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# Reactive-flow luminescence detector for gas chromatography<sup>☆</sup>

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## Abstract

A stable, several centimeters-long luminescent column is easily formed by a hydrogen–air mixture ascending through a glass capillary toward a glow-sustaining flame on top (which combusts the excess hydrogen with auxiliary air as a flame ionization detector). This encased glow can be used for the photometric determination of gas chromatographic effluents of sulfur and phosphorus, in what may be termed a “reactive-flow detector” (RFD). The RFD behaves in many —though not in all— respects similar to the well-known flame photometric detector (FPD). This manuscript reports analytical figures-of-merit for an RFD prototype that are as good as, or better than, those of a typical FPD.

## 1. Introduction

This study describes a new detector for gas chromatography (GC), which mimics some of the properties of much older and well-established GC detectors. Its concept hails from a general study [1,2] of the survival/transformation rates of organic molecules in a multi-capillary, high-capacity reactor. That reactor supported, enclosed, and compared low-temperature hydrogen–air flames of many varieties: fuel-rich and air-rich, diffusion and premixed, doped and undoped, etc. Effluents from the reactor were collected and analyzed by GC for intact molecules.

Two among the several processes this study attempted to explore were the formation and excitation of small molecules like  $S_2$ , HPO, SnH, etc.; and the peculiar type of quenching that

befalls such emitters in the presence of hydrocarbonaceous materials. This quenching seriously hampers the use of the flame photometric detector (FPD) [3–9] and related analytical devices. Accordingly we often used gas streams doped with small amounts of sulfur compounds as probes of flame shape and conditions prevailing at the reactor’s multicapillary burner head.

To gain further insight into the stability of flames at capillary orifices, single jets were also used. These jets were made of glass. Glass jets in open and encased versions could be produced fast, cheap, and in the laboratory; they were relatively inert; and they revealed the location of flames by the orange atomic emission of sodium traces emanating from their hot surfaces. Owing to the great general importance of combustion processes and various forms of spectroscopy, tomes are available on the physical behaviour, optical characterization, and analytical use of multifarious flames (cf. [9–17]).

While working with capillary glass jets, we

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noticed that premixed gases would often form elongated glows; glows that were situated beneath (and were dependent on the presence of) stable flames burning on top. Typically, such glows would extend over 1 to 4 cm in capillaries of 1.5 to 3 mm I.D., and would fill the available volume between the upper rim of the capillary and some lower restriction. If, however, a true flame (as judged by shape and heat, i.e. by the attendant sodium emission) would establish itself at the restriction, the glow above it would vanish.

The latter situation (though not used in, and of no direct relevance to, the current study) calls to mind the “separated” flame described by Smithells and Ingle [18] more than a century ago. A similarly configured hydrogen-flame burner, cooled to enhance the Salet effect of the divorced  $S_2$  and HPO emissions, has in fact been put to good spectral and analytical use [9]. Tongue firmly in check, the by far most detailed, trustworthy and readable monograph on the flame spectroscopy of non-metals has even suggested that “the device would make a lovely ornament for restaurant tables in place of the usual candle” [9]. Present some stretch of imagination, its design might also have served as forerunner of today’s dual flame photometric detector (FPD) flames [19,20]. Yet, to our knowledge, a “glow” (as we describe it here) was never found in such devices—not surprisingly so if one considers the *dual-flame* design, as well as the dimensions, materials and operating conditions—of the Smithells separator.

Our glow used a hydrogen-rich premixture, thereby raising the question whether it is the typical premixed flames that should be considered its forerunners or that could serve as its points of reference. Premixed low-temperature hydrogen flames have indeed been used for molecular luminescence, but they proved less efficient than diffusion flames [21]. In exploratory studies by our own group, premixed single flames (produced by fitting typical FPD jets with perforated hollow caps) performed sometimes similar to, but never better than, the original diffusion flames [22]—and they were harder to control. The only other device that to our

knowledge used flame gases premixed (though not premixed with the column effluent), was the welder’s torch FPD design of Moye [23].

