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The influence of temperature on the pyrolysis of household materials

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ABSTRACT

We have previously demonstrated the successful application of multivariate statistical (i.e. chemometric) techniques to the classification of casework fire debris based on gasoline content, with the objective to expedite the data interpretation process for the forensic analysis of fire debris. We have also shown that it is possible to classify simulated fire debris based on gasoline content using simulated fire debris; however, models trained on simulated debris are not applicable to casework samples without a significant loss in model accuracy. A previously developed simulation protocol that works well for generating debris to train human analysts was inadequate for training either partial least-squares discriminant analysis (PLS-DA) or soft independent modelling by class analogy (SIMCA) models to identify casework debris due mainly to its inability to generate a sufficient amount of benzene, toluene, ethylbenzene, and xylenes (BTEX) and non-aromatic hydrocarbon compounds. This method relied on pyrolyzing materials at 400 °C. Here we examine the effects of pyrolysis conditions on household materials, including spruce plywood, vinyl sheet flooring, polyethylene terephthalate (PET) carpet, Nylon 6 carpet, polyurethane (PU) foam carpet underlay, asphalt shingle, medium-density fireboard (MDF) shelving, and spruce timber at temperatures above 400 °C, in an attempt to generate additional BTEX and non-aromatic hydrocarbon compounds for the realistic simulation of fire debris. The work presented here showed that C_3- to C_5-alkylbenzenes, which are abundant in gasoline, were generally absent from the pyrolysates of all materials studied and at all temperatures studied (400, 700 and 900 °C), only appearing in trace amounts on rare occasions. Based on our results, we propose that accurate simulation of fire debris could be achieved with a mixture of carpets, carpet underlay, and vinyl flooring pyrolyzed at 700 °C; spruce plywood pyrolyzed at 900 °C, and asphalt shingles pyrolyzed at 400 and 700 °C. These conditions generated a substantial amount of BTEX and non-aromatic hydrocarbons in the debris matrix background. The testing of this "recipe" for generating simulated debris for training chemometric models that can classify casework debris is left for future experimentation.

1. Introduction

Combustion and pyrolysis reactions are the dominant processes that occur in a fire, with combustion being described by two processes: flaming combustion and smoldering combustion [1,2]. Flaming combustion is the most common type of combustion with characteristic flames for which it is named. This process involves a reaction between oxygen and fuel in the gas phase. Smoldering combustion is a flameless process involving the reaction of atmospheric oxygen directly with the surface of a solid fuel in an environment with limited ventilation [1–3]. Since flaming combustion is an entirely gas-phase process, solid and liquid fuels must undergo a phase change or a chemical change to enter the gas phase. For some fuels this is achieved by simple evaporation; however, for the vast majority of substrates, pyrolysis is required to support flaming combustion.

Pyrolysis is the process whereby (typically large) organic compounds undergo thermal decomposition at elevated temperature. Strictly speaking, the pyrolysis reaction occurs in the absence of oxygen; however, in the context of fires where oxygen may still be present, pyrolysis refers to thermal decomposition due to heat without involving oxygen [1,4,5]. Pyrolysis products (pyrolysates) are generated via multiple mechanisms and are smaller, more volatile compounds than the parent molecules. Thus pyrolysates are better able to support flaming combustion. Common pyrolysis products include alkanes, alkenes, alkadienes (e.g. from pyrolysis of polyethylene) [4], and aromatic compounds such as benzene, toluene, ethylbenzene, and xylenes (BTEX), as well as styrene and

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naphthalene (e.g. from polyvinylchloride) [4]. The wide variety of materials used in building construction, coupled with the different temperature zones and atmospheric compositions present during a structural fire will generate a complex and unpredictable background matrix of pyrolysis products. During forensic fire investigations, the presence of pyrolysis products is the main factor complicating the identification of ignitable liquids in fire debris.

Much work has been devoted to understanding the combustion and pyrolysis behaviour of flooring materials and the interference potential of pyrolysis products with the detection of ILs. Smith [6] characterized the volatiles generated by charred carpet obtained from fire scenes and observed styrene and BTEX. Howard and McKague [7] demonstrated the pyrolysis of styrene-butadiene copolymer material in a test tube with a Bunsen burner to compare the volatiles generated from this polymer with those from charred carpet volatiles collected at fire scenes. Later, DeHaan and Bonarius [8] performed a full scale simulation of a structural fire for the identification of volatiles produced from pyrolysis of a few different types of flooring products, including nylon carpet, polyethylene/polypropylene carpet and polyurethane foam underlay. The goal was to investigate whether the volatile products from these materials could be distinguished from those found from common petroleum distillates (ILs) or synthetic blends. Bertsch [9] pyrolyzed carpet and carpet underlay in one-gallon paint cans over a Bunsen burner. In this study, styrene, methylstyrene, ethylbenzene, naphthalene and methylnaphthalenes were identified as pyrolysis products. Chasteen et al. [10] burned building materials under four different sets of conditions and constructed a library of pyrolysis products based on their results. Fernandes et al. [11] burned three types of carpet (polypropylene, nylon, and wool) with sponge rubber underlay using a Bunsen burner. All three samples generated toluene, and polypropylene carpet also generated styrene and limonene.

Over the last few decades, research has also been conducted to investigate the pyrolysis products formed from various types of natural and synthetic polymers [12–19], the results of which may be useful for deducing the behaviour of polymers containing household products in fires (for example: poly(ethylene terephthalate) (PET) containers and textiles, nylon carpets, polyurethane (PU) foam underlay, and polyvinyl chloride (PVC) sheet flooring). Smith [15] established a library of pyrolysis products generated from different types of synthetic polymers including polystyrene, polyethylene and nylon. The characteristic pyrolysis products used to identify each polymer were also listed. Bednas et al. [20] studied the pyrolysis of PET fabrics at 700 °C and 900 °C using flash pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Benzene, vinyl benzoate, benzoic acid, and biphenyl were observed as the main pyrolysis products. Dzięcioł and Trzeszczyński [21–23] conducted several studies on the influence of temperature and atmosphere on the pyrolysis of PET granulate. They pyrolyzed samples at constant temperatures from 200 to 700 °C in constant nitrogen or air flow. Moltó et al. [24] also heated used polyester fabrics isothermally under these two atmospheres to temperatures of 650–1050 °C. McNeill and Memetea [14] identified 60 products from the pyrolysis of PVC under helium atmosphere up to 1000 °C. The pyrolysis products of PVC were found to contain aromatics and polycyclic aromatic hydrocarbons (PAHs) such as BTEX, naphthalene, biphenyl and their substituted products [12–14]. Alajbeg characterized the pyrolysis products of PVC window blinds [13], rigid polyurethane foam [18], and commercial phenol-formaldehyde resin foam [25] in a flow reactor with a mixture of oxygen and nitrogen atmosphere (1:1) at three different temperatures: 550, 750, and 950 °C. Nylon 6 and Nylon 6,6 are two types of polyamide fibres commonly used to produce carpets. The former produces caprolactam as the major pyrolysis product [15,16], while Nylon 6,6 pyrolysates exhibit a characteristic cyclopentanone peak [15–17]. PU is a polymer frequently used in the production of carpet underlay, the pyrolysis of which was found to generate considerable amounts of benzene, toluene, styrene, aniline, benzonitrile, 1-propenyl-bezene and naphthalene [18,19].

Wood is the primary structural material used in residential construction and is also found in flooring and furniture. Wood consists mainly of cellulose (approximately 50%), hemicellulose (approximately 25%) and lignin (approximately 25%) [2]. Pyrolysis of wood generally produces guaiacols and phenols which originate from lignin, as well as levoglucosan which originates from cellulose [26–30]. Asphalt shingles are another combustible material, commonly used as a roofing material in North America, fabricated from the residual bottoms remaining after the vacuum distillation of crude oil. This petroleum-based product yields pyrolysates comprising primarily *n*-alkanes, alkenes, aromatics and PAHs [31,32].

Pyrolysis products such as BTEX (benzene, toluene, ethylbenzene, xylenes), alkanes, and PAHs will often be present in fire debris collected from residential structural fires. In particular, the C_2-alkylbenzenes are an important group of diagnostic compounds for many petroleum products [1] and so interference from pyrolysis products can make the interpretation of data from forensic samples more challenging. Currently, the interpretation of chromatographic data from samples of fire debris is a laborious manual process requiring one experienced analyst to interpret the data, and a second experienced analyst to confirm the results. Data interpretation can take anywhere from 20–60 min per analyst, per sample. With the goal of speeding up the data interpretation workflow, our group has previously demonstrated the application of partial least-squares discriminant analysis (PLS-DA) and soft independent modelling by class analogy (SIMCA) to the detection of gasoline in simulated [33] and casework arson debris [34]. While the individual models for simulated and casework debris were successful, models trained by debris simulated in a laboratory were not able to classify casework debris samples based on gasoline content without introducing an unacceptable number of false positives and false negatives [35]. It was shown that while C_2-alkylbenzenes and aliphatic alkanes are typically abundant in real (casework) fire debris, the debris simulation method [36] did not produce a sufficient concentration of these compounds to cause the model optimization algorithm to ignore these features when identifying which peaks to retain for modeling. Consequently, C_2-alkylbenzenes and aliphatic alkanes were chosen by the model as marker compounds for indicating the presence of gasoline. This, in turn, resulted in a model which would frequently misclassify casework debris samples where these compounds appear frequently in the matrix. Thus a refinement of the simulation protocol is required to generate simulated debris that is adequate for the automated construction of a chemometric model for classifying casework debris samples.

Pyrolysis temperature and atmospheric composition can affect the chemical profiles of the resultant pyrolysates of household materials. During a fire, the temperature of a room within a structure will change over time as the fire develops. Although several studies have been conducted to investigate the influence of temperature on pyrolysis products, to our knowledge there has been no research using ramped-temperature profiles that mimic temperature rise in a real fire. Additionally, to our knowledge there has been no comprehensive study of the pyrolysis of a broad range of building materials under identical conditions. In this research, we evaluate the influence of temperature and heating profile on the pyrolysis products of eight types of household materials commonly submitted for arson analysis, and use this information as a step toward developing a lab-scale fire debris simulation protocol that will likely result in more realistic debris samples suitable for training chemometric models.