

**CONFIDENTIAL**

**HIGH-THROUGHPUT REACTOR  
FOR SIMULATING THE  
FLAME PHOTOMETRIC DETECTOR**

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## ABSTRACT

Quenching of luminescing species by co-eluting hydrocarbons has been widely reported in the flame photometric detector (FPD). This paper describes a novel method of investigating the chemical behavior of both analyte and quencher molecules in the FPD. The method attempts to reproduce the FPD's behaviour on a large scale by using a custom-built reactor. The high-throughput reactor's multi-capillary burner, situated inside a glass housing, is well suited to approximate the low-temperature, fuel-rich conditions of the conventional FPD. It also allows the study of various other flame phenomena. Wide regions of gas composition can be accessed by both diffusion- and premixed-type flames, and products can be easily sampled. Effluent collection demonstrates that as much as 82% or as little as 2% of various organic compounds may survive passage through the diffusion flame and be recovered intact. The recovery of several hydrocarbons - used here primarily to mimic the behaviour of quenchers - was found to decrease with increasing carbon number. Hetero-atoms such as sulfur, nitrogen, or oxygen greatly decrease the recovery of molecules vis-a-vis their pure-hydrocarbon analogues. Compared to a diffusion flame, the recoveries of n-alkanes from a premixed flame are much lower and largely independent of carbon number or volatility.

## INTRODUCTION

The flame photometric detector (FPD), whose classical form dates back to Brody and Chaney, is well known for its sensitive and selective response to sulfur [1-4]. It has been extensively used for this element, both as a continuous analyzer and as a gas chromatographic (GC) detector [5-8]. Perhaps its greatest limitation in practice is the peculiar quenching of sulfur response that occurs in the presence of hydrocarbons [1,3,8,9]. This quenching can seriously interfere with the analysis of complex samples such as petroleum products. Considerable attention has therefore focused on the quenching mechanism [1,8,10]. The most common explanations for this phenomenon propose collisional deactivation of the excited  $S_2$  emitter, and the scavenging of S or H atoms by hydrocarbons or their fragments [8,11]. While most scenarios assume, implicitly or explicitly, that hydrocarbons and organo-sulfur compounds do fragment in the detector flame, very little is known regarding the extent to which such fragmentation occurs.

In an earlier article, Aue and Sun demonstrated that the response of FPD-active elements (i.e. of P, Sn, Fe, Mn, and Cr) was quenched to a very similar extent as that of sulfur [12]. This finding was taken to suggest that hydrocarbons in the FPD “quench the exciting flame rather than the excited analyte”. However, other scenarios, such as diffusion-controlled quenching, were not ruled out. In those quenching studies, methane was used as the model compound. But it might have been interesting to test different hydrocarbons to see whether all types of quenchers were effective to a similar degree for all analyte elements; and whether reactivity, size or volatility of the quencher molecules played any role. Furthermore - if hydrocarbons do indeed “quench the exciting flame” -

it would have been important to know whether this function was performed by a single, hydrocarbon-derived flame species common to all quenchers. Such considerations suggest a quantitative study of hydrocarbon fragmentation in the conventional FPD flame. Flame sampling by mass spectrometry might have provided some of the information; however, the necessary instrumentation was unavailable in our laboratories.

A potentially interesting approach to FPD mechanisms is the collection and analysis of organic compounds passing through (or being formed in or above) the detector flame. However, this approach is neither convenient nor easy to carry out, considering the tiny volume of a typical FPD flame and the submicrogram per second quantities of carbon flow that define the upper limit of its linear range. It would take a single FPD - or even several FPDs - a long time to collect the amounts necessary for gas chromatographic analysis. This limitation strongly suggests the combination of several FPD jets into a single burner head. In conventional flame spectroscopy, large burners have often been constructed from assemblies of multiple capillaries, mainly to serve mechanistic studies [13-15]. The best of these burners provide a large, evenly distributed, laminar gas flow arising from the combined output of individual capillaries.

This paper describes the construction and characterization of such a high-throughput, FPD-like reactor. Its multi-capillary burner and glass housing were designed to simulate the low-temperature, hydrogen-rich conditions that support the chemiluminescent response of the conventional FPD. Beyond this immediate purpose, the reactor was constructed to sustain a wide range of gas flows (i.e. from air-rich to very hydrogen-rich); to accommodate different methods of introducing compounds (i.e. through and/or above the flame); and to test different kinds of flames (i.e. diffusion

versus premixed types). As a possible future application, the reactor was also built to allow the collection of potential reaction products of stable flame species (themselves derived from fuels or additives) with compounds introduced into the radical-rich area above the flame. A glass housing was chosen to provide inertness and permit the flame and any luminescent phenomena to be kept under visual or instrumental observation. Details regarding the construction and operation of the reactor, and some preliminary results obtained by introducing organic materials and collecting their residues, are discussed below.

## **EXPERIMENTAL**

### **Burner Design and Construction**

The burner was constructed by assembling pieces of type 316 stainless steel capillary tubing (1/16" o.d. x 0.030" i.d., Chromatographic Specialties Ltd., Ontario, Canada) in a hexagonal close packing arrangement. Rows of 2-inch capillaries were layered between rows of 2-inch and 5-inch capillaries, all meeting flush at the end of the burner head to be. High-temperature epoxy (Duralco 4525, McMaster-Carr Supply Co., New Jersey, USA) was poured within 0.5" from the ends of the short capillaries to hold the pieces together. The burner end was ground off to an even, flat, hexagonal surface, measuring 1" across at its widest point. Figure 1 presents a top view of the burner surface, illustrating the short (empty circles) and long (filled circles) tubes used to deliver hydrogen and air, respectively. At the surface, each air tube (37 in total) was surrounded by six hydrogen tubes (147 in total), simulating the diffusion-flame design of a typical

FPD burner, in which the central air supply is surrounded by a flow of excess hydrogen plus carrier gas.

This capillary assembly was placed into a 4"-long stainless steel tube (1.25" o.d. x 1" i.d.) and the burner head positioned 6 mm above the edge in order to prevent overheating [15]. A 1/8" i.d. gas port, previously drilled through the side of the tube, was also used to deliver a 0.5" wide layer of epoxy to seal the unit into place at each end. The longer capillaries, protruding from the end opposite the burner head, were ground flush to the edge of the tube.

The burner tube was secured into a 1.5" - 1.25" stainless steel reducing union, fabricated from the bisection and welding of two regular unions, with a 1.25" cap on the end (Swagelok). The union was modified so that air could be introduced through a 1/8" o.d. reducer fitting in the bottom cap, and hydrogen and nitrogen could flow through a similar fitting in the side gas port that terminated inside the burner tube. With the unit swaged gas-tight, air was delivered to the burner head from the bottom through the long capillaries, while hydrogen and nitrogen were introduced through the short capillaries via the cavity between the two layers of epoxy.

A 7" long glass tube (1.5" o.d. x 1.38" i.d.) was held tightly around the burner head by silicone rubber o-rings, and fitted with a 14/20 clear glass joint for connecting it to a cold trap containing the collection solvent in an ice bath. A 1/8" i.d. and a 1/4" i.d. port were included for placing a thermocouple and an igniter, respectively, close to the burner head surface. A 1.5"-1.25" stainless steel reducing cap was similarly connected to the top end of the burner glass tube by using silicone rubber o-rings. This simple cap can be easily taken off for cleaning the reactor. It can also be replaced by a more complex

cap, not shown here, that contains a stainless steel tube with longer, protruding capillaries, in an arrangement similar to that of the bottom piece. The adjustable position of this tube within the cap allows the introduction of samples into, and/or the sampling of, different regions above the flame. In this study, however, the simpler reactor version represented by figure 2 was used, which forces all flame gases through the side port and into the collection solvent.

## **Procedure**

Extra dry air, prepurified hydrogen, and reagent grade nitrogen (Linde) were used as flame gases. The typical diffusion flame, based on the setting that produces the optimal sulfur luminescence, was operated with 1000 mL/min hydrogen, 550 mL/min air, and 150 mL/min nitrogen. The typical premixed flame was operated with a mixture of 1400 mL/min hydrogen, 1000 mL/min air, and 500 mL/min nitrogen being introduced through the short capillaries. In an additional, comparative set of experiments, a diffusion flame was operated with exactly the same flows as the premixed flame. (Note: the premixed flame is unstable at settings typical of the diffusion flame, hence the latter had to be adjusted for a proper comparison of recovery rates between the two types of flames).

Organic compounds were introduced into the reactor by a flow of nitrogen passing through a sampling vessel and sweeping the vapor of the dopant into the hydrogen/nitrogen line and up to the burner head. The amount of compound delivered during an experiment was determined by accurately weighing the sampling vessel before and after each trial. The rate of delivery, controlled by the nitrogen flow and, occasionally, the temperature of the sampling vessel, was selected such that the reactor

operated close to maximum luminescence (i.e. that the flow of dopant corresponded roughly to the upper end of its linear range in an FPD). All chemicals were of reagent-grade purity (Aldrich and Fisher Scientific).

Compounds were passed through the reactor in two corresponding runs: the first with the flame unignited, the second with the flame ignited. Except for the flame being off or on, both runs used identical gas flows and conditions. Samples were typically collected in two ice-cooled bubbler traps in series, with the help of a suitable collection liquid. The collected reactor effluents were then analyzed by a Tracor model 550 gas chromatograph equipped with a flame ionization detector (FID) and a 2 m x 1.8 mm i.d. borosilicate column packed with 10% Apiezon L on Chromosorb W 45/60 mesh (about 350-250 micron particle diameter). The response ratio of the amount of compound collected in the “ignited-flame” trial to that in the “unignited-flame” trial was termed the “percent recovery” [i.e. (ignited/unignited) x 100%]. A collection efficiency close to 100% from the “unignited-flame” trial was considered a precondition for continuing the experiment in the chosen circumstances. All other instrumental or procedural details are described in the text.

Prior to any experiments with compounds, a rough overview of the operating limits of the reactor and of the approximate temperatures at a fixed location near the burnerhead were obtained for as wide an array of hydrogen/air flows as possible. The resulting temperature contours are outlined on the flame stability chart shown in figure 3.

## RESULTS AND DISCUSSION

Although the flame stability chart shown in figure 3 adequately delineates the area of gas flows in which the flame can be expected to be stable, the thermal information it includes simply describes the temperature as measured at a fixed point near the burner surface. Since flame size and shape change with flow conditions, the fixed-position thermocouple readings near the edge of the burner are at best approximate representations of flame temperature. They should therefore not be used for exact comparisons between different flames, nor should they be considered “maximum” temperatures, nor should they even be taken to imply that every point of the same height above the burner surface had this particular temperature. Nonetheless, for the hydrogen-rich conditions used throughout this study, separate (and frequently repeated) measurements, in which a manually controlled thermocouple was moved across the burner surface, produced very similar temperatures to those measured near the edge.

As can be seen from figure 3, the reactor provides steady flames for a wide range of gas flows. In this initial investigation, stable operation of the reactor with as little as 150 mL/min (i.e. about 1 mL/min per capillary) or as much as 10 L/min was achieved for hydrogen. Extremely air-rich operation of the reactor could not be probed to the same extent. In fact, some of the larger air flows increased the fixed-thermocouple temperature to over 700 °C. Since these conditions started to erode the epoxy, the attempt to further extend the graph along the air axis was halted.

In any case, large air flows hold little relevance for FPD simulation. For that task, the most interesting and relevant area exists around 1000 mL/min hydrogen and 550 mL/min air. In this relatively low-temperature (~ 300 °C), fuel-rich region, the reactor

operates with a nearly five-fold stoichiometric excess of hydrogen. On average for each air capillary (upon which a flame resides in the fuel-rich atmosphere), the flows are about 15 mL/min air and about 42 mL/min hydrogen through the 6 capillaries that surround it\*.

*\*Footnote: As can be easily calculated, the average flow through one hydrogen capillary is  $1000/147 = 6.8$  mL/min. Thus, for the typical middle-of-burner arrangement of one air tube surrounded by six hydrogen tubes – each of which abuts yet another air tube – the formal flow of hydrogen per air tube equals  $6.8 \times 6/2 = 20.4$  mL/min. The average “hydrogen flow per air tube” for the total burner head is slightly larger, i.e.  $1000/37 = 27$  mL/min. This is because the air tubes on the periphery of the burner surface (cf. figure 1) are surrounded by higher-than-average hydrogen flows toward the edge of the burner. The above calculation is, of course, formal: it does not take into account mixing effects, possible differences in capillary flow resistance, etc.*

These values are similar to the optimum gas flows of the conventional FPD [1]. The reactor flame behavior bears this out. For instance, the maximum carbon luminescence in the reactor under these conditions was visually estimated to correspond to an overall carbon flow of 4  $\mu\text{g/s}$ , which agrees with the FPD’s upper response limit to carbon [1]. More importantly, small amounts of sulfur dopants resulted in an intense blue emission, floating as an even disc directly above the burner head. Given these operational similarities between the multi-capillary burner and the typical FPD, the reactor conditions as described above could now be used with confidence to examine the behavior of organic compounds in the multi-capillary flame, and to presume that such compounds would behave likewise in the single-jet flame of the FPD.

To gain an initial understanding of how organic molecules behave in an FPD-flame environment, a modest assortment of representative alkanes and hetero-organic

compounds were individually introduced into the reactor, and their remains collected and analyzed. The “percent recovery” (see **Experimental** for definition) was used as a measure of fragmentation or decomposition in the flame. The results are displayed in table 1. As can be seen, only small amounts of the organic sulfur, nitrogen, and oxygen compounds were recovered. This agrees with what would be expected from a typical FPD flame. Indeed, many of the conventional excitation mechanisms for FPD-active elements are based on the disassembly and reduction of hetero-organic molecules into small, often atomic fragments [1,8,11]. While typical analyte molecules thus behaved according to expectation, the behavior of pure hydrocarbons was decidedly different.

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The results of table 1 indicate that considerable amounts of the alkanes were not decomposed by the hydrogen-rich diffusion flame. In fact, for the hydrocarbons containing less than 8 carbon atoms, amounts of 50% or more were recovered from the flame. For compounds containing 8 carbon atoms or more, the percent recovery decreased from near 30% to almost zero (i.e. close to disappearance).

Other interesting observations, with reference to the structure of the hydrocarbons studied, are that the recoveries for 1,7-octadiene and 1-octyne were lower than for n-octane, obviously as a result of the functional groups. However, there was no significant difference between the recoveries of, say, benzene and cyclohexane. Nor was there any significant difference in the recoveries of cyclohexane and cyclopentane as compared to their n-alkane analogues. Further, while the recovery of benzene was significantly larger than the recovery of a series of butylbenzene isomers, these C-10 compounds did show

recoveries in the n-nonane/n-decane range. Branching in pure aliphatic structures, as in the case of the methylpentane isomers, also made no difference in recovery.

The most interesting aspect of table 1 is the fact that, as the carbon number increases in the n-alkane series, the percent recovery decreases from 82% for n-pentane to 2% for n-decane. This seems to argue against mechanisms proposing that hydrocarbons decompose completely to single carbon species in FPD-type, hydrogen-rich flames [10]. In regard to larger “product” molecules, it must be noted that no peaks indicating the formation of such products were ever observed in chromatograms of flame effluents - although the collection procedure efficiently captured compounds as small (i.e. as high in volatility) as n-pentane.

Another interesting consideration regards the aromatic ring. One might have expected to find substantially different recovery rates for benzene vs. cyclohexane vs. hexane, since these C-6 compounds, while of comparable volatility, do differ in their chemical behavior in many systems. For instance, when these compounds are analyzed by the conventional FPD, the relative response of benzene is much higher than that of the two other compounds. Indeed, aromatic compounds in general respond stronger in the FPD than do aliphatic ones, and they do produce a different spectrum (i.e. mainly CC\* vs. CH\*) [16]. Clearly, therefore, aromatics and aliphatics must produce different yields of carbonaceous species in the conventional FPD diffusion flame.

In an earlier, different type of premixed flame system, aromatics and aliphatics were found to respond equally well and produce the same spectrum [17]. In fact, significantly reduced quenching effects and other response differences have often been

noted in those instances where the analyte was premixed partially, or entirely, with air [6,18,19]. Therefore, with the reactor of this study well suited to the task, it became interesting for us to determine the recovery of the same series of n-alkanes in a hydrogen-rich premixed flame.

Figure 4 compares the recovery of n-alkane molecules from the reactor operating in diffusion (circles) and premixed (triangles) flame modes. In order for the reactor to sustain a premixed flame, moderately larger gas flows were required than for the diffusion-flame (table 1). Therefore the measurements were performed again, with both the diffusion and the premixed flame operating at identical gas flows. As can be seen from figure 4, the results of the diffusion-flame experiment reflect those found in table 1, albeit at an overall lower percent recovery due to the somewhat higher reactor temperature ( $\sim 450$  °C versus  $\sim 300$  °C, as determined at the fixed thermocouple site). The same trend is observed in the diffusion flame, as alkane recoveries decrease from a plateau region around 20% for n-pentane and n-hexane, to near zero for n-decane. However, for the premixed flame, which also showed a roughly comparable temperature measurement ( $\sim 400$  °C), the same compounds are recovered in much lower quantities and, except for the case of pentane, in quantities much closer to one another. Considering that the reactor conditions and stoichiometry of the flame gases were comparable in both cases, this observation must be attributed to the difference in flame type. Only pentane appears to behave differently, and it is unclear why this border molecule is less affected by the change in burner operation than the other alkanes. Analogous relationships in the mass spectra of straight-chain hydrocarbons (for which it is well known that fragments containing more than four carbon atoms are relatively less abundant) may be relevant

here. However, a much more extensive series of compounds would have to be tested before such far-reaching speculations could be reasonably entertained.

One possible reason for the discrepant alkane recoveries between diffusion and premixed mode could be related to the way in which the molecules contact the different flames. Note, for comparison, that in the design of the conventional FPD diffusion flame, a mixture of column effluent and hydrogen fuel flows around the central tube that supplies the air (and upon which the visible flame is situated). In typical FPD operations, the outer flow is often much larger than the inner one. This leads to a smooth laminar flow profile, whereas the reverse situation creates more turbulence and mixing [20]. Thus it may be possible that some compounds from the GC column merely skirt the flame and thereby escape fragmentation. Such a “blow-by” effect is also theoretically possible in the diffusion flames of the reactor, and may even be slightly more pronounced at the edges and corners of the burner head (see figure 1). However, when colored by a sulfur compound, the blue flame disc appeared perfectly even and horizontal, with no apparent anomalies around the periphery. One would thus assume that if “blow-by” does indeed occur to a significant extent, it may be less prevalent in this reactor than in some FPD constructions.

