



Recovery of oxygenated ignitable liquids by zeolites, Part I: Novel extraction methodology in fire debris analysis



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ABSTRACT

The recovery of low molecular weight oxygenates in fire debris samples is severely compromised by the use of heated passive headspace concentration with an activated charcoal strip, as outlined in ASTM E-1412. The term “oxygenate” is defined herein as a small, polar, organic molecule, such as acetone, methanol, ethanol, or isopropanol, which can be employed as an ignitable liquid and referred to in the ASTM classification scheme as the “oxygenated solvents” class. Although a well accepted technique, the higher affinity of activated carbon strips for heavy molecular weight products over low molecular weight products and hydrocarbons over oxygenated products, it does not allow for efficient recovery of oxygenates such as low molecular weight alcohols and acetone. The objective of this study was to develop and evaluate a novel method for the enhanced recovery of oxygenates from fire debris samples. By optimizing conditions of the heated passive headspace technique, the utilization of zeolites allowed for the successful collection and concentration of oxygenates. The results demonstrated that zeolites increased the recovery of oxygenates by at least 1.5-fold compared to the activated carbon strip and may complement the currently used extraction technique.

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1. Introduction

Fire debris analysis provides analytical information to fire investigators and attorneys by identifying traces of ignitable liquid residues (ILRs) in fire debris samples. Caution must be exercised when reporting the results of analyses, due to the fact that the presence of an ILR does not necessarily indicate an incendiary fire. There are many legitimate reasons for ILRs to be present on or within samples submitted for fire debris analysis [2,3]. One challenge presented to the fire debris analyst is the identification of ILRs when compounds produced by pyrolysis, combustion, or those originating from the sample material are also present. Low molecular weight oxygenates have reportedly been produced through pyrolysis and incomplete combustion [2–4]. The term “oxygenate” is defined herein as a small, polar, organic molecule, such as acetone, methanol, ethanol, or isopropanol, which can be employed as an ignitable liquid and referred to in the ASTM classification scheme as the “oxygenated solvents” class.

ASTM 1618: standard test method for ignitable liquid residues in extracts from fire debris samples by gas chromatography–mass spectrometry, provides guidelines for the classification of ILRs from fire debris samples [5]. This reference standard states that “a large excess of the compound (at least one order of magnitude above other peaks in the chromatogram)...” must be present before any significance is given to the identification of an oxygenate [5]. As previously mentioned, oxygenates are encountered as products of incomplete combustion or pyrolysis as well as in the manufacturing and maintenance of many common household items, creating difficulty in establishing a clear threshold for determining the significance of identifying an oxygenate. However, without a well-defined threshold an analyst must use his or her discretion when reporting the significance of an oxygenate present in a fire debris sample.

Acetone, methanol, ethanol, and isopropanol are examples of compounds that may be found in several different household items either naturally, through their manufacturing or maintenance, as a product of pyrolysis or as a product of incomplete combustion. The flammability of these oxygenates and their readily available nature make them attractive accelerants for a fire, and thus important considerations to the fire debris analyst. However, the high volatility and polarity of these compounds make them difficult to

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recover from fire debris samples with the current recovery techniques. The methods used are optimal for the recovery of heavy hydrocarbon-based products rather than low molecular weight oxygenates.

Although arguments have been made that the high volatility of low molecular weight alcohols and acetone would prevent their recovery from fire debris samples, research has shown that they are easily recovered from samples in controlled house burns [2]. The literature has reported the difficulty of recovering acetone and low molecular weight alcohols in the presence of higher molecular weight compounds when using the heated passive headspace concentration method with activated charcoal strips as an adsorbent medium [2,6]. The greater affinity of carbon for hydrocarbons over oxygenates and high molecular weight compounds over low molecular weight compounds compromises the recovery of low molecular weight oxygenates such as methanol, ethanol, isopropanol, and acetone. Due to the boiling point of low molecular weight oxygenates, they are the first components to vaporize into the headspace of the sample container and adsorb onto the suspended activated carbon strip. As heating continues, the higher molecular weight components vaporize into the headspace and also interact with the activated carbon strip, ultimately displacing the low molecular weight oxygenates which have a weaker affinity for the activated carbon strip. This process can lead to skewed results and an inaccurate interpretation of the findings. The development of a new technique to improve the recovery of oxygenates from fire debris samples was necessary for several reasons, including: (1) the difficulty of recovering oxygenates with the current extraction technique when heavier molecular weight compounds are also present in the sample, (2) the difficulty in establishing a well defined threshold for interpreting the significance of identifying an oxygenate in a fire debris sample and (3) the likelihood of identifying a low molecular weight oxygenate in a fire debris sample which may be attributable to pyrolysis products, products of incomplete combustion, the sample matrix, the manufacturing of the sample, or the maintenance of the sample.

