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COMPARATIVE METHODS FOR THE TRACE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN COMPLEX ENVIRONMENTAL MATRICES

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ABSTRACT:
We have compared the analysis of trace level (nanograms per liter) volatile organic compounds on two types of automated laboratory preparatory instruments to present the possibility of their use in the development of methods to analyze difficult environmental matrices such as wastewater, soil, or animal tissues for those compounds. In addition to this comparison, we present general theory behind the performance of these methods. We note that while these methods are extremely sensitive when coupled to gas-chromatography/mass spectrometry (GC/MS) detectors used in the selective-ion monitoring (SIM) mode, they might still be affected by interferences from the laboratory environment.

KEY TERMS:
Volatile Organic Compounds, Environmental, Headspace Analysis, Solid Phase Micro-extraction, Dynamic Headspace

The volatile byproducts and process contaminants of wastewater treatment have long been analyzed under federal and state regulation by laboratories conducting drinking water analysis (Xie, 2003), but they have historically not been monitored or regulated in final effluent waste streams from treatment operations (Rostad, 2002). Due to their intrinsic volatility and hydrophobicity, they aren't generally regarded as problem contaminants for open bodies of surface water due to their tendency to rapidly partition from aqueous media into the atmosphere. Accordingly, wastewater treatment facilities often finalize treatment processes with chlorination, possibly generating and releasing volatile halogenated organic compounds into the environment through treated effluent (Jones, 2005). These compounds and other released volatile organic contaminants are unlikely to remain in the released aqueous media, but may quickly enter sludge, soils, or plant and animal tissues (Crosby, 1998). An area of current concern for environmental chemists is the fate of compounds in the effluents of wastewater treatment plants and the effects of those compounds (either individually or synergistically) on exposed biota.

Analysis of volatile organics (VOCs) by GC/MS (gas-chromatography/mass-spectrometry) at trace equilibrium levels in tissue samples or in complex matrices has often been a difficult task requiring either special sample handling techniques for purge-and-trap instrumentation or conventional headspace analysis, both of which can limit analysis to higher concentrations (parts-per-billion to parts-per-million levels). Since direct contact with the sample matrix often results in contamination of sensitive equipment or interference with the analytical result, headspace methods are preferred to purge-and-trap in our investigations of "dirty" matrices, but they have historically been regarded too insensitive for trace analysis. Headspace analytical methods are also excellent ways to speciate organic contaminants by their volatility and eliminate a large amount of analytical complexity in the MS signal. Newer technologies have overcome the obstacles presented by headspace analysis and commercial instrumentation has brought to it the robust features required for automated sample analysis (Kolb, 2006).

Two modern analytical techniques favor the analysis of volatile organic disinfection by-products and volatile water contaminants at trace (parts-per-trillion to parts-per billion) levels. Solid phase micro-extraction (SPME) is one technique of choice for the analysis of VOCs in difficult matrices. This methodology involves trapping volatile compounds in the analytical headspace of a sample vial within a thin polymeric film on the outside of a silica fiber. Analytes are adsorbed by the film and later desorbed into a heated GC inlet for quantitative or qualitative measurement by GC/MS. The relatively expensive robotic technology employed generally limits the technique to laboratories with extensive instrumentation budgets, but samples may be analyzed manually with a specialized syringe (Pawliszyn, 1997). Figure 1 is an example of volatile organic analysis performed in our laboratory in human blood using a SPME fiber.