Certainly some radicals continue to exist beyond the visible boundary of the flame (e.g., H atoms are present at concentrations much above their recombination equilibrium value). Under these conditions, hydrocracking may exert greater effects on larger molecules and, in particular, hetero-organic compounds. This would be in agreement with table 1, and also with the results of doping experiments carried out above an FPD

flame [21]. By contrast, the compounds processed by the premixed flame (figure 4) were transported directly into its primary reaction zone, thus having a much greater, and more equal, probability of being decomposed.

The degradation of alkanes by H atoms in flames has been known for some time [22,23]. Studies involving the air-rich flame of the FID have shown that hydrocarbons are largely, if not completely, pyrolyzed to methyl or methane fragments in the hydrogen atmosphere just beneath the flame, and also within parts of the flame itself [24,25]. These processes were postulated to be responsible for the FID's "equal-to-carbon" response. Clearly, the flames of the FID and the FPD are not directly comparable, since they differ in their overall stoichiometry (i.e. air-rich *vs.* hydrogen-rich) and temperature (i.e. high *vs.* low). Yet in the FID the analytes are forced through the primary reaction zone, similar to the premixed flame of this study. Thus, the initial hydrocarbon degradation observed in the FID, and like processes in the reactor, may be influenced in comparable ways by the mode of analyte introduction into the flame.

## CONCLUSIONS

A multicapillary burner was constructed for (primarily) fuel-rich operation at low temperature and high throughput, in order to study chemiluminescent flame processes, particularly those of the hydrogen-rich FPD. Through 37 capillaries carrying air, intimately surrounded by 147 capillaries carrying hydrogen, the reactor provides stable flames over a wide range of gas compositions, from about 100 to over 1000 mL/min of hydrogen and from about 400 to over 1000 mL/min of air. Under the hydrogen-rich conditions simulating an FPD flame, visual observation of sulfur chemiluminescence

shows a remarkably even flame disc across the flat burner head. Flow conditions for maximum carbon response are similar for the reactor (per air capillary) and the conventional FPD, suggesting that the reactor allows the investigation of typical FPD processes on a much larger scale.

Initial experiments performed with the reactor indicate that hydrocarbons fragment to very different degrees in the hydrogen-rich diffusion flame, and that those with higher carbon numbers (i.e. those of larger size and lower volatility) are much more strongly degraded. In stark contrast to the diffusion flame, a premixed flame of the same gas flows was found to decompose these hydrocarbons to an overall similar and much greater extent. Organic sulfur, nitrogen, and oxygen compounds were decomposed almost entirely, in both hydrogen-rich diffusion and premixed flames. These findings strongly suggest that in the typical analysis of complex samples by the FPD, a significant amount of the volatile sample matrix (i.e. of the compounds that quench analyte luminescence) may be present as intact molecules. This permits, *inter alia*, the consideration of relatively large molecules collisionally deactivating the electronically excited state of the analyte. However, how quenching actually occurs - whether through energy transfer to molecules or their fragments from the excited analyte, or through energy transfer from the energetic flame species directly or indirectly responsible for analyte excitation - is not addressed by the current experiments.

While these preliminary studies have led to some interesting observations for the behavior of organic compounds in a hydrogen-rich diffusion flame, much more work would need to be done with the reactor in order to establish mechanisms and interpret

these in terms of the analytical characteristics of the FPD. For the more immediate purpose of constructing a fuel-rich flame system of high throughput in order to investigate the chemistry of the conventional FPD, the developed reactor performed to our satisfaction and provided a simple and inexpensive method for studying the behavior of organic compounds in some unique types of flames. As well, such a device may yet prove useful in spectral studies, by producing greater emission intensity for the unidentified emitters of those elements that yield only a low photometric response in the FPD. Further afield, the reactor might also serve synthetic aims, by allowing the collection of products from radical-radical or radical-molecule reactions in and/or above its fuel-rich flame.

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**TABLE 1: Survey of Analyte Decomposition in the Reactor**

<b>Compound</b>	<b>Number of Carbon Atoms</b>	<b>Recovery From Flame (%)</b>
n-pentane	5	82
n-hexane	6	79
2-methyl pentane	6	74
3-methyl pentane	6	80
n-heptane	7	58
n-octane	8	32
1,7-octadiene	8	18
1-octyne	8	13
n-nonane	9	23
n-decane	10	2
n-butylbenzene	10	3
iso-butylbenzene	10	7
sec-butylbenzene	10	6
tert-butylbenzene	10	11
benzene	6	73
cyclohexane	6	74
cyclopentane	5	76
n-butylether (O)	8	5
tetrahydrothiophene (S)	4	7
pyridine (N)	5	10
piperidine (N)	5	9

**FIGURE CAPTIONS**

- Figure 1:** Top view of the multi-capillary burner head indicating the respective tubes for air (filled circle) and hydrogen (empty circle).
- Figure 2:** Schematic representation of the assembled reactor.
- Figure 3:** Flows (mL/min) of hydrogen and air through the reactor that produce a stable diffusion flame. The temperatures indicated for each region are a) <300 °C, b) 300-400 °C, c) 400-500 °C, d) 500-700 °C, and e) >700 °C, as measured from the same point within the reactor close to the surface of the burner head. See details in the text.
- Figure 4:** Recovery of a series of n-alkane molecules introduced into the reactor operating with 1400 mL/min of hydrogen and 1000 mL/min of air, in either the diffusion flame (circles) or the premixed flame (triangles). See text for details.