Thus we are not aware of any case where glows similar to ours have been observed; much less where, containing analyte, they have been used to analytical ends. However, the range of interests that may have produced such glows is very large indeed, and we stand to be corrected on our presumption of absolute novelty. For instance, typical plasma afterglows and certain other low-pressure gas-phase chemiluminescences (cf. [24–28]) may be considered distant cousins to the ambient-pressure premixed hydrogen–air glows encountered here. Our glows may also be collateral relatives—in kinetic principles if not in initiation, composition and spectral performance—to the “pre-ignition glows” and “cool flames” {slow, luminescent oxidations of hydrocarbons to peroxides, aldehydes, etc. (e.g. [10,15,17])} of classical spectroscopy. Yet there does not appear to have existed any kindred (much less any legitimate next-of-kin) device to the glows described here.

## 2. Experimental

The metal jet of the flame ionization detector (FID) on an old Tracor Model 550 GC was replaced by a borosilicate capillary. The capillary had an inner diameter of 1.8 mm and a restriction of 1 mm I.D. about 3.5 cm down from the top. (These dimensions are typical and, for the most part, not crucial. Quartz capillaries also worked well.) When present in excess, background luminescence was suppressed with heavy injections of tetraethyllead [29]; deposits were removed with injections of Freon-113 ([cf. [30]). (Usually these tricks work, occasionally they do not).

For initial experiments, the outside of the capillary was painted with high-temperature black paint—of the type used on car exhausts—leaving a ca. 0.5 cm broad ring untouched (painting the capillary later turned out to be unnecessary). A 6 in.  $\times$  1/4 in. O.D. (1 in. = 2.54 cm) glass image conduit (No. 38307; Ed-

mund Scientific, 101 E. Gloucester Pike, Barrington, NJ 08007-1368, USA), shielded from light by a protective metal pipe, was inserted through the detector wall and moved against (the transparent section of) the capillary. The other end of this optical feed-through terminated vis-à-vis the photocathode of Hamamatsu 268 or 374 photomultiplier tubes (PMTs with nominal wavelength ranges of 300 to 650, and 300 to 850 nm, respectively), leaving a gap wide enough to insert an optical filter if desired. The PMT housing could be easily opened, giving the operator the chance to observe the reactive flow through the image conduit. The detector housing was reconstructed to prevent ambient light from entering, but no effort was made to change the Tracor detector base and FID-type design, or to minimize dead volume. Fig. 1 offers to-scale schematics of this first reactive-flow detector (RFD) version. (It does so mainly to placate an astute referee, provide an accurate record, and please the avid reader; however, an optimized RFD built from scratch would obviously have been different).

Test compounds were separated on an already installed, old 2 m × 1.8 mm I.D. borosilicate

column, packed with 10% Apiezon L on Chromosorb W, 45–60 mesh (roughly 350–250  $\mu\text{m}$  particle diameter), and purged by a nitrogen stream of ca. 12 ml/min. The signal from the Tracor electrometer was routed through a laboratory-made three-pole filter set at an resistance/capacitance (RC) = 0.5 s time constant, before being displayed on a strip-chart recorder. Other props and procedures were conventional as well; where important they will be described in the text or in the captions to the figures.

### 3. Results and discussion

Our glows, which developed easily inside the capillary carrying an FID-type flame on top, would turn brilliantly blue in the presence of small amounts of sulfur. Their visual appearance was certainly unlike that of any conventional flame—difficult, however, it may be to define what does and what does not constitute a “flame” [10]—but of something that we, for lack of a better term, like to refer to as “reactive flow”.

This reactive flow is not self-sustaining: it

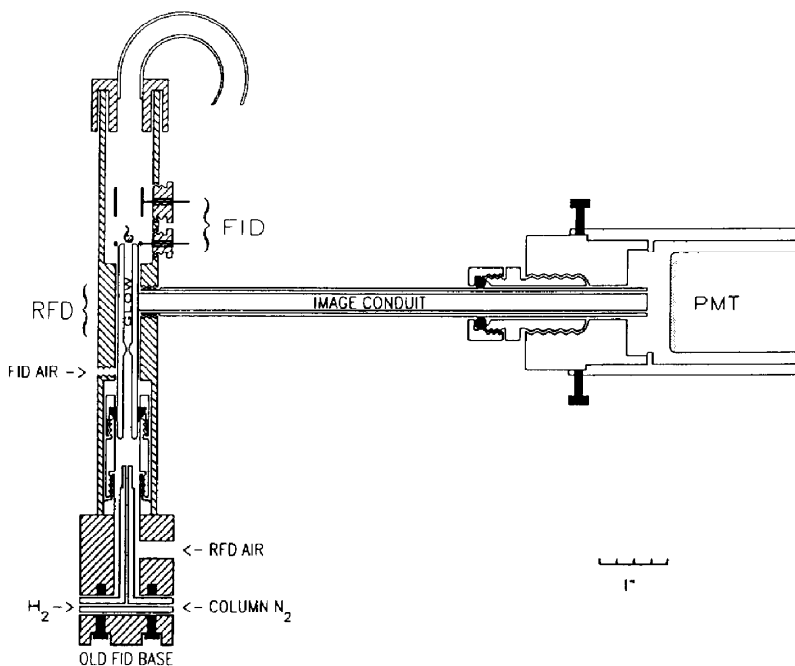


Fig. 1. Schematic of RFD prototype.