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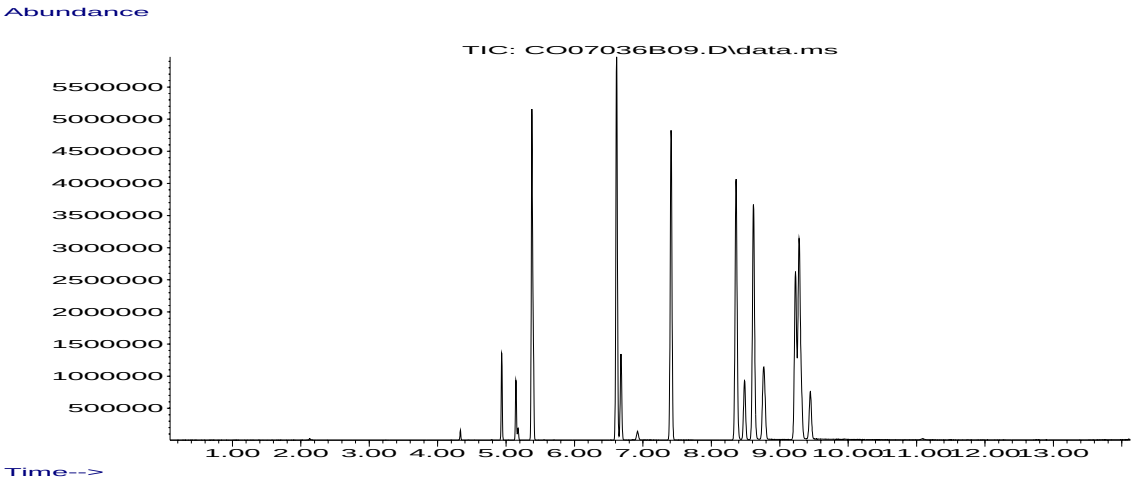

Figure 1. Analysis of a mixture of volatile organic compounds in human blood by GC/MS. This chromatogram indicates the analysis by a SPME-based instrument of a mixture fortified at 250 µg/L (parts-per-billion). Others have performed this analysis in the same manner with low parts-per-trillion level detection limits (Cardinali, 2000).

In contrast to SPME, dynamic trapped headspace technologies replace the trapping of volatile organic compounds with a trap similar to those used in purge-and-trap analysis. This instrumentation not only allows for a direct transfer of analytes concentrated over time from the headspace of the sample into the GC inlet via an airtight and chemically inert line, but also maintains the analytes of interest in a tightly concentrated area of the moving flow during the process (Markelov, 2002) In relation to analytical work in difficult matrices, dynamic headspace appears to offer the advantage of VOC separation without the requirement of the cryogenic cooling used in SPME, possibly offering cost-savings and a lower level of technical expertise required for instrumental operation. Our experiences with dynamic headspace equipment indicate that the parts-per-trillion level detection limits obtained by others using SPME are achievable at a reduced cost, and that comparable data quality may be realized. Figure 2 shows data from an analytical run performed by our laboratory in sheep's blood of a mixture of volatile organic compounds.

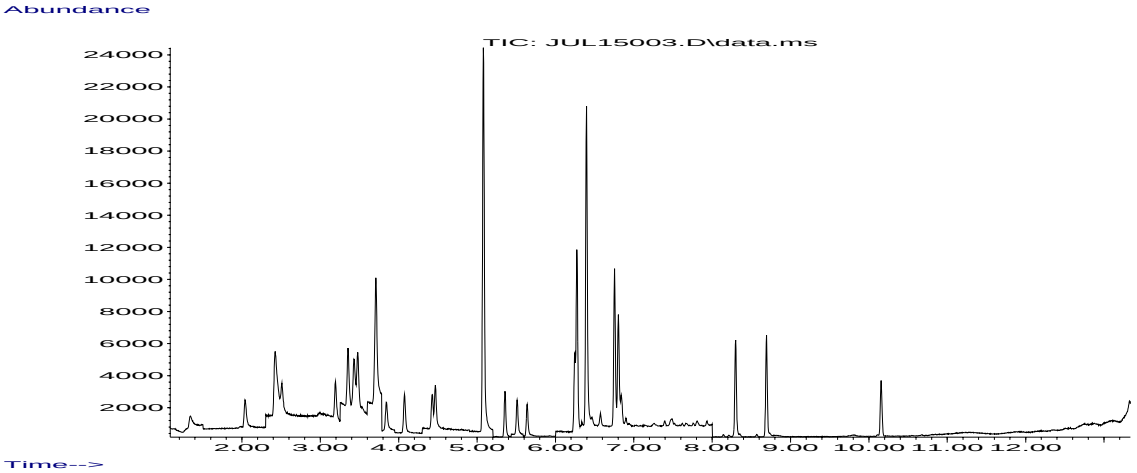

Figure 2. Analysis of a mixture of twenty-six volatile organic compounds in blood by dynamic headspace GC/MS. This chromatogram indicates the analytes at a trace level of 50 ng/L (parts-per-trillion).

In addition to the instrumentation used to prepare the sample for GC/MS analysis, special considerations need to be made in terms of the instrument parameters used to detect these compounds. Since instrument noise at extremely low levels can interfere with compound identification, analysts generally employ selective ion mode (SIM) detection, which limits the instrument to chosen masses, rather than scanning through a range. This does, however, reduce the amount of information available for compound identification. We have found, along with others, that SIM MS along with chromatographic resolution is sufficient to identify volatile species at trace levels (Cardinali, 2000).

As with any analytical methods that seek data at extremely low levels, instrument and laboratory background become concerns, especially with contaminants present in building materials, those used in solvent extractions, and those present at background levels in the external environment. We have attempted to reduce or eliminate some of these interferences by baking sample preparation materials at elevated temperatures in a vacuum oven, ultra-purifying water utilized in the analysis, and cleaning the air in the sample preparation area and hood with activated carbon filtration. These problems were identified in research by others and are likely to vary according to individual laboratory's levels of background contamination (Cardinali, 1994). As figure 3 indicates, analytes of interest are still found in blank samples at concentrations that might interfere with quantitative analysis.

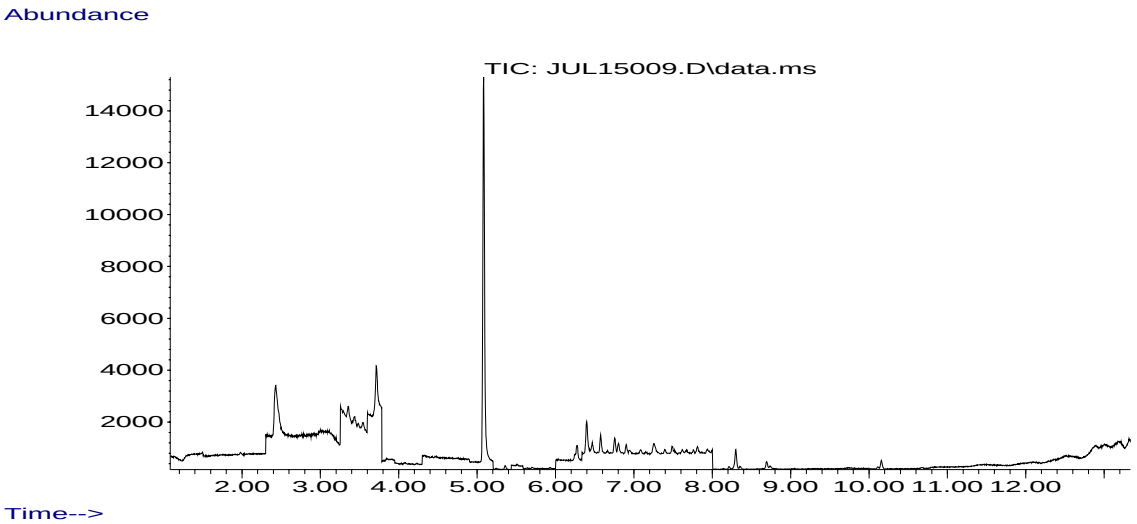

Figure 3. Blank contamination present in a sample analyzed by dynamic headspace. The large peak at 5 minutes on the chromatogram is toluene. Other contaminant peaks include methylene chloride, chloroform, carbon tetrachloride, benzene, and xylenes.

The purpose of this presentation is to compare the alternatives to a standard method of volatiles analysis that might prove useful in the trace-level evaluation of matrices that may have been considered too problematic to analyze. By offering an overview of the basic theoretical nature of both methods and comparing the chromatography obtained, we seek to educate on new possibilities of trace volatile analysis for environmental monitoring when matrix limitations need to be considered. We hope that a proper understanding of the technology available and the analytical possibilities might lead to further important discoveries in environmental chemistry and toxicology.

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