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Reactive-flow luminescence with flame ionization detection[☆]

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Abstract

The existence of the glowing, hydrogen-rich column of a reactive-flow luminescence detector (RFD) depends on the presence of a stable, air-rich flame burning at its top. The latter shows flame ionization detector (FID) behavior, despite the fact that it is being fed highly degraded analyte by the reactive flow below. The electrical (and optical) responses of the resulting RFD–FID combination are characterized by model compounds containing CH, O, N, S, P, Sn and Mn. The electrical response is qualitatively similar to that of a comparable FID; although —at conditions optimized for a stable reactive flow and maximum optical emission— it is quantitatively weaker by about a factor of two. The RFD–FID can thus function as a dual-channel detector, with simultaneous, sensitive, and orthogonal responses being offered by the two channels.

1. Introduction

Recently we described a novel type of chemiluminescence-based sensing device for gas chromatography and, for lack of a more descriptive term, called it the “reactive-flow detector” (RFD) [1,2]. Much of its response appears similar to that of the flame photometric detector (FPD); except that quenching by hydrocarbons does not take place in the RFD and, perhaps interrelatedly, that the RFD does not seem to discriminate between aliphatics and aromatics.

Briefly recalled, the “reactive flow” is a luminescent gas column formed by a H₂-rich, hydrogen-air mixture flowing inside a capillary, which

can be monitored photometrically for compounds containing sulfur, phosphorus, tin, manganese and other luciferous species. On top of the capillary, the excess hydrogen is burned off with auxiliary air. This flame on top is necessary: extinguishing it would mean extinguishing the reactive flow beneath it.

The flame thus does yeoman’s duty: it provides the reactive flow with free-radical sustenance, and it gets rid of its excess hydrogen. These chores accomplished, though, it just might become a sensor of its own, generating ion pairs from chromatographic peaks. In other words, its role would be that of an additional flame ionization detector (FID) [3–5] fed directly by the reactive flow.

All this because the flame has one crucial quality: it is *air-rich* and, while certainly not optimized for FID duty, should yield much better ionization performance than the *hydro-*

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gen-rich flame of the FPD. The latter has, of course, been used for its conductivity as well: several FPD manufacturers offer the easily installed and inexpensive option of an electrical channel. Unfortunately, the FPD's electrical background current and its noise are rather large. It is therefore not surprising that the detection limit for carbon compounds by ionization in an FPD-type flame is nowhere near that of the FID proper. (Note, however, that hydrogen-rich—or richer—flames can, under particular circumstances, yield larger ionization currents than typical air-rich flames [6,7].)

On the other hand, many types of FPD-based analyses do benefit from—and may even require—an additional FID channel: for that, the petroleum, perfume, and pesticide industries (to name but three) offer an abundance of examples. There, the column effluent is usually divided between two independent detectors, with all the drawbacks such an arrangement entails in terms of split-ratio constancy, peak correlation, and detection limits. Still, two different detectors are usually preferable to a single detector with two different channels [e.g. 8,9].

In this context, a very recent, sequential-detection development should be mentioned because it might prove competitive with the common parallel-detection approach. A pulsed flame photometric detector has been described in which the hydrogen-rich effluents from one pulse (i.e. a flame or detonation front) flow into a second chamber and are mixed there with additional air, to be recombusted by the subsequent pulse. The electrical conductivity of the second chamber thus provides FID-type response [10].

Our group has for the past few years dabbled in dual- or multiple-channel detector systems for the determination of signal ratios; and for the related, computer-aided generation of subtraction, correlation, and response-ratio chromatograms [11–15]. For this purpose, amplitudinally independent but temporally concurrent channels offer the most basic, most accessible, and most interesting systems to investigate. The already existing flame atop the RFD would fit right in.

The question is only to what qualitative and quantitative degree the reactive flow would de-

liver to the flame the (FID-active parts of) various analytes; i.e. the degree to which the flame atop the reactive flow would be able to respond like a conventional flame ionization detector fed the same (but intact) analyte molecules. Some ionic conductivity could probably be obtained. But how much and from what compounds?

On one hand, the column effluent has to travel a few centimeters in a reactive flow that is chemically corrosive. It is obvious from the generation of mono-, di- and tri-atomic luminescers—including the strong 431-nm $0 \rightarrow 0$ band of CH ($A^2\Delta-X^2\Pi$) from relatively stable compounds such as *n*-dodecane and naphthalene—that the reactive flow has the ability to break analytes apart. On the other hand, if our earlier experience regarding effluents collected from a large-capacity, low-temperature, hydrogen-rich flame reactor [16,17] provides any analogy for the reactive flow, some hydrocarbon molecules could still escape unscathed.

Even if hydrocarbons were to break down completely in the glowing reactive-flow column and never reach the top flame, electrical conductivity might still be obtained there from suitable fragments. The reaction most often considered to provide the FID with its chemiionization response [3–5,18 and references cited therein] is



and CH is a securely established and relatively stable—though, yieldwise, undefined—product of carbon compounds traversing the reactive flow.