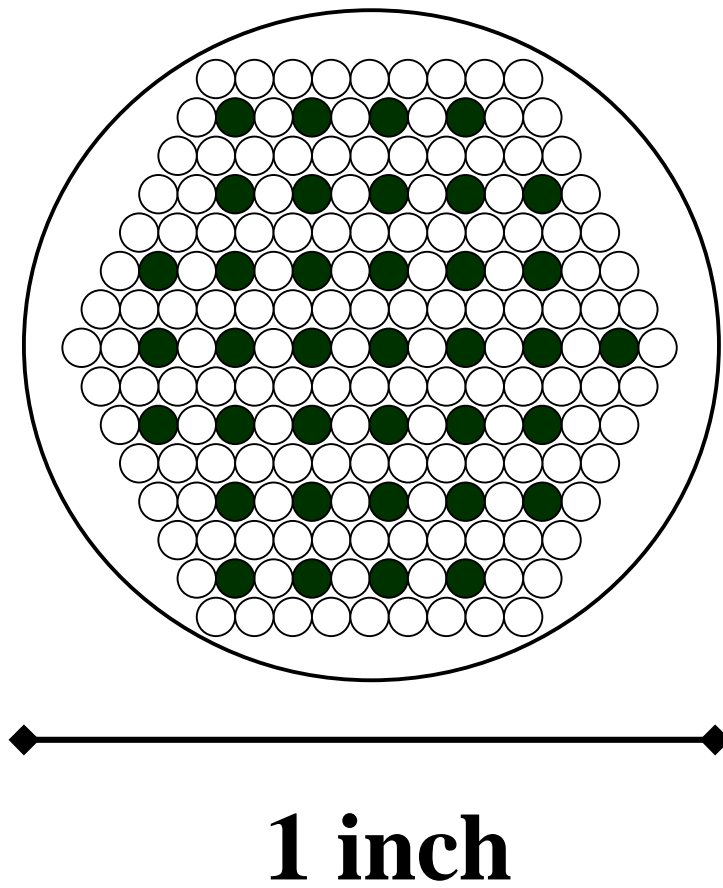


Figure 1

