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Evaluation of a miniaturised single-stage thermal modulator for comprehensive two-dimensional gas chromatography of petroleum contaminated soils

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ABSTRACT

A novel miniaturised single-stage resistively heated thermal modulator was investigated as an alternative to cryogenic modulation for use in comprehensive two-dimensional gas chromatography (GC × GC). The single-stage thermal modulator described herein yielded average retention time relative standard deviations (RSD) of ≤0.2% RSD (first-dimension) and ≤3.4% RSD (second-dimension). The average peak widths generated by the modulator were 72 ± 3 ms, and the peak area precision was better than 5.3% RSD for a range of polar and non-polar test analytes. GC × GC analysis can be performed using this modulator without the requirement for cryogenic cooling or additional pressure control modules for flow modulation. The modulator and associated electronics are compact and amenable towards field analysis. The modulator was used for qualitative and quantitative characterisation of petroleum-contaminated soils derived from a sub-Antarctic research station at Macquarie Island. The limit of detection compared to standard 1D GC analysis was improved from 64 to 11 mg kg^{-1}. An automated method of analysing and categorising samples using principal component analysis is presented.

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1. Introduction

Comprehensive two-dimensional gas chromatography (GC × GC) has been a topic of great interest due to the expanded possibilities of this technique to analyse very complex mixtures of compounds [1,2]. One-dimensional gas chromatography (GC) separations with long (60–100 m) columns often fail to resolve large numbers of compounds due to limited peak capacity [3]. GC × GC vastly increases the peak capacity of GC by augmenting the first-dimension separation with a continuous series of rapid separations that are carried out every few seconds in the second dimension [1]. This peak capacity increase can be accomplished without significantly increasing the analysis time. A device known as a modulator installed at the interface between the first- and second-dimension columns is critical to the quality of separations obtained using GC × GC [4,5]. A modulator must provide narrow injection bandwidths to the second-dimension column to maximise the performance of the multidimensional separation.

Several types of modulators have been developed for GC × GC, based on either carrier gas flow manipulation or solute focusing. Flow based modulation in the form of high speed Deans' switching and pulsed-flow modulation uses a high auxiliary flow of carrier gas to rapidly inject small portions of effluent from the first-dimension to the second-dimension column to provide modulation [6,7]. While these systems can be set up at low cost, the high flows required for operation cause a significant loss in second-dimension column efficiency and make coupling of the system with MS difficult (although research into low-flow modulation has gone a long way towards overcoming the latter limitation [8]). Alternatively, solute-focusing modulation can be used whereby solutes are focused within a modulator. The modulator is then periodically heated to mobilise trapped solutes to the second-dimension column, thereby providing modulation of effluent from the first-dimension column. The focusing of solutes is often enhanced cryogenically by using liquid nitrogen, carbon dioxide or refrigerated air to ensure that volatile compounds are adequately focused and cryogenic modulation has subsequently become the dominant modulation strategy [1]. The main drawback of this strategy is the need for a refrigeration unit or a supply of expensive liquid cryogen,

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which limits the adoption of this technique for routine and portable analysis.

Resistive heating has been shown to be very effective for providing temperature programmed GC analysis [9], and this technique was used during the initial development the GC × GC technique [10]. Harynuk and Górecki used resistively heated stainless steel (SS) trapping capillaries (530 μm ID, packed with a macro porous organic polymer, Tenax TA) using both liquid nitrogen cryogen, and air-cooling for solute focusing [11]. Capacitive discharge facilitated rapid mobilisation of trapped components with the application of electrical current to the SS capillary. Libardoni *et al.* later developed a single-stage thermal modulator with another SS capillary (180 μm ID) coated with a non-polar stationary phase (MXT-1, 0.2 μm d_f), however this design was reliant on refrigerated air or cryogen for solute focusing [12,13].

Recent research by Colin *et al.* highlighted how alternative modulator stationary phases could be beneficial for thermal modulator designs, compared to conventional stationary phase coatings [14]. The use of a highly polar room temperature ionic liquid stationary phase coating within a micro-fabricated GC × GC modulator minimised stationary phase bleed from the modulator while temperature pulses were being applied compared to conventional polydimethylsiloxane based coatings that have been utilised in the past as the basis of thermal modulators [15]. Mascalu *et al.* similarly reported the development of novel thermally stable stationary phase coating for single-stage thermal GC × GC for the analysis of polychlorinated biphenyl compounds [16]. While dual-stage modulators are typically used to prevent solutes from passing through a modulator without being focused, a number of authors have demonstrated that optimisation of a single-stage modulator design can minimise the potential for breakthrough without recourse to an additional focusing stage [12,16]. The aim of the present article is to evaluate a miniaturised single-stage thermal modulator that incorporates an adsorptive stationary phase coating and high-speed resistive heating for comprehensive two-dimensional GC × GC modulation. This modulator was evaluated used a range of compounds and then applied to the analysis of petroleum hydrocarbon spills affecting a sub-Antarctic research station, for the purpose of evaluating ongoing remediation efforts.