As well, the catabolic mechanisms that generate the particular carbon species responsible for the “equal-carbon” response behavior of the FID are still open to debate. To us, the hydrogen-atom induced decomposition [18] seems attractive: if it does indeed represent the main process of analyte fragmentation in the *air*-rich FID flame, then the same analyte in the *hydrogen*-rich RFD flow—or in the *hydrogen*-rich FPD flame—should be even more prone to degrade. We also like to use the concept of H-atom cracking processes as a working hypothesis because it fits some circumstantial evidence

that we managed to obtain in effluent-collecting experiments with the above-mentioned reactor [16,17], and in (unrelated) quenching experiments with the FPD [19–21].

The results of the latter favor, in our opinion, chemiluminescence and quenching mechanisms that are *similar* for most FPD-active elements; for instance mechanisms that both use hydrogen atoms and that hence both correlate with the rapidly interacting, quasi-equilibrium mixture of free radicals in the flame. Oversimplified, this has been described as the quencher quenching the exciting flame rather than the excited analyte [21]. The excitation of optical emitters via the recombination of flame radicals is, of course, a commonly invoked process in “spectroscopic” flames [22–24].

If the (hydrogen-rich) reactive flow leaves some hydrocarbons intact and/or transforms others to reduced single-carbon species, then the receiving top (air-rich) flame should be capable of FID-type response—effective carbon number [3–5,25,26] and all. The purpose of this manuscript is to test this presumption.

2. Experimental

The RFD is the same unit as described earlier [1,2]. The contraption looks very much like the original FID, except for the light guide piercing its side and peering at its reactive flow. Fig. 1 shows in detail the relevant section of an earlier published blueprint [1].

To test the FID properties of the flame that burns the excess hydrogen on top of the RFD capillary, the reactive flow below it is switched on and off, back and forth, as the test compounds are repeatedly injected. This procedure is considered preferable to comparing the output of a separate, conventional FID, since FID response depends very strongly on various constructional and operational details—not just for overall performance but, much more disturbingly, for the relative responses between differently structured compounds [e.g. 4,27, and references cited therein].

For this study, the “run-along” RFD channel

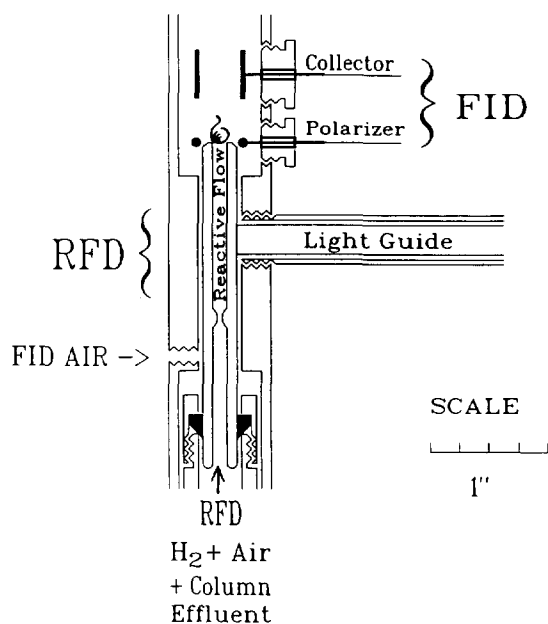


Fig. 1. Detail of RFD–FID, showing the relative positions of optical and electrical points of measurement. 1 in. = 2.54 cm.

is monitored by a Hamamatsu R-268 photomultiplier tube (nominal range 300 to 650 nm) without optical filter. Note, however, that the inexpensive glass image conduit transmits only from (a nominal) 400 nm on [28].

The old Tracor gas chromatograph, Model 550, is used with a 2 m × 1.8 mm I.D. borosilicate tube packed with 10% Apiezon L on Chromosorb W, 45/60 mesh (an ancient column that simply happened to be available), and a typical nitrogen flow of 12 ml/min. Unless stated otherwise, 40 ml/min hydrogen and 60 ml/min air are added to the column effluent before the mixture enters the RFD capillary. The auxiliary air flow (for the FID flame) is kept around 150 ml/min.

3. Results and discussion

The primary question of this study is obviously whether the flame produces chemiionization when carbon compounds enter it *through the reactive flow*. The answer is clearly yes. The only exceptions—as expected—are carbon com-

pounds such as CO that are known to respond only feebly or not at all in the conventional FID.

This raises immediately a series of secondary questions: (1) What is the relationship between the (gas supply) regime under which analytes produce maximum electrical conductivity in the air-rich flame and the one under which they produce maximum optical emission in the hydrogen-rich reactive flow? (2) Does the presence of the reactive flow exert a beneficial or a detrimental influence on the response of analytes in the FID flame above it? How does its effect on analytes compare with that of a hydrogen-rich flame? (3) Does the presence of the reactive flow alter the relative FID responses of different types of compounds, e.g. stable vs. labile, luminescing vs. non-luminescing, oxygen-containing vs. non-oxygen-containing ones? (4) Similarly, what are the analytical figures of merit for the FID flame in the presence and in the absence of a reactive flow? How do they compare in terms of linear range, baseline noise, and detection limit?

3.1. Flame ionization vs. reactive-flow luminescence: regions and trends

Testing FID responses is obