B143 The Estimation of True Compositions of Volatile Compounds in Headspace Via Solid Phase Microextraction (HS/SPME) and Inverse Gas Chromatography (IGC)

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Learning Overview: The goal of this presentation is to demonstrate a strategy of the estimation of true compositions of volatile compounds in headspace via solid phase microextraction (HS-SPME) and inverse gas chromatography (IGC). The compositions of volatile compounds in headspace (HS) analyzed by a solid phase microextraction (SPME) sampling method usually differ from true compositions mainly because the partition coefficients for these compounds between headspace and a SPME fiber are not equal. In this presentation, the author reports an analytical strategy to more accurately quantify relative compositions of selected hydrocarbons present in gasoline residue by employing inverse gas chromatography (IGC) coupled with a HS-SPME sampling method.

Impact on the Forensic Science Community: This presentation will impact the forensic science community by proposing a way to estimate true compositions of target compounds in headspace as well as solid substrates using partition coefficients obtained via inverse gas chromatography (IGC). The results produced in this work and future studies can be applied to the quantification of target volatile/semi-volatile compounds in various forensic samples including fabric, cardboard, and carpet.

Headspace concentration method, coupled with solid phase microextraction (HS-SPME), provides an easy and convenient sampling method for analyzing volatile/semi-volatile compounds such as gasoline residues present in solid samples. Compared to traditional sampling techniques such as passive headspace concentration with activated carbon and subsequent solvent extraction, it is a solvent-free sample preparation technique that integrates sampling, isolation, and concentration with enhanced sensitivity. Its simplicity of use, relatively short sample processing time, and fiber reusability have made SPME an attractive choice for many forensic analytical applications.

Despite its successful sampling from various solid substrates, a quantitative analysis of target compounds present in solid substrates via HS-SPME cannot be done in a straightforward manner. It is primarily because SPME fibers are not evenly sensitive to all target compounds in headspace. In addition, all compounds present in solid substrates do not equally diffuse into headspace. Thus, the relative peak areas in chromatograms via HS-SPME do not properly represent the true compositions of all compounds present in solid substrates. Both partition coefficients of volatile compounds at headspace/SPME and headspace/solid substrate are required to obtain true compositions of target compounds present in the solid substrate via HS-SPME.

In this work, an analytical strategy to more accurately quantify relative compositions of selected hydrocarbons present in three model headspace systems using estimated partition coefficients between headspace and a PDMS is presented. First, inverse gas chromatography measurements using a column packed with a solid support coated with polydimethylsiloxane (PDMS) were conducted to obtain the thermodynamic and chromatographic data needed for the estimation of the relative partition coefficients for *n*-heptane, toluene, and *1,2,4*-trimethylbenzene between headspace and a PDMS SPME fiber at 100°C and 130°C.

Then, three model headspace systems containing different compositions of vaporized *n*-heptane, toluene, and *1,2,4*-trimethylbenzene were prepared. Chemical analysis of these model headspace systems was conducted via a PDMS SPME sampling method at 100°C and 130°C. The true relative compositions of these vaporized compounds in three model headspace systems were estimated using compositions from a PDMS SPME sampling method and the relative partition coefficients from inverse gas chromatography. Estimated relative compositions were compared to true compositions which were obtained from direct headspace analysis. Except for the composition of *1,2,4*-trimethylbenzene in one model headspace at 100°C, the estimated compositions agree with experimental compositions within a relative error of less than 10%.

As presented in this work, inverse gas chromatography can provide an alternative way for the estimation of partition coefficients of volatile compounds at the solid/headspace interface which are critical for the quantification of the actual headspace compositions. Although only three vaporized components were used to establish model headspace for chemical analysis in this work, there is the ability to expand inverse gas chromatography measurements to more components to estimate partition coefficients at various solid/headspace interfaces. In addition, partition coefficients estimated via inverse gas chromatography measurements need to be validated under different experimental conditions such as the presence of more components with various quantities. The results produced in this work and future studies can be applied to the quantification of target compounds in various forensic samples. To achieve goal, inverse gas chromatographic measurements with columns packed by various materials such as fabric, cardboard, and carpet for more hydrocarbons are currently underway.

HS/SPME, Inverse Gas Chromatography, Partition Coefficient