Short communication

Increased flow rate compatibility for universal acoustic flame detection in liquid chromatography

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ABSTRACT

The liquid chromatography (LC) flow rate tolerance of the universal Acoustic Flame Detector (AFD) is characterized and significantly expanded through using larger bore burners. For example, increasing the burner i.d. from 1.00 to 4.00 mm increases the AFD upper flow rate limit from 20 to 100 μL/min. While signal and noise each reduce as the burner i.d. widens, the best current performance is obtained with a 2.30 mm i.d. burner. This approach also allows AFD operation over a broader range of mobile phase temperatures. As a result, the overall increased flow rate compatibility of the detector can facilitate improved chromatography and further development of LC-AFD applications.

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1. Introduction

Over the years, a recurring challenge in many liquid chromatography (LC) analyses is the lack of robust, simple, and sensitive universal detection techniques [1]. For instance, such devices are often sought for non-chromaphoric analytes that do not respond in the conventional ultraviolet–visible absorbance detector [2]. While refractive index and evaporative light scattering methods can frequently detect such analytes, they often elicit a variable response factor for molecules of differing optical properties or volatility, respectively [2–4]. As such, there remains a need for the development of universal LC detectors that can uniformly respond to all organic compounds.

In recent years, we have introduced the Acoustic Flame Detector (AFD) as a novel universal detector for LC [5,6]. This device is based upon the frequency of a unique oscillating hydrogen/oxygen flame that continually flashes partially downward into a burner delivering a steady upward flow of pre-mixed flame gases. Each of these cycles forms an acoustic burst which translates into an audible detector pitch near 1000 Hz. When organic analyte is present, it decreases the flame burning velocity and the depth that it penetrates into the pre-mixed gases, thereby increasing the oscillation

frequency. As a result, the detector pitch increases as a function of analyte carbon content and provides a uniform response toward hydrocarbons that is qualitatively similar to a standard flame ionization detector, but quantitatively more on par with an evaporative light scattering detector [5–8]. Thus, considering its relatively straightforward inexpensive design, the AFD can potentially offer a useful and easily accessible universal LC detection method.

One challenge in working with the AFD is its limited capacity to accommodate LC mobile phase flow rates. For instance, if values typically exceed 20–25 μL/min, the AFD flame is overwhelmed and the detector response terminates. This is problematic since it primarily limits AFD usage to low-flow, packed capillary micro or nano LC applications and restricts the ability to optimize separation flow rates. Additionally, it can also impede LC separations at elevated temperatures, where efficiency and mobile phase velocity can increase. While post-column flow splitting has been attempted to alleviate these problems, it frequently poses undesirable consequences such as variable split-ratios among analytes and an overall degradation in detection limit. Therefore, any means of removing this boundary and increasing flow rate capacity in the AFD could improve its operating flexibility and usage.

Recently, we discovered that carefully changing both the AFD burner diameter and the ignition sequence of the flame had a very positive effect on the flow rate capacity of this detector. Here, we present this phenomenon and discuss its impact on LC-AFD operation.

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2. Experimental

2.1. Instrumentation

The AFD construction used here has been detailed previously [5–7]. In particular, the heated burner configuration introduced earlier [6] was employed in these experiments. The conventional flame burner is made from a 100 mm × 6.00 mm o.d. × 1.00 mm i.d. quartz tube. Others explored here also include 2.00, 2.10, 2.30, 2.95, and 4.00 mm i.d. tubes. Note that these i.d. measurements are accurate within less than 0.01 mm. A Vespel ferrule secures the burner to the detector port.

The separation column is housed in a GC oven, which is usually maintained at 30 °C. Separations are performed using either a commercial LUNA C_{18} column (150 mm × 1 mm i.d.; 3 μm particles; Phenomenex, Torrence, CA, USA) or an in-house packed capillary column (150 mm × 0.25 mm i.d. fused silica; 5 μm silica particles, Silicycle, Quebec City, Canada). A 45 cm length of undeactivated fused silica tubing (50 μm i.d.; Polymicro, Phoenix, AZ, USA) leads directly from the column outlet into the burner, where it terminates 20–40 mm below the flame. Although unlikely, to prevent exposure to any potentially hazardous mobile phase combustion by-products, all flame exhaust is carefully directed into a fume hood.