requires continuous access to a stable flame. A both tautological and talkative description of the phenomenon may assert that steady-state free-radical reactions are initiated and supported by the stable flame at the upper border of the reactive flow, and extend downward through the capillary to the lower border formed by the nearest stabilizing restriction; in a process that is sustained by the counter-reactionary mass movement of the premixed, excited gases.

As mentioned before, the reactive flow can give birth to a second flame at the restriction (present a suitable composition and supply rate of the hydrogen–air mixture). Yet if it does, it is quickly starved to death by its own offspring. Sans metaphor, the reactive flow is simply extinguished by a flame burning *below* it.

But still, the reactive flow needs a flame *above* it. If the flame atop the reactive flow is slowly suffocated—i.e. by carefully diminishing the auxiliary air supply—the reactive flow dies with it. The reactive flow may also succumb to, say, a sudden influx of solvent. But that is merely *petit mort*: As the injection solvent enters, the reactive flow appears to leap out of the capillary into the upper flame, which in turn becomes large and bright. Then, with the solvent gone, the flame shrinks and dulls again, sending the reactive flow back into the capillary. The extreme stages of this process are often accompanied by characteristic sounds.

Oscillations and singing flames are, of course, well-known phenomena, even in chromatographic detectors [31,32]. In the RFD, such events occur only under extreme, i.e. gas supply boundary or analyte overload conditions. Our typical reactive flow was silent and did not visibly fluctuate (as judged by the human ear, the human eye, and the oscilloscopic trace from a PMT); it was tolerant of considerable variation in flow conditions; and it was stable in time.

That a typical reactive flow is free of fluctuations (but that it can be easily made to fluctuate if so desired) is mechanistically interesting and analytically important. It is easy to calculate the minimum (i.e. the fundamental, quantum-related) noise from the photon flux [33]. A calculation of that kind showed that the RFD noise

consisted, predominantly if not entirely, of photon shot noise. By definition, therefore, fluctuation noise was absent.

This, plus the unexpected brightness of the blue  $S_2$  bands in the reactive flow (though in part due to visual compression by the capillary) suggested that we explore the RFD's analytical potential with organosulfur and, because of its striking similarity with the FPD, with organophosphorus compounds as well.

Fig. 2 shows the typical gas supply range for a reactive flow, as judged by the resulting signal-to-noise ratio ( $S/N$ ) for test compounds of sulfur and phosphorus. Clearly, reactive flows could be established at quite a variety of conditions. In the upper portions of the curve, the hydrogen input was about two thirds in excess of stoichiometric. (Note that a certain excess of hydrogen was necessary to support the top flame and thereby provide radical sustenance to the reactive flow.) The thermocouple temperatures at four different flows of Fig. 1 were all in the 200 to 230°C range. (These measurements were done with the detector housing removed, the ther-

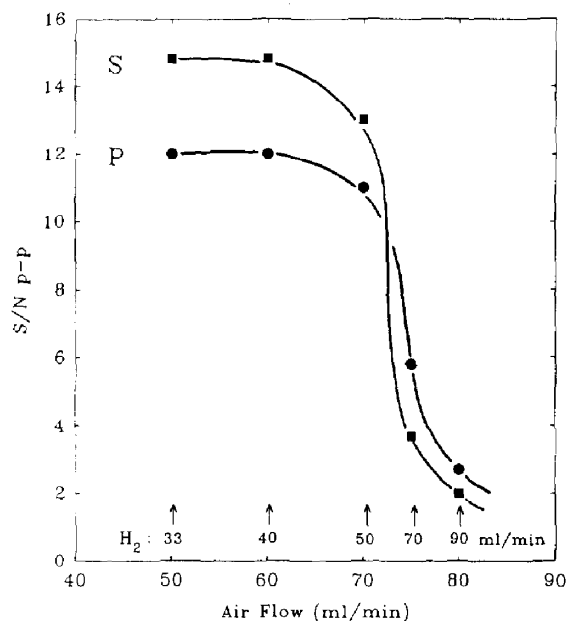


Fig. 2. Response of sulfur and phosphorus test analytes in reactive flows of different gas velocity and composition. No optical filter, R-268 PMT.