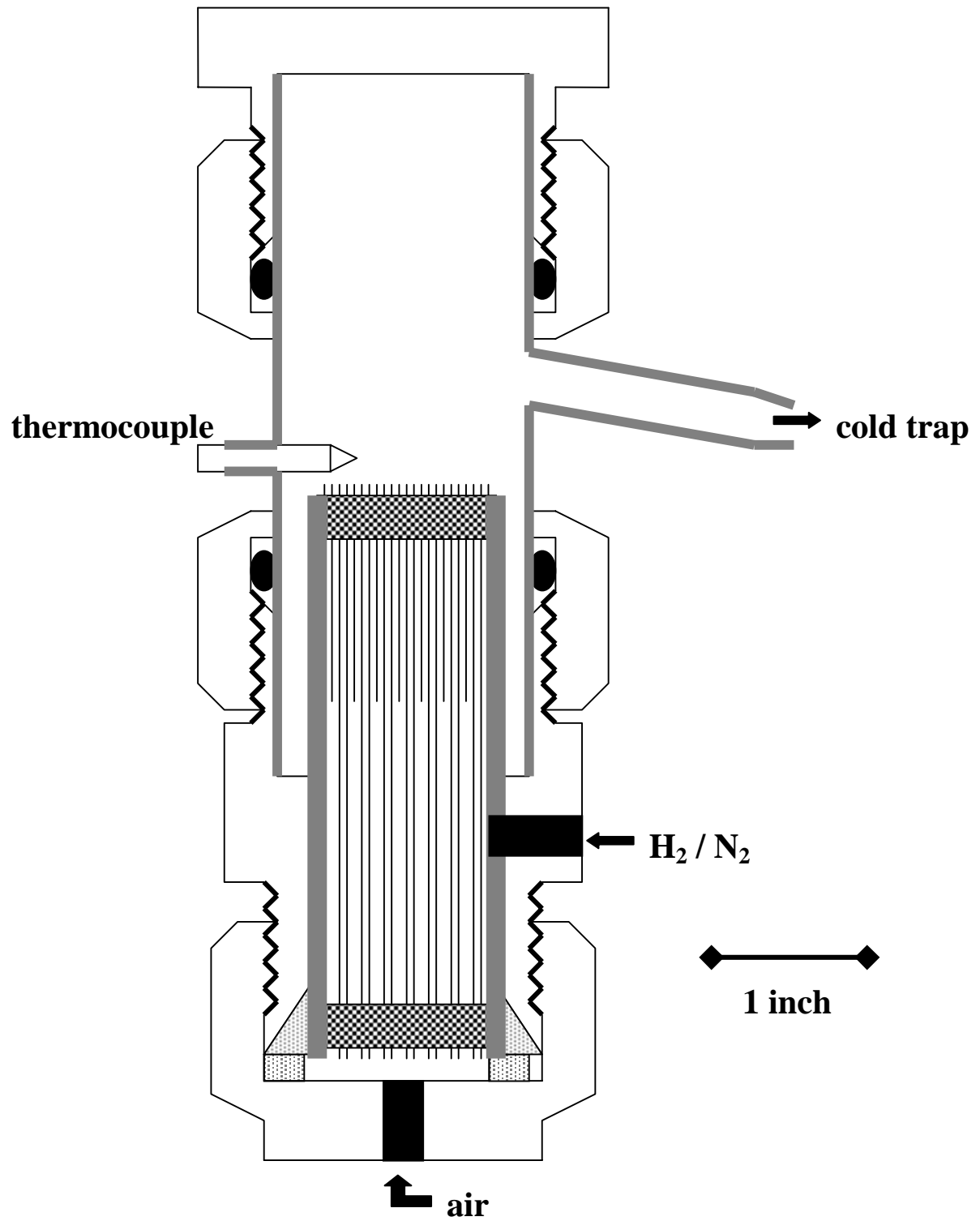


Figure 2

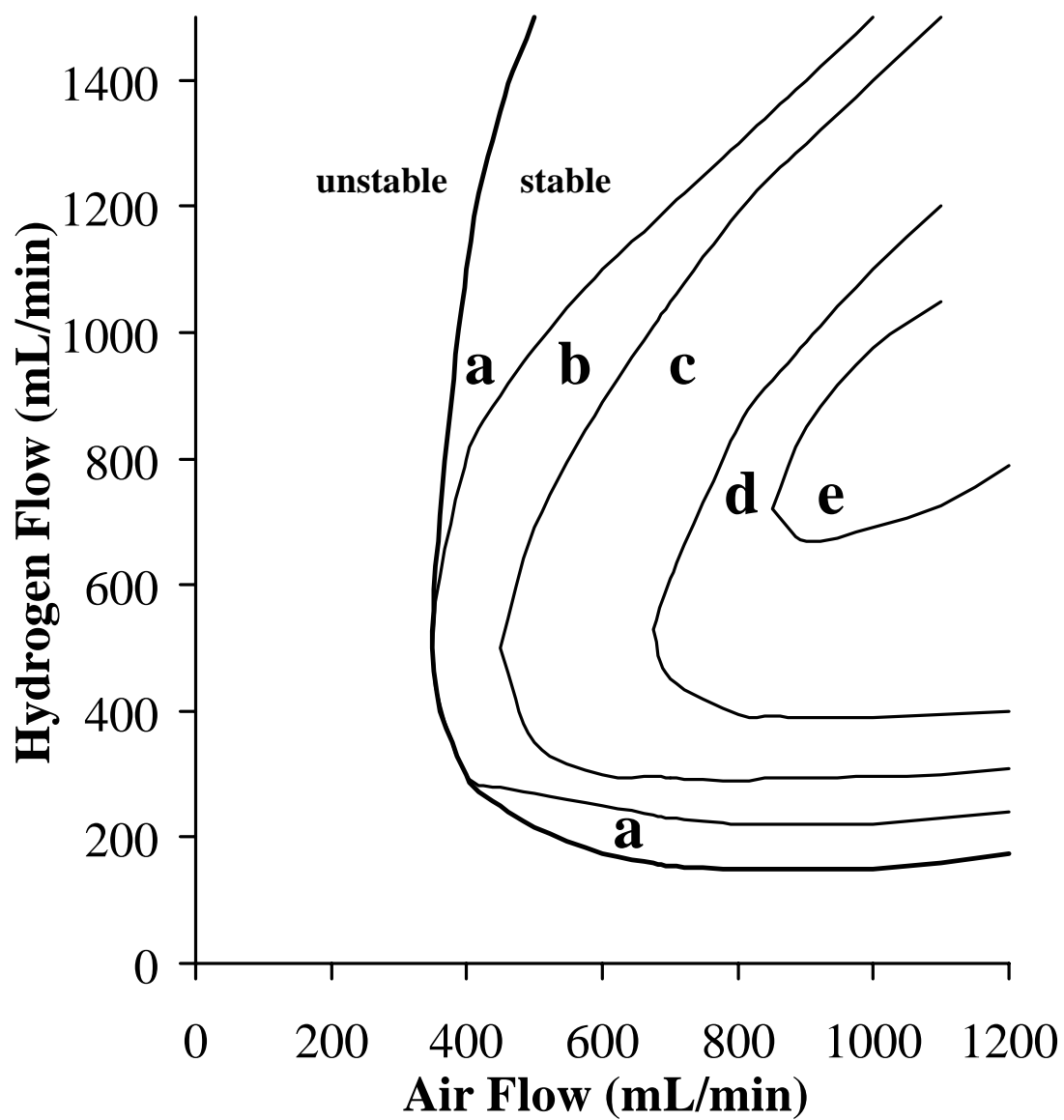