AFD signals are collected and processed using Spectrogram acoustic software (Version 6.6, Richard Horne author, www.visualizationsoftware.com) and Praat phonetics software (Version 4.0.26, Paul Boersma and David Weenink authors, University of Amsterdam, www.praat.org/).

2.2. Reagents and conditions

Toluene (99.5%) and HPLC grade acetonitrile are used as a test analyte and mobile phase, respectively (Aldrich, Oakville, Canada). Medical grade oxygen, high purity hydrogen and air are purchased from Praxair (Calgary, Canada). Typical AFD settings employ 7 mL/min oxygen, 75 mL/min hydrogen, and 250 mL/min auxiliary air. Normally the detector block temperature is 100 °C while the resistively heated burner [6] is 250 °C. Any variations and other details are in the text.

3. Results and discussion

In contrast to our previous efforts [5–7] where the AFD flame is ignited and stabilized prior to introducing mobile phase, we recently found that if as little as 1 μL/min of mobile phase is introduced prior to ignition, then considerably larger burners and flow rates can indeed be successfully used in the AFD.

This arises because hydrocarbons reduce the flame's burning velocity and its ability to penetrate into the burner [5,8,9]. A larger burner i.d. also physically moderates the linear velocity of the effluent at larger flow rates.

Fig. 1 displays the maximum column flow rate attainable in the AFD as a function of burner i.d. As seen, the flow rates increase considerably as the burners expand. For example, while the 1.00 mm
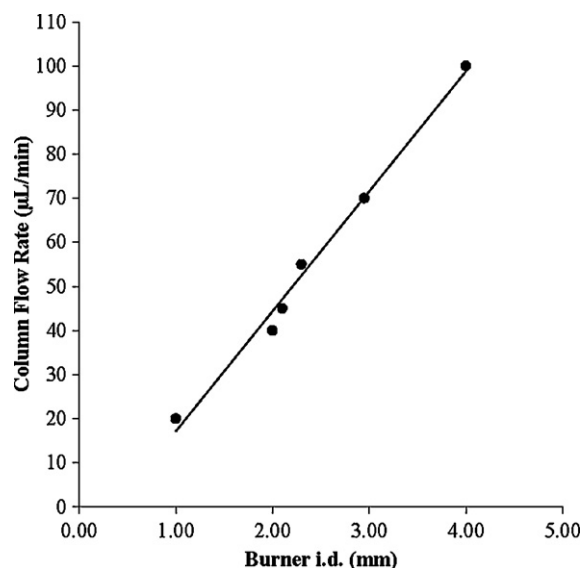

Fig. 1. Maximum LC column flow rates in the AFD as a function of burner i.d. A LUNA C_{18} column (150 mm × 1 mm; 5 μm) is used.

i.d. burner tolerates up to 20 μL/min as expected, this linearly increases 5 times to 100 μL/min as the burner i.d. enlarges to 4.00 mm. This increase is very significant since even as little as 30 μL/min has never previously been successfully used in the AFD. Following this, an optimal configuration was determined by further exploring the properties of these AFD burners.

Table 1 lists the general operating characteristics of the various burners for comparison. As observed, the overall supporting gas flows naturally increase about 7 times as the burners widen. Over this same range, the flame volume oscillating inside the burner also increases considerably from about 2 to 40 μL (reasonably estimated from the cylindrical depth of the flame below the surface). These findings are somewhat anticipated given the larger burners employed. However, despite this apparent growth, the ratio of oxygen to hydrogen remains near 0.2 in most of these trials. As well, the resulting effluent linear velocity resides around 100 cm/s in many cases. Thus, while AFD flame parameters physically change for the burners of Table 1, these core operating attributes appear to remain relatively consistent throughout.