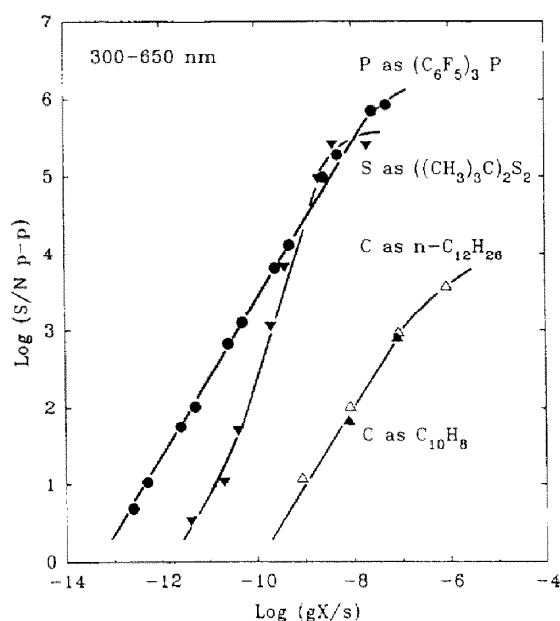


Fig. 3. Calibration curves of phosphorus ( $X=P$ ), sulfur ( $X=S$ ) and hydrocarbon ( $X=C$ ) analytes without optical filter. Hamamatsu R-268 PMT. Gas supply rates: hydrogen 40, air 60, nitrogen (from column) 12 ml/min. Linear portions drawn at exactly slope 1 (for P and C) or exactly slope 2 (for S).  $N_{p-p}$  is the peak-to-peak noise of the baseline, with drift and spikes excluded.

mocouple tip touching the reactive flow, and only minor heat emanating from the detector base.)

The most important criterion for setting gas supply rates was the creation of the reactive flow itself. Changing gas rates within its stability band (region of existence) contributed but little to its

relative sensitivity for sulfur and phosphorus. If this should be confirmed as a characteristic trait of the RFD in broader-based future investigations, the detector could be used at one and the same condition for all elements to which it responds. That would greatly simplify analytical methodology, albeit at some cost in selectivity. (Note that, with the possible exception of Joonson and Loog's dual-chamber model [34], most FPDs use distinctively different gas supply rates for sulfur and phosphorus determinations [4].)

Fig. 3 shows calibration curves of sulfur and phosphorus analytes, and allows their comparison with aliphatic and aromatic hydrocarbons, in the "open", i.e. filterless mode. The straight-line portions of these log-log calibration curves are deliberately drawn at slopes of precisely 1 (for P and C) or 2 (for S).  $N_{p-p}$  is the peak-to-peak noise of the baseline, with spikes and drift excluded (cf. [35,36]);  $S$  is the signal (peak height).

Graphically, the calibration curves end at the common chromatographic detection limit of  $S/N_{p-p} = 2$ . If the  $S/RMS = 3$  detection limit is preferred—where RMS (root mean square) denotes the standard deviation of the baseline noise—the plot should be extrapolated farther down to an ordinate value of about  $-0.3$  [35]. Table 1 charts these limits and, of more original appeal, Fig. 4 pictures them as peaks of sulfur and phosphorus rising out of the baseline noise.

The most interesting aspect of the results shown in Fig. 3 and Table 1 emerges from their comparison with the characteristic performance

Table 1  
RFD detection limits

Compound	X	At $S/N_{p-p} = 2$		At $S/RMS = 3$	
		g Compound	gX/s	g Compound	gX/s
Di-tert.-butyl-disulfide	S	$7 \cdot 10^{-11}$	$2 \cdot 10^{-12}$	$2 \cdot 10^{-11}$	$5 \cdot 10^{-13}$
Tris(pentafluorophenyl)phosphine	P	$2 \cdot 10^{-11}$	$8 \cdot 10^{-14}$	$4 \cdot 10^{-12}$	$2 \cdot 10^{-14}$
Naphthalene	C	$3 \cdot 10^{-9}$	$2 \cdot 10^{-10}$	$8 \cdot 10^{-10}$	$5 \cdot 10^{-11}$

$S$  = Signal (peak height);  $N_{p-p}$  = peak-to-peak noise, with drift and spikes excluded; RMS = root mean square (the standard deviation in a Gaussian distribution).

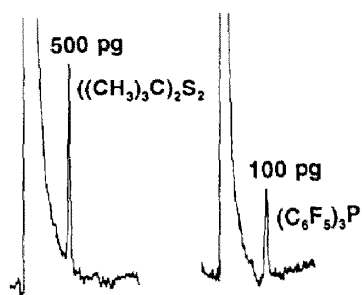


Fig. 4. Peaks of tris(pentafluorophenyl)phosphine and di(*tert.*-butyl)disulfide near their detection limit. The RC filter time constant is 0.5 s. Conditions as in Fig. 3.

of the FPD. Dressler states in his monograph [4] that "the minimum detectable mass rate ranges from about  $1 \cdot 10^{-13}$  g/s to  $2 \cdot 10^{-12}$  g/s of P for phosphorus compounds and from about  $2 \cdot 10^{-12}$  g/s to  $5 \cdot 10^{-11}$  g/s of S for sulphur compounds" (his reference numbers deleted). In other words, the minimum detectable amounts in the RFD are equal to or better than those of the FPD. (They are, however, notably worse than those of the "pulsed-flame photometer", the "atomic emission detector", the "sulfur chemiluminescence detector", and various related detection devices [8,24,28,36–43]).

It may be noted that, at present, the RFD remains a simple prototype, designed to evaluate analytical potential in the shortest possible time and with the least instrumental effort. For instance, the type of inexpensive light conduit it uses restricts the optical range to the visible (whereas some of the strongest S<sub>2</sub> bands lie in the UV). It also samples only a fraction of the light generated by the reactive flow.

The shapes of the RFD phosphorus and sulfur calibration curves typically match those of the FPD. The bend-off to a first-order slope at the bottom of the sulfur curve is a common occurrence [44]; in fact, it can already be found in the seminal FPD paper by Brody and Chaney [45]. Also as in the FPD, temperature programming causes only minor, if indeed any, baseline drift.

The few data points for *n*-dodecane and naphthalene were added to Fig. 3 as an afterthought,

just to indicate how strongly (or weakly) matrix hydrocarbons might show up in the RFD. As is well known, aromatics respond in the FPD stronger (and with a different spectrum [35]) than aliphatics. This seems not to be the case here. While that matter is of only minor interest under the present circumstances, it may well warrant careful study in a future context.

One (but not the only) reason for such future study is that our measurements of hydrocarbon survival in hydrogen-rich flames—using the "reactor" mentioned in the Introduction—showed considerable differences between diffusion and premixed systems. Whereas in diffusion flames compounds with high carbon numbers were less likely to survive intact than compounds with low carbon numbers, such discrimination was not found in premixed flames. Also, the overall survival rates of organics in premixed flames were generally much lower than those in diffusion flames of the same flow and overall stoichiometry [2] (this may, however, have been due to differences in local temperature as well as local gas-phase composition). Yet, much more work would need to be done on such systems before clear connections between the large-volume reactor experiments, the typical performance of the FPD, and the still largely unexplored behavior of the RFD could be established.

In analytical practice, sulfur and phosphorus luminescences in the FPD are monitored through interference filters. We therefore include calibration curves for two popular wavelengths in Figs. 5 and 6. No unexpected features appear to be present. The minimum detectable amounts are slightly worse than under filterless conditions, as one would expect [46].

We also include, via Fig. 7, the calibration curve for "linear sulfur" [47] (HSO [48]). Increasing the relative response of the red HSO vs. the blue S<sub>2</sub> bands through the use of different hydrogen–air ratios, while helpful in the flame, proved of only limited value in the glow. Instead, the RFD was operated at an overall larger supply rate of reactant gases; an approach that appeared to depress S<sub>2</sub> slightly more than HSO. Also, a red-sensitive PMT was used and two