This study proposed and evaluated a novel methodology for optimizing the recovery of acetone and low molecular weight alcohols, including methanol, ethanol, and isopropanol, from fire debris samples using zeolites as an adsorbent medium. Zeolites are both naturally occurring and synthetically produced crystalline aluminosilicate mineral structures with high thermal, chemical, and mechanical stability and unique molecular sized pores and cavities [7]. The primary structure of a zeolite is a tetrahedral framework of silicon (Si), aluminum (Al), and oxygen (O) atoms balanced by a cation. The number of oxygen atoms contained within the framework determines the pore size of the zeolite. The unique pore sizes allow zeolites to host guest molecules, which fit into their pores and ultimately separate molecules from mixtures [8].

Based on the composition and geometry of the structure, different guest molecules will have a greater or lesser affinity for different zeolites [9]. Hydrophilicity is one factor determining which molecules will interact with the zeolites by entering into the pores and adsorbing onto the interior surfaces. The hydrophilicity of the zeolite is partially dependent on the Si/Al ratio as well as on the nature of the cation. The lower the Si/Al ratio and the more hydrophilic the cation, the more hydrophilic the zeolite will be. Zeolites A, X, and Y have Si/Al ratios between 1 and 1.5, making these zeolites very hydrophilic adsorbents [10]. Also aiding to the hydrophilicity of the zeolite are intercrystalline boundaries and defects within the structure, which terminate in silanol (Si–OH) groups increasing the hydrophilicity of the zeolite in these locations [11].

Separation of mixtures utilizing zeolites occurs through both selective adsorption and molecular sieving [12]. The most well known applications of zeolites are in water treatment where they are used as molecular sieves and in catalytic cracking where they are used in the process of converting hydrocarbons into high-octane compounds [9–11]. Discrimination of components within a mixture by zeolites is accomplished based on differences in pore sizes, shape, and adsorption preferences [13]. One of the basic components for separation using zeolites is size exclusion [8].

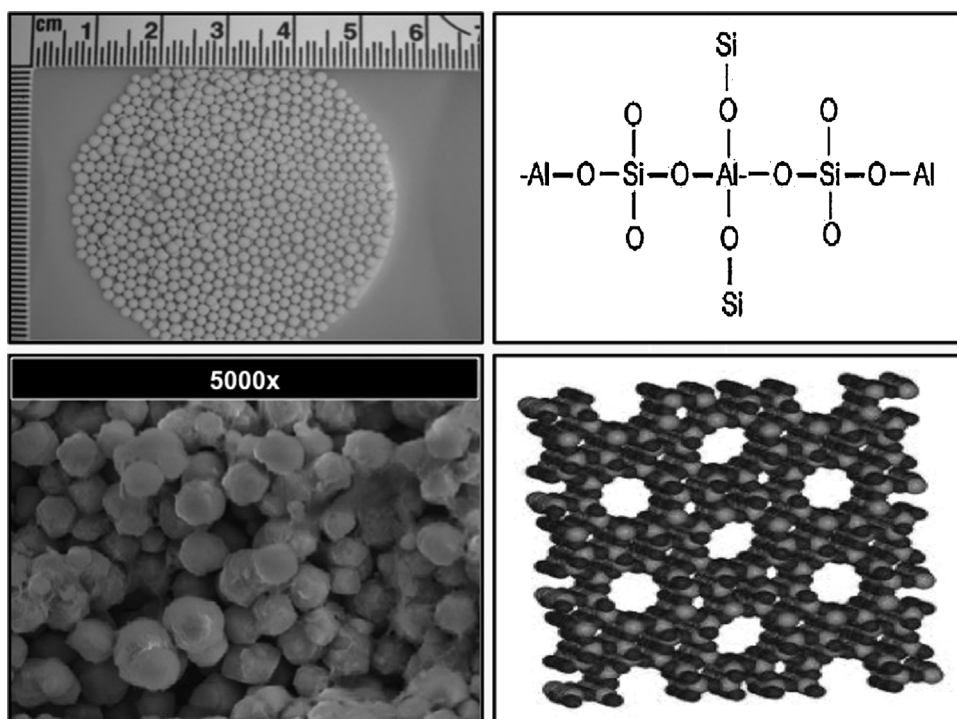


Fig. 1. 13X zeolite structure: Zeolites are crystalline, aluminosilicate, mineral structures with unique molecular sized pores and cavities. The primary structure of a zeolite is a tetrahedral framework of silicon (Si), aluminum (Al), and oxygen (O) atoms balanced by a cation.

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