Also in Table 1, the typical AFD baseline frequency observed decreases by 700 Hz as the burner i.d. increases. This is likely due in part to mobile phase dilution as the flame volume expands, since AFD frequency is fundamentally proportional to hydrocarbon concentration in the flame [5–7,10]. It should also be noted that the 500 Hz baseline value quoted for the 2.00 and 2.10 mm burners is only typical of the range observed and not the exact value measured each time. In fact, for the 2.00 mm burner, these conditions later yielded a baseline value near 600 Hz in other experiments independent of those in Table 1.

Another artifact of altering flame volume is that a general decrease in absolute AFD response is also observed as burner bore

Table 1
General operating characteristics of various-sized AFD burners.

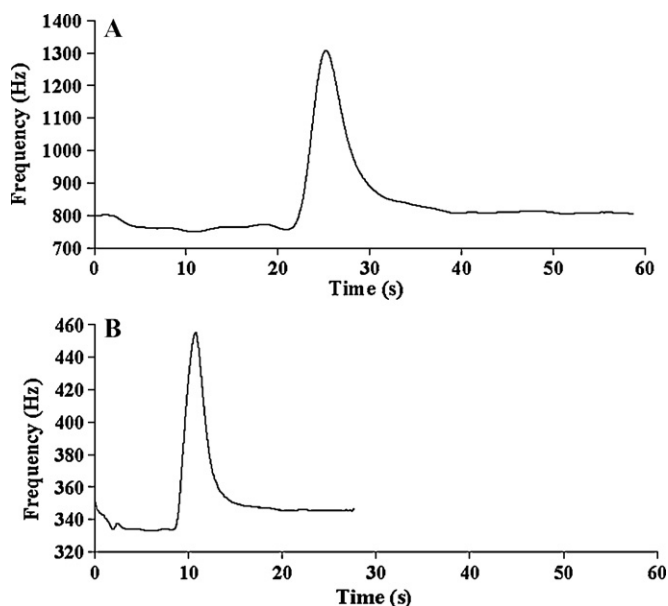| Burner i.d. (mm)	Maximum flow rate (μL/min)	H_2/O_2 flow ratio (mL/min)	Oscillating flame volume (μL)	Typical baseline frequency (Hz)
1.00	20	28/21	1.9	800
2.00	40	143/26	11.0	500
2.10	45	160/32	12.1	500
2.30	55	238/48	14.5	350
2.95	70	272/59	23.9	300
4.00	100	308/72	44.0	100

Fig. 2. LC-AFD chromatograms of toluene using (A) a 1.00 mm i.d. burner with a flow rate of 20 μL/min and (B) a 2.30 mm i.d. burner with a flow rate of 55 μL/min. A silica column (150 mm × 0.250 mm; 5 μm) is used and 200 μg of analyte is injected.
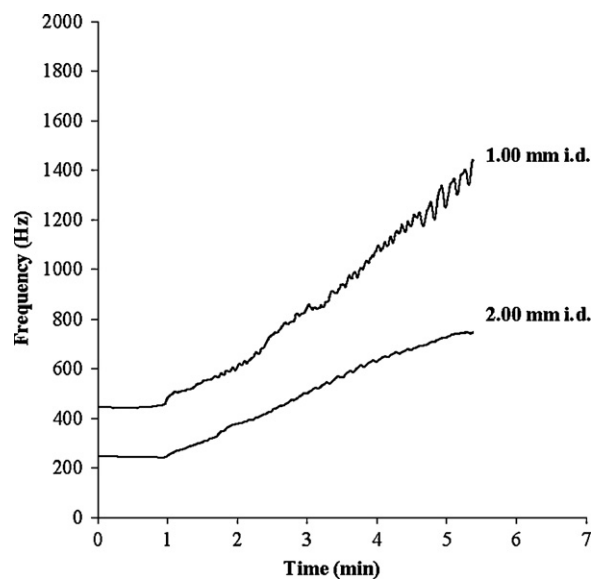