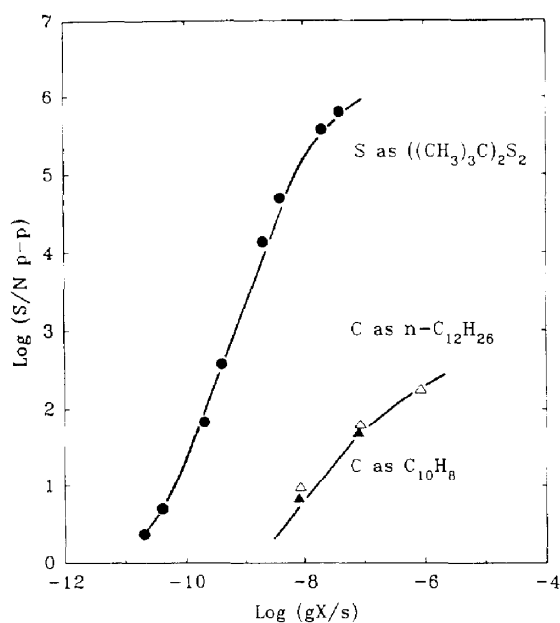


Fig. 5. Calibration curves of sulfur and hydrocarbon analytes through a 405-nm narrowband interference filter of 11 nm bandpass. Other conditions as in Fig. 3.

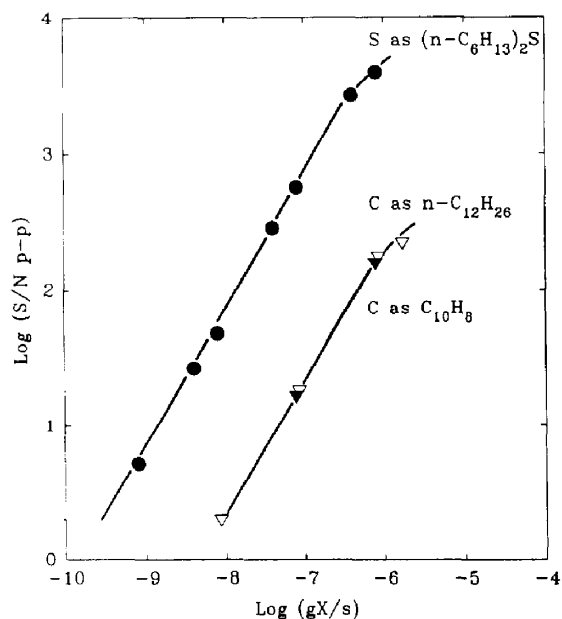


Fig. 7. Calibration curves of sulfur ( $X = S$ ) and hydrocarbon ( $X = C$ ) analytes through a 750-nm wideband interference filter of 40 nm bandpass, with a 600-nm longpass colored-glass filter added for increased blocking. Hydrogen 100, air 85 ml/min; Hamamatsu R-374 PMT. Both lines are drawn at exactly unity slope.

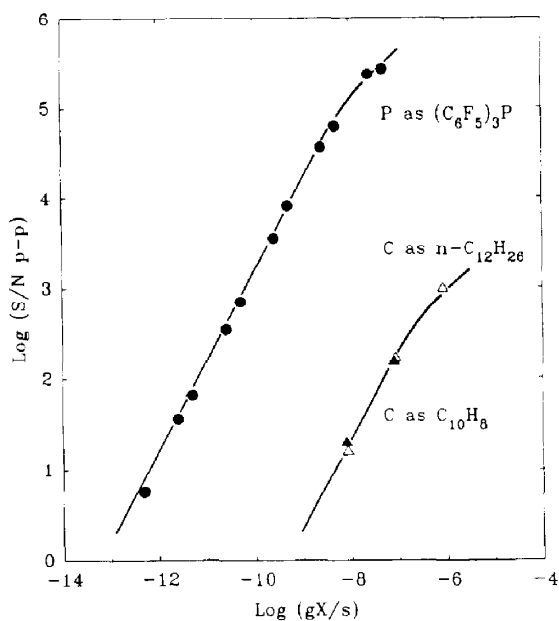


Fig. 6. Calibration curves of phosphorus and hydrocarbon analytes through a 524-nm broadband interference filter of 40 nm bandpass. Other conditions as in Fig. 3.

optical filters restricted the light input to the  $0 \rightarrow 1$  750-nm band of HSO ( ${}^2A' \rightarrow {}^2A''$ ) [48]. The HSO luminescence was not as strong in the glow as it had been in the FPD flame [47]; also, its selectivity against carbon was lower. It is interesting to note in this context that, in the RFD, carbon compounds give rise to conventional peaks, while in the FPD they usually produce negative peaks (decreases in baseline luminescence) at wavelengths above, very roughly, 600 nm.

