B53 Preservation of Trace Compounds From Headspace Analysis in Adsorbent Capillaries

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Learning Overview: After attending this presentation, attendees will better understand the stability of gasoline-derived compounds captured by dynamic headspace sampling with alumina as the adsorbent. This presentation considers evidence stability as a function of storage conditions and storage interval to address situations in which evidence must be preserved prior to analysis (hours to days) or for re-analysis (weeks to months).

Impact on the Forensic Science Community: This presentation will impact the forensic science community by describing experimental and statistical methods to quantify the distribution of compounds captured by an adsorbent. These methods may support archival of forensic samples collected by headspace methods, including fire debris extracts, by providing quantitative evaluation of chromatogram reproducibility.

Headspace vapors are collected to extract trace compounds from complex solid matrices (e.g., fire debris) or in other situations where the solid or liquid under investigation cannot be directly analyzed. Static headspace sampling is appropriate for volatile compounds; headspace concentration must be employed for low-volatility compounds. The National Institute of Standards and Technology (NIST) has developed a dynamic headspace sampling method that utilizes alumina Porous Layer Open Tubular (PLOT) capillaries to concentrate headspace vapors. In this method, an inert carrier gas sweeps headspace vapors through the capillary, which can be cooled if needed, depending on the volatility or stability of the analyte(s), to promote adsorption. The capillaries can be eluted with solvent and analyzed by any analytical technique, typically Gas Chromatography with Mass Spectrometry (GC/MS).

PLOT dynamic headspace sampling was originally developed to identify compounds in the headspace of low-volatility explosives and has been successfully applied to the detection of gravesoil, among many other applications.[1,2] PLOT dynamic headspace sampling can be performed in the field with a portable briefcase-sized unit. The method detection limit has been determined for diesel fuel, and explosives- and gravesoil-related compounds have been detected inside a simulated shipping container.[3,4]

This report investigates the distribution of compounds recovered from alumina capillaries after storage in heat-sealed polyester/polyethylene laminate evidence bags. To generate large populations of nominally identical samples, individual headspace vials containing a known liquid sample were sampled with individual capillaries. The liquid sample was 50% weathered gasoline, which contains a variety of volatile compounds ranging from C_7 (e.g., toluene) to C_{11} (e.g., methylnaphthalene). The headspace vial was equilibrated in an oven at 60°C, and the cryostat containing the "trap" portion of the capillary was cooled to 0°C. Headspace vials were purged with carrier gas at 0.6mL/min, and the total collection volume was 1.5mL. Capillaries were heat sealed in evidence bags and randomly assigned to room temperature storage or refrigeration and to various storage intervals.

GC/MS analysis included total ion chromatograms and selected ion monitoring (m/z) for alkanes (57, 71, 85, 99), cycloalkanes (55, 69, 83), aromatics (91, 105, 119), indanes (117, 118, 131, 132), and polynuclear aromatics (128, 142, 156). Principal component analysis was applied to probe differences between time points and among samples from the same time point. The analyses investigated variations in the carbon number, carbon class, and total mass of retained compounds. Individual compounds were also monitored. These statistical methods quantitatively demonstrate the reproducibility of the collection method; however, after six weeks, room temperature storage leads to the loss of low molecular weight compounds. Furthermore, the samples lost compounds in a divergent manner. The methods described here can be used to evaluate any adsorbent material stored for any time period and should be applied to situations in which vapor samples must be collected in a field setting and preserved until analysis.

Reference(s):

1. Tara M. Lovestead and Thomas J. Bruno. Trace Headspace Sampling for Quantitative Analysis of Explosives with Cryoadsorption on Short Alumina PLOT Columns. *Analytical Chemistry* 82 (2010) 5,621–5,627.
2. Tara M. Lovestead and Thomas J. Bruno. Detecting Gravesoil with Cryoadsorption on Short Alumina PLOT Columns. *Forensic Science International* 204 (2011) 156–161.
3. Megan E. Harries, Santiago Bukovsky-Reyes, and Thomas J. Bruno. Field Portable Low Temperature Porous Layer Open Tubular (PLOT) Cryoadsorption Headspace Sampling and Analysis Part II: Applications. *Journal of Chromatography A* 1429 (2016) 72–78.
4. Megan E. Harries and Thomas J. Bruno. *Field Demonstration of Portable Headspace Sampling in a Simulated Cargo Container*. Submitted.

Fire Debris Analysis, Evidence Stability, Principal Component Analysis

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