Variable-energy electron ionization for blood VOC profiling

Lena M. Dubois[a], Katelynn A. Perrault[b], Pierre-Hugues Stefanuto[a], Jean-François Focant[a]

[a] Organic and Biological Analytical Chemistry Group, University of Liège, Liège, Belgium
[b] Forensic Sciences Unit, Chaminade University of Honolulu, Honolulu, HI USA

The detection of blood at a crime scene can provide critical information about the nature of events that occurred, the order of events, and possibly the identity of the individuals involved. Therefore, the detection of blood has always been an important aspect of forensic investigations. Establishing an accurate volatile organic compound (VOC) profile of blood can assist with developing and improving existing forensic methods to locate blood. This can be relevant at a crime scene or may also apply to the search for living and deceased individuals using scent detection canines or portable detection devices. In recent years, the possibility to train scent detection canines on blood has become more popular by forensic agencies. In order to provide more information about such applications, comprehensive two-dimensional gas chromatography (GC×GC) coupled to time-of-flight mass spectrometry (TOFMS) has been proposed as a novel analytical tool that can increase the ability to separate and identify blood VOCs. The introduction of new analytical approaches and technological developments requires the critical assessment of instrumental parameters and their combination. Mass spectrometric detection was performed using electron impact ionization (EI) carried out at 70 eV and lower energies (12, 14, and 16 eV). The use of variable-energy (ve) EI allowed mass spectra to be produced with less fragmentation and an increased presence of structurally significant ions and the molecular ion. This provided additional confidence in peak assignments, especially for closely eluting isomers often observed in the profiling of the headspace of blood. Variable-energy EI TD-GC×GC-TOFMS blood data sets were statistically processed using principal component analyses (PCA) and hierarchical cluster analyses (HCA). These techniques demonstrated that the effect of aging was greater than the inter-individual variation on the blood VOC profile. The combination of retention indices, low and high EI MS spectra served as a strong basis to gain more confidence in analytical identification by excluding identities proposed by mass spectral databases (70 eV) for compounds contributing to the separation of blood of different ages which will assist in developing forensic search methods for blood and victims of mass disasters or homicide. The results demonstrated that by taking advantage of a broad array of instrument technical capabilities, blood VOC analysis will be able to reach its full potential in the future and contribute to practical advancements in the forensic sciences.