Figure 3

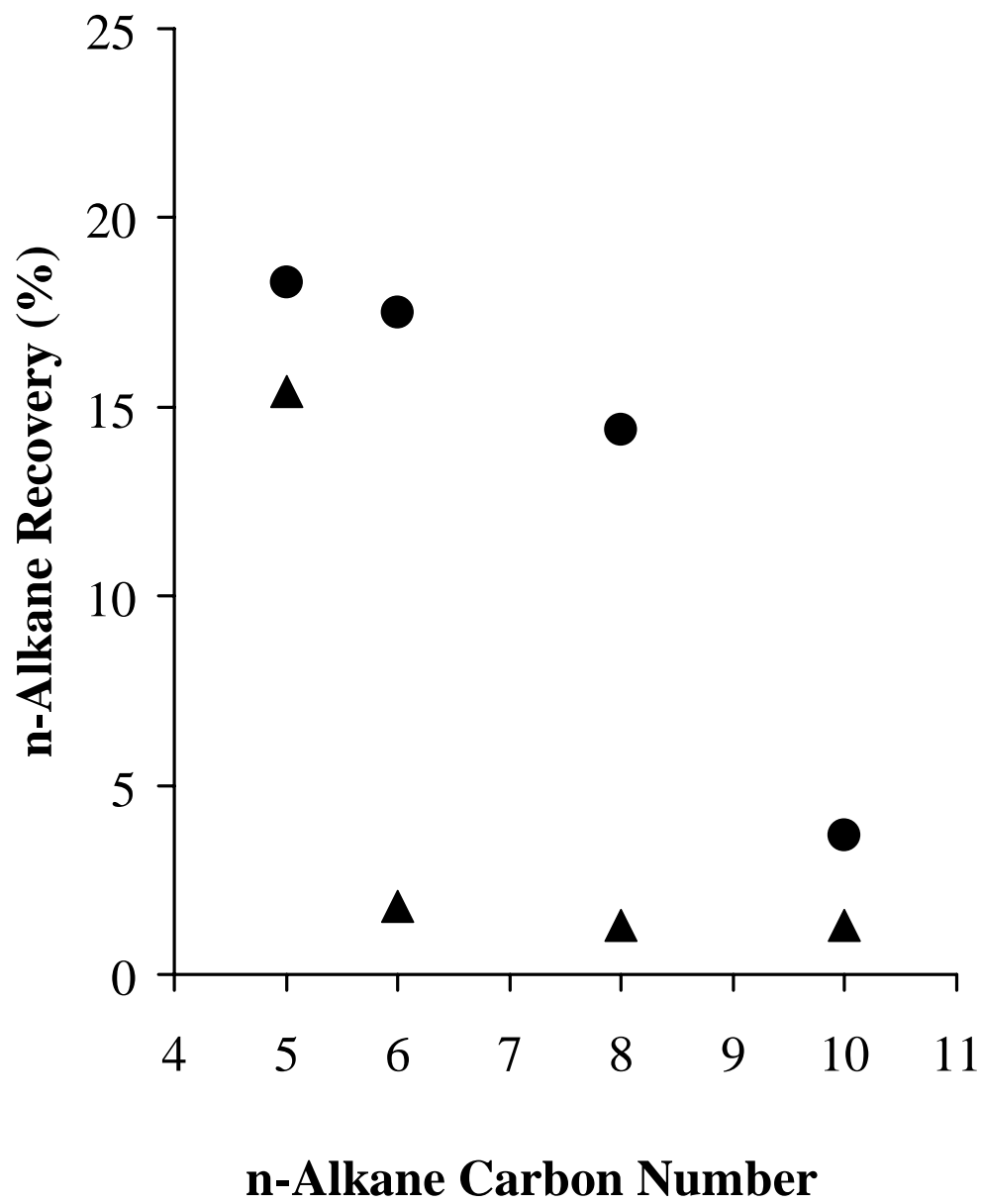


Figure 4