Taken together, the RFD behavior vis-à-vis sulfur, phosphorus and carbon suggests that the glow responds frequently, though not always, in a manner similar to that of the FPD. But why? It could be argued, of course, that the FPD flame should contain a region similar in composition to the reactive flow. Yet the existence of such a region is neither a necessary nor, obviously, a

sufficient criterion for observing luminescence. When, in an unrelated earlier study, sulfur compounds were introduced into an FPD from the top, strong sulfur response could still be obtained [49,50]. Since both the point of introduction and the luminescent region were situated clearly above the (visible) flame region in those early experiments, we are forced to conclude that high-energy species (e.g. hydrogen atoms) had to transcend the visible flame in large enough numbers to excise a significant fraction of sulfur atoms from the analyte molecules above {and perhaps excite (cf. [3,5,9]) them to the  $S_2(B^3\Sigma^-)$  [51] state}. By general principle as well as optical analogy, such free radicals (H, OH, peroxy-type structures, etc.) must likewise be present in reactive flows.

The suggested excision scenario is also in general agreement with the measured survival rates of various hetero-organics (containing N, O or S) en route *through* the low-temperature, hydrogen-rich flame of the above-mentioned reactor: their survival rates are much lower than those of the pure hydrocarbons [1,2]. It is also possible to introduce test compounds *above the flame of the reactor* (in fact, that is what the reactor was in part designed for). However, no thorough study of analyte survival under such conditions has yet been carried out.

Nor, indeed, have the contents of typical *reactive flows* been collected and analyzed for residual molecules of, or products from, hydrocarbons and hetero-organics of interest. These analytes/reagents are easily added as vapors—via a continuous doping stream or as chromatographic peaks—to the premixed hydrogen–air supply gas. Such an “RFR” (a reactive-flow reactor) may indeed prove attractive to some of the earlier-mentioned areas of spectral or kinetic cognates; it may even appeal to synthetic interests.

That would certainly be helpful: the RFD is in dire need of basic understanding (a need not unlike that of the FPD; never mind the latter’s much longer history [4–9]). Similar to many other chromatographic detectors that appear to represent simplicity itself—and certainly similar

to the FPD—the RFD may yet turn out to be much appreciated before it is much understood.

#### 4. Note added in revision

Our reviewer suggested that we “discuss the applicability of this detector to capillary GC”. Aware of the dinosaurian aura of packed columns, we are pleased to oblige. We do not, however, want to test the RFD with capillary columns: for us, packed columns are easier to use. More importantly, still, they offer a bigger challenge to detector performance because of their greater bleed, their larger solvent volumes, their broader analyte peaks. Thus, the RFD should, if anything, perform better with capillary than with packed columns.

That leaves only one problem to be addressed in this context: the detector speed (cell time constant). Some detectors broaden sharp peaks. Will the RFD do likewise? Judged from Fig. 1, considerable deadspace exists near the detector base. To reduce it is easy: by a tighter construction; by combining the hydrogen–air premix with the column effluent within the capillary flow regime; or by simply inserting the capillary column right up to restriction. But it would not be as easy to reduce the volume of the glow itself. Could *it* contribute to peak broadening?

The glow used in this study is a cylinder of 1.8 mm diameter and 35 mm length—of which, say, 10 mm are within view of the 6-mm diameter image conduit. The typical supply flow-rates are hydrogen 40 and air 60 ml/min. That amounts to a detector cell constant of ca. 15 ms, or to an analyte residence time within the whole reactive flow region of ca. 50 ms—far shorter than the chromatographic dispersion of even the sharpest capillary peak.

#### 5. Note added in proof

One of us described briefly the RFD in a recent lecture [52]. In the ensuing discussion it



was noted that a micro-flame ionization detector–radioactivity detector ( $\mu$ FID–RAD) [53], which used a premixed oxy–hydrogen flame, had also monitored photometric flame response. This multi-channel detector should therefore be included in our literature citations (see second page) of *premixed flames*.

### Acknowledgements

The consummate artistry of J. Müller (glassblowing) provided the capillaries for the new detector; the cooperative assistance of M.R. Conrad and C.G. Eisener (machining) succeeded in putting it together; and the cost-conscious adaptations of B. Millier and C. Wright (electronics) helped to monitor its response. Only this full array of Departmental support made our study possible and allowed it to proceed with minimal drain on our much appreciated financial support, NSERC research grant A-9604.

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