



Recovery of oxygenated ignitable liquids by zeolites, Part II: Dual-mode heated passive headspace extraction



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ABSTRACT

Previous studies performed by our research group have suggested that zeolites are a suitable adsorbent for the recovery of oxygenates from fire debris through heated passive headspace extraction. Zeolite 13X, in particular, has been shown to be effective for recovering analytes with molecular diameters smaller than 10 Å.

The primary aim of this study was to evaluate the addition of zeolite 13X to heated headspace extraction for the recovery of ignitable liquids. Comparative recoveries of petroleum and alcohol-based ignitable liquid mixtures were studied utilizing activated charcoal strips and zeolites, individually and in tandem. In the presence of both adsorption media within the same sample can, activated charcoal strips recovered the majority of gasoline components, while zeolites recovered the majority of oxygenated compounds. This phenomenon was attributed to the size exclusion properties, polarity, and available surface area of zeolites. This research supports the use of zeolites with activated charcoal strips in a “dual-mode” preparation for casework in which the presence of an ignitable liquid is suspected. The described method allows for the recovery and concentration of ignitable liquid residues in a single extraction procedure, whether the ignitable liquid is petroleum-based or oxygenated in nature.

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1. Introduction

Heated passive headspace concentration for the extraction of ignitable liquid residues (ILRs) from fire debris samples is a simple, sensitive, and nondestructive method that can often be performed within the original sample packaging. Activated charcoal strips, which do not interact with water or nitrogen, are typically used to adsorb ignitable liquid (IL) compounds as they have a high affinity for hydrocarbons and are resistant to oxidation. The technique is highly efficient for recovering petroleum-based ILs, however, it has had limited success with adsorbing and concentrating oxygenated species [1].

In 1991, Dietz outlined an optimized passive headspace technique [2]. Activated charcoal was placed inside sample containers and used to capture volatilized components of ILs as

they entered the container headspace. The charcoal was then desorbed in carbon disulfide (CS₂). Activated charcoal strips were effective in recovering a standard accelerant mixture composed of gasoline, kerosene, and diesel by heating for as little as an hour or storing at room temperature for 24 h. Examination of the effects of time, temperature, size of charcoal strip and concentration of sample were later performed to provide an optimal analysis scheme for the extraction of petroleum-based ILRs from fire debris samples [3]. Heated passive headspace continues to be the favored concentration method for ILRs from fire debris samples due to its ease, robustness, nondestructive nature, and precedent of court admissibility.

Phelps et al. later described success in recovery of trace levels of methanol, ethanol, isopropanol, and acetone from laboratory samples using activated charcoal strips with CS₂ [1]. While oxygenates were recoverable in the presence of kerosene, they were greatly reduced relative to the recovery that had been obtained without kerosene present. The current use of activated charcoal strips in heated passive headspace extraction works well for low levels of petroleum-based, non-polar compounds. In the presence of larger molecules, or comparatively more non-polar molecules, evidence of an oxygenate may not be detected.

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Additionally, if a laboratory uses a solvent delay in its GC run parameters, there is a high likelihood that early-eluting oxygenated compounds will not be detected.

Oxygenates are highly volatile and are easily lost at a fire scene, by evaporation due to high heat and by the application of water in fire suppression efforts. While at present it is not possible to combat the loss of oxygenated compounds due to harsh fire scene conditions, it may be possible to improve the extraction efficiency of oxygenated ILRs from fire debris samples.

St. Pierre and co-workers recently demonstrated the capability of zeolite 13X to recover low molecular weight polar compounds, at higher levels than were obtained using activated charcoal [4]. The study described an optimized method of heated passive headspace extraction with zeolite adsorption media, resulting in two to three-fold increases in recovery reported for acetone, ethanol, and isopropanol compared to recovery using charcoal strips. It was proposed that the size exclusion property, large surface area, and polar surface of zeolite 13X together make it an ideal adsorbent for the recovery of oxygenated ILs.

The purpose of this research was to examine the utility of a dual-mode heated passive headspace extraction setup using a protocol that supplements the current headspace concentration technique for petroleum products with zeolite 13X, increasing the ability to simultaneously recover oxygenated IL compounds from fire debris samples. The data from this investigation were obtained in ideal laboratory conditions and serve as a foundation for further study into the use of zeolites in heated passive headspace extraction for practical applications in fire debris casework.

