has been studied.

References

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