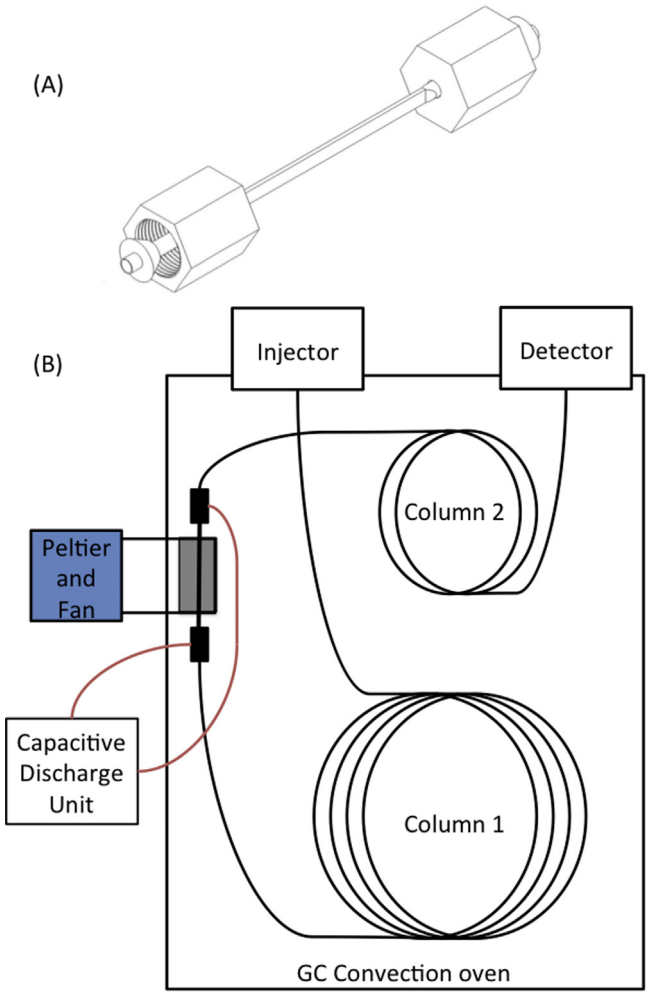

Fig. 1. Schematic diagram of the resistively heated single-stage modulator (A), and a diagram showing the modulators installation in a GC convection oven (B).

2. Experimental

2.1. Instrument configuration

An Agilent 6850A Gas Chromatograph (Agilent Technologies, Wilmington, DE, USA) equipped with a spilt/splitless injector, an automatic liquid sampler 7683B Series (Agilent) and an FID was used for all analyses. The first-dimension column was a DB5-MS 25 m × 250 μm ID × 0.25 μm d_f (Agilent) coated with a low-polarity silarylene based stationary phase equivalent to 5% diphenyl- 95% dimethylpolysiloxane. This column matched the stationary phase type utilised previously for petroleum spill analysis at Macquarie Island [17]. The second-dimension column was an Rxi 17Sil MS 1 m × 100 μm ID × 0.1 μm d_f (Restek, Bellefonte, PA, USA) coated with a mid-polarity silarylene stationary phase equivalent to 50% diphenyl- 50% dimethylpolysiloxane, which was selected due to its high efficiency and rapid separation speed. This stationary phase combination has been shown to be very effective in providing GC × GC separations of petroleum based samples [1].

The modulator was constructed from a segment of SS capillary (4 cm long, 0.28 mm ID) coated with an adsorptive stationary phase coating prepared using a proprietary procedure [16]. The modulator was installed within the GC convection oven and connected to the first- and second-dimension columns using two SilTite mini unions (Trajan Scientific & Medical, Ringwood, Australia). The modulator was compressed between a pair of ceramic pads mounted on a hinged device that was installed through the wall or roof of the GC convection oven as shown in Fig. 1. The compression device served as a heat conduit, ensuring that the modulator was kept at sub-oven temperature. The device was made of copper and cooled using a pair of fans (12 V) and thermoelectric cooling pads (5 V, 2.6 A) that were mounted outside of the convection oven. The trap was connected to a programmable (0–40 V) capacitive discharge power supply (4 × 44,000 μF capacitor array) using two glass fiber braid insulated copper wires.

2.2. Modulator performance testing

A test mixture containing a range of different compounds was injected (1 μL) into the split/splitless inlet at a split ratio of 100:1 and all analytes were determined in triplicate. The inlet temperature was 250 °C, and a 4 mm SGE split liner (Trajan) was used. The carrier gas was hydrogen, with a constant flow rate of 1.0 mL min^{-1}; the initial head pressure was 87.08 kPa at 30 °C. The GC temperature was initially 30 °C for 1 min and then temperature programed at a rate of 5 °C min^{-1} to 200 °C. The FID temperature was 250 °C, and operated at a data sampling rate of 200 Hz, to ensure adequate detection of the narrow peaks generated during modulation [18,19]. The capacitive discharge power supply was programmed to provide a modulation period of 3.0 s, with a discharge voltage of 21.0 V.

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