2. Materials and methods

Zeolite 13X (ZeoChem L.L.C., Louisville, Kentucky, USA), has a reported available surface area of approximately 400–800 m²/g [5,6]. Following the procedure introduced by St. Pierre, zeolite packets were constructed by placing approximately 0.5 g of zeolites into porous loose tea bags (Teavana Corporation, Atlanta, Georgia, USA). The quantity of the zeolites was determined by weight to account for the wide variation in bead diameter, a 1.6 mm average [7]. The tea bag was then pierced through the center by a paper clip (Staples, Inc.) tied to a length of unwaxed dental floss (CVS pharmacy brand). Activated charcoal strips (Albrayco Technologies Inc., Cromwell, Connecticut, USA) with 1128 m²/g available surface area [8] were halved to each measure 10 mm × 10 mm and weigh 0.04 g. Strips were pierced with a paper clip, and tied to a length of unwaxed dental floss. Each adsorbent was suspended within the headspace of the sample container. In some cases, both adsorbents were prepared individually as previously described, and suspended in tandem during the extraction process.

Airtight quart-sized metal cans and pressure lids (Fisher Scientific, Pittsburgh, Pennsylvania, USA) were utilized as sample containers. One Kimwipe (KimTech Science, Kimberly Clark Professional, Roswell, Georgia, USA) per can served as a sample substrate; unspiked Kimwipes were used as negative controls. All oxygenates of interest (ethanol, 1-propanol, 1-butanol, isopropanol, and acetone) and desorption solvents (methanol and carbon disulfide) were obtained from Fisher Scientific, Acros Organics (part of Thermo Fisher, Waltham, Massachusetts, USA), or Pharmco-AAPER (Brookfield, Connecticut, USA) and were spiked onto the sample using Finnpiptette™ adjustable pipettes (Fisher Scientific). Gasoline and diesel were obtained from Hess Corporation at local fueling station pumps (Boston, Massachusetts, USA).

An Agilent 7890A gas chromatograph (GC) system coupled to an Agilent 5975C inert XL EI/CI mass selective detector (Agilent Technologies, Wilmington, Delaware, USA) was utilized for analysis of sample extracts. GC separations were performed using helium gas through an Agilent J&W HP-5MS column, 30 m in

length with a 0.25 mm internal diameter and a film thickness of 0.25 μm (see Table 1 for specific method parameters). MSD ChemStation software, version E.02.00.493, was utilized for the analysis of chromatographic data. Integration of peak area was performed using the auto integrate feature on total ion chromatographic data (TICs), with the exception of ethanol and acetone peaks. Due to the co-eluting nature of these two analytes, extracted ion chromatograms (EICs) were rendered by the software before auto-integration. For acetone, *m/z* 43 was used, while both *m/z* 31 and 45 were utilized for ethanol. All GC vials, liners and caps were obtained from Fisher Scientific.

2.1. Single-mode extraction studies

In order to evaluate the efficacy of a dual-mode extraction procedure, the recovery of oxygenates and petroleum products were examined first using a single adsorbent medium. To perform this study, 10 μL of ethanol, 1-propanol, 1-butanol, isopropanol, acetone, diesel, or gasoline was spiked separately onto a Kimwipe within a quart-sized metal paint can. Either a 13X zeolite packet or an activated charcoal strip was suspended within the headspace of each can. Samples were heated for 2 h at 85–90 °C before desorption of zeolites in methanol (MeOH) and charcoal strips in MeOH or CS₂. MeOH was utilized with charcoal strips to evaluate whether desorption with a polar solvent could improve the recovery of polar oxygenated compounds. All tests were performed in triplicate. Extracts were analyzed by GC/MS; resulting chromatographic peaks were integrated and averaged across the three replicates.

Additional extraction setups in which both oxygenated and petroleum-based compounds were spiked within the same sample cans were also investigated. The procedure was followed as above, using single adsorbents in each can, but 10 μL of all five oxygenates and 10 μL of diesel or gasoline were spiked. For samples that included hydrocarbons, three compounds were monitored: *n*-dodecane, *n*-pentadecane and pristane for diesel, and toluene, *p*-xylene, and 1,2,4-trimethylbenzene for gasoline. While using only three components would certainly be insufficient for evaluating the presence of an IL in forensic casework, a select few compounds were chosen for each neat IL that could be readily picked out for integration and that had retention times which spanned the earlier, middle and later parts of the chromatogram. As in the previous study, extracts were analyzed by GC/MS; resulting chromatographic peaks were integrated and averaged across the three replicates.

2.2. Dual-mode extraction studies

The affinity of five oxygenates for an adsorption medium when both zeolites and activated charcoal were present within the same sample can was examined. To perform this study, 10 μL of a single IL (as listed above) was spiked onto a Kimwipe within three paint cans. Both a 13X zeolite packet and an activated charcoal strip were

Table 1
Optimized parameters of GC/MS method utilized in this study.

Total run time	30 min
Program	40 °C for 4 min, then 10 °C/min to 280 °C for 2 min
Inlet mode	Split 1:20
Injection volume	1 μL
Pressure	4.76 psi
Split flow	15.98 mL/min
Solvent delay	1.30 min
Average velocity	32.414 cm/s
MS mode	Scan
Low mass	31 amu
High mass	350 amu
Timed events	Specific to solvent (detector off during solvent elution)

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