Fig. 3. Effect of column temperature on the LC-AFD baseline frequency when using (A) a 1.00 mm i.d. burner and (B) a 2.00 mm i.d. burner with moderate initial flow rates of 10 and 20 μL/min, respectively. The temperature program is 35 °C initially for 1 min, then increasing manually at 17 °C/min to 110 °C. The column used is the same as in Fig. 2.

increases. For example, the 1.00 and 2.00 mm i.d. burners differ about 6 times in flame volume and a proportionate decrease in response results due to analyte dilution. Specifically, under identical chromatographic test conditions, this 6 fold difference is clearly reflected in 200 μg toluene injections, which elicit 396 and 66 Hz signals, respectively for these burners. Comparatively, analyte response with the 4.00 mm i.d. burner is often very low and difficult to detect making it currently less practical for use.

Interestingly, baseline noise in the AFD also decreases with increasing burner i.d. For example, using maximum allowable flow rates, the natural peak to peak AFD noise reduces 10 times just between the 1.00 mm i.d. (e.g. noise of 42 Hz) and 2.30 mm i.d. (e.g. noise of 3.8 Hz) burners alone. Thus, this welcome observation dictates that analyte detection does not necessarily erode by using larger burners. In fact, we have found that signal to noise ratios are often slightly better by a factor of about 2 between the 1.00 and the 2.30 mm i.d. burners. Considering this, overall the 2.30 mm i.d. burner generally offers optimal performance in the current set of experiments.

Fig. 2 demonstrates LC-AFD test chromatograms of a toluene analyte using both conventional and larger flow rates as a result of increased burner size. As seen in Fig. 2A, the peak elutes at 26 s with a half-width of about 4 s when using the conventional 1.00 mm i.d. burner and its maximum allowable column flow rate of 20 μL/min. Conversely, in Fig. 2B, the peak elutes at 11 s with a much narrower half-width of about 2 s when using the 2.30 mm i.d. burner at a flow rate of 55 μL/min. Thus, the greater column flow rates now possible in the AFD can facilitate faster chromatography and flexibility in optimizing conditions. Of note, the LUNA C_{18} column used in this study has a recommended optimal flow rate of 50 μL/min that was previously unattainable in LC-AFD experiments, but is now readily employable.

These improvements can also facilitate AFD usage in high temperature LC applications where the mobile phase is heated near or above its boiling point [11–16]. In particular, the conventional 1.00 mm i.d. burner is little compatible with such changes leading to significant mobile phase expansion, while the larger bore burners appear to more readily accept such conditions. For example, acetonitrile mobile phase applied at 80 atm to the column of Fig. 2 results in 15–20 μL/min of flow for temperatures up to the boil-

ing point of 81 °C. However, as temperatures approach 140 °C, the resulting flows increase beyond 30 μL/min where only a larger bore burner could make AFD operation feasible.

Fig. 3 illustrates this difference in temperature tolerance for the 1.00 and 2.00 mm i.d. burners each operating with moderate initial flow rates at 35 °C. As the temperature increases to 110 °C and the mobile phase greatly expands, the resulting increased flow into the flame is still manageable for the larger burner, while the smaller responds more erratically and AFD operation approaches termination. Further, the background increase is much steeper for the 1.00 mm i.d. burner by comparison. For example, over the range examined this burner produced a baseline offset of roughly 1000 Hz, whereas the 2.00 mm i.d. burner yields about half this value and provides a much smoother signal even though it operates with twice the amount of mobile phase.

4. Conclusion

The ability to increase LC flow rates in the AFD can be attained through using larger bore flame burners. Such burners can accommodate a greater flow of mobile phase while still maintaining flame oscillation. The resulting flame volume and analyte dilution therein are key factors in optimization. Overall, this approach provides greater flexibility in method development and improved detector operation.

Acknowledgement

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