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Discussion

Setting the record straight about the capabilities of the rotating heater as a modulator for GC × GC

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Recently, Dallüge et al. published a review of comprehensive two-dimensional gas chromatography (GC × GC) in this journal [1]. In a history of modulator design, the authors identify the first commercially-available modulator as the rotating heater developed by Zoex Corporation (Lincoln, Nebraska, USA). This modulator is often called the "Sweeper" because a slotted heater sweeps over a section of capillary column to desorb and launch sharp concentration pulses onto the second column. The authors state that "the major disadvantage of the Sweeper was its limited application range." They list a maximum compound elution temperature of 230 °C, and a usable eluent boiling point range of 125–450 °C. This belief that the rotating modulator has a narrow and limited application range has become pervasive in the recent literature [2–5]. However, these facts are wrong and we would like to set the record straight. In short, rotating modulators are capable of effectively modulating compounds from butane (C_4) to tetracontane (C_{40}) and beyond. The record of published data generated with a rotating modulator will prove our position.

In 1998, Gaines et al. quantified oxygenates and benzene, toluene, ethylbenzene and xylenes (BTEX) in groundwater [6] in which the earliest eluting peaks reported were methyl-*tert*-butyl ether (MTBE, bp 55.2 °C) and 2,3-dimethylbutane (bp 89.7 °C) which coeluted on the non-polar first column. This was also the case when Frysinger et al. quantified BTEX and heavier aromatics in gasoline [7]. Frysinger and Gaines later quantified oxygenates in gasoline [8] in which the earliest eluting peak identified was butane (bp −0.50 °C). In these studies, thick-film modulators (d_f = 3.5 and 5.0 μm) were used for compound trapping. The most volatile compounds like butane required sub-ambient cooling (−40 °C) of the GC oven and modulator tube. These three published studies demonstrate that rotating modulators can modulate compounds with boiling points as low at 0 °C, which is significantly below the 125 °C lower limit offered by Dallüge et al. [1].

In 2001, Frysinger and Gaines were the first to extend the boiling point range of the rotating modulator beyond about C_{24} (bp 391 °C). By incorporating a thin-film modulator tube (d_f = 0.5 μm) in a separate heated zone that was programmed to be 40 °C cooler than the first column temperature, the modulation range was extended to tetracontane (C_{40}, bp 522 °C) [9]. A detail about the rotating modulator that needs clarification is the actual temperature reached on the trapping capillary column as the rotating heater passes over it. Although the temperature of the heater is 100 °C hotter than the oven, the transient temperature increase on the capillary, which depends primarily on the rotation velocity of the heater, is only 60–70 °C above the oven temperature [10]. For compounds like C_{40} at the upper end of the modulation range, the typical oven elution temperature is about 320 °C, but the thin-film trapping capillary that is located in a separate, cooler zone is 280 °C. Therefore, the rotating heater produces a transient to about 350 °C during modulation. This is not a temperature that will damage a thin-film, non-polar phase capillary column, so modulation to C_{40} with a rotating heater is possible in both theory and practice.

In practice, Frysinger and Gaines used the rotating heater modulator to separate a number of high molecular weight biomarkers, including steranes, hopanes, and triaromatic steranes from a crude oil sample [9]. Frysinger et al. also separated and identified a wide variety of sedimentary pollutants including polyaromatic hydrocarbons (PAHs),

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steranes and hopanes in a complex marine sediment extract [11]. These compounds eluted in the alkane range from C_{17} to C_{38} (bp range: 302–511 °C). In their review [1], Dallüge et al. show their previously unpublished GC × GC chromatogram of steranes, sterols, and steroidal ketones and claim that "cryogenic modulation was essential since heated modulators (such as the Sweeper), and valve-based modulators cannot be used at such high temperatures." They are incorrect. In our laboratory, we used a rotating modulator to separate and identify steranes in crude oil and sediment extracts in work that was published in 2001 [9] and 2002 [11]. In other work, we used the rotating modulator to separate and identify C_{35}–C_{39} long-chain alkenones in Black Sea sediment extracts [12]. These compounds eluted in the alkane range of C_{36}–C_{41} (bp range: 497–527 °C). These three published studies demonstrate that rotating modulators can modulate compounds with boiling points as high as 527 °C, which is significantly beyond the 450 °C upper limit specified by Dallüge et al. in Table 2 of their paper [1].

In summary, when the rotating modulator is configured with a thick-film trapping capillary ($d_f = 3.5$ or 5.0 μm), samples with compounds ranging from C_4 to about C_{24} can be modulated. When the rotating modulator is configured with a thinner film capillary ($d_f = 0.5$ μm), the modulation range shifts to about C_8–C_{40}. Opinions about the "robustness" of the rotating thermal modulator vary. We agree that column assembly and alignment of the rotating heater were problematic. However, the facts about the application range of the rotating thermal modulator are undeniable. It has been demonstrated to successfully modulate compounds with a boiling point between 0 and 527 °C (corresponding to compounds from C_4 to C_{40}) with GC column elution temperatures of 320 °C or greater. We request that all future descriptions of rotating modulator performance incorporate these facts.

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