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Comprehensive two-dimensional gas chromatography – time-of-flight mass spectrometry and simultaneous electron capture detection/nitrogen phosphorous detection for incense analysis

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ABSTRACT

This study reports comprehensive two-dimensional gas chromatography hyphenated to time-of-flight mass spectrometry detection (GC × GC/TOFMS) for characterisation and identification of components generated by four different types of powdered incense headspace (H/S) and incense smoke. GC × GC/TOFMS allowed simultaneous separation and identification of compounds emitted into the atmosphere as a result of combustion of incense powder. The smoke stream comprised compounds originating from the incense powder, and combustion products such as saturated and unsaturated hydrocarbons, essential oil type compounds, nitromusks, fatty acid methyl esters (FAMEs), polycyclic aromatic hydrocarbons (PAHs, which possibly include oxygenated and nitrated PAH), N-heterocyclics, pyrans and furans, which were detected and tentatively identified by GC × GC/TOFMS. GC × GC-electron capture detector/nitrogen phosphorous detector (ECD/NPD) potentially offers the prospect of providing selective chemical compositional information of incense powder and smoke, such as nitrogen-containing (N-containing) and halogenated compounds. Results of GC×GC-ECD/NPD showed that both incense powder and smoke generated emission of N-containing and halogenated compounds. A significant number of halogenated and N-containing compounds were emitted during the incomplete combustion of incense. However, one further objective of this paper is to demonstrate the capacity of comprehensive two-dimensional gas chromatography coupled to specific and/or selective detectors such as those used in this study (GC × GC-ECD/NPD) for the detection of particular classes of compounds such as N-containing and halogenated compounds at trace level concentrations in complex smoke samples.

1. Introduction

People have used incense for religious or spiritual, aesthetic and therapeutic reasons for centuries. Nowadays, incense is still used for these purposes, as well as for creating a pleasant atmosphere and scent to enhance the ambience of a home or in shops. Because of its long history of use, incense has evolved into many different types, colours, forms, scent, shape and the way it burns. The most common form of incense is stick incense, the gum or resin from which the incense is made coats a long thin stick that burns slowly to release the particular fragrance that it comprises. Fragrances are created from different organic plant materials, derived from animal such as musk, and essential oils that are extracts of either or both. The fragrance can be a single scent found naturally or a combination of two or more ingredients; the combinations of incense scents are endless. Nevertheless, smoke particulates generated from incense burning is a major source of indoor and air pollution, particularly in most Asian

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countries, since incense burning is a traditional practice in many religions throughout Asia. Hundreds or thousands of incense sticks with different sizes are burnt during major ceremonies. Incense has also been used for other purposes including aromatherapy and air fresheners. The burning of incense causes the emission of toxic compounds including polycyclic aromatic hydrocarbons (PAH) (Lin et al., 2002; Yang et al., 2007), and metallic elements (Lin et al., 2007) into the atmosphere. Particulate matter such as PM_{10}, and $PM_{2.5}$ (Jetter et al., 2002; Wang et al., 2007) were also found to be generated during incense burning.

Particles less than 10 μm in diameter include both fine and coarse dust particles. These particles pose the greatest health concern because they can pass through the nose and throat, and into the lungs.

Particles larger than 10 μm that are suspended in the air are referred to as total suspended particulates (TSP), and can cause irritation to the eyes, nose and throat in some people, but they are not likely to be delivered to the lungs. Other studies demonstrated that incense smoke generated from different types of incense sticks exhibit different smoke-generating properties and characteristic size distributions (Chang et al., 2007). Most recently, See et al. (2007) studied physical characteristics of nanoparticles emitted from incense smoke and their results showed that the airborne particles in the nanometre range (5.6–50 nm), in the ultrafine range (50–100 nm) and in the accumulation mode range (100–560 nm) accounted for 1–6%, 16–55% and 40–60% of the total particle counts, respectively, depending on the brand of incense.

This paper reports on the continuation of earlier incense work (Tran and Marriott, 2007), where solid-phase microextraction (SPME) was used as an extraction and sampling method followed by GC × GC-FID for the analysis of incense powder and smoke volatiles. GC × GC was able to detect many more compounds present in incense powder as well as in the smoke than 1D GC, where many compounds coeluted in conventional (1D) GC. Different column configurations (e.g. non-polar/polar and polar/non-polar) were investigated to compare and contrast the separation of compounds in both incense powder and smoke. In addition to this, GC/quadrupole MS (qMS) was used for identification of components in incense powder and smoke. However, only about 100 compounds in incense powders and 200 compounds in the incense smoke were identified using this technique, principally due to resolution limits in 1D-GC, which caused peak overlapping; trace level compounds were not detected. In other words, this means that conventional GC cannot provide sufficient resolution to separate such a complex mixtures as this. Although inadequate and/or incomplete information will be extracted from GC/qMS, the compounds that were identified by this technique indicated that potentially there are various toxic compounds present in the smoke. Therefore in order to more completely characterise the components emitted into the atmosphere by incense burning, a technique such as GC × GC in tandem with high-speed mass spectrometry is required.

From previous work, comprehensive two-dimensional gas chromatography (GC × GC-FID) after solid phase microextraction appeared to be a suitable method for fingerprinting of incense smoke volatiles and comparison of different incense types. The aim of the work is to extend the above approach of SPME with GC × GC in tandem with time-of-flight mass spectrometry (SPME-GC × GC/TOFMS) to improve analytical resolution and characterisation through GC × GC with mass spectral information. Due to its high ion extraction speed, the TOFMS analyser is able to generate up to 500 spectra s^{-1}. Since all fragment ions are almost simultaneously detected with little or no spectral bias, this technique allows clean, unique spectra to be produced and also partially multi-component co-eluting compounds may be deconvoluted in the MS domain. This technique has been successfully applied to various applications including, coffee bean volatiles (Ryan et al., 2004), honey volatiles (Cajka et al., 2007), pepper volatiles (Cardeal et al., 2006), monoterpenoids in grapes (Rocha et al., 2007) and recently, PAH in olive oils (Purcaro et al., 2007). Likewise, other selective detectors such as nitrogen phosphorous detection (NPD) and micro-electron capture detection (μECD) may be used for the detection of nitrogen-containing (N-containing) and halogenated compounds in both incense powder and smoke. The fundamental operation of GC × GC-NPD was reported by Ryan and Marriott (2006), demonstrating GC × GC-NPD for the analysis of nitrogen containing compounds and pyrazines in coffee bean headspace. This technique was later applied to the analysis of N-containing compounds in heavy gas oil (von Muhlen et al., 2007) and nanoparticles in roadside atmosphere (Ochiai et al., 2007). GC × GC-ECD also had been widely applied to the analysis of organohalogenated compounds (Korytar et al., 2005), polychlorinated biphenyls (PCBs) in sludge (Kristenson et al., 2005), and food samples (Bordajandi et al., 2005). This study therefore also reports observations on GC × GC-ECD/NPD for simultaneous (i.e. parallel) detection of N-containing and halogenated compounds emitted by incense burning.

2. Experimental

2.1. Samples and SPME procedure

Sources and descriptions of four different types of incense used in this study were described previously (Tran and Marriott, 2007). Incense samples were chosen based on their uses, fragrances and appearances; the mass of incense powder burnt for different incenses varied according to their shapes and sizes. Incenses used included lotus-scented incense stick, red Tibetan incense stick, brown smokeless stick and medicine herb cone. Detail of SPME sampling procedures of incense powder volatiles and smoke were described elsewhere (Tran and Marriott, 2007). SPME sampling was carried out using a polydimethylsiloxane/divinylbenzene (PDMS/DVB) coated fibre (65 μm; Stableflex, Supelco Inc.). Extraction for 60 min at room temperature was used for incense powder and 20 min for incense smoke. After extraction, manual SPME injections were made to thermally desorb analytes at 250 °C for 3.5 min in the glass liner of the GC injector under splitless mode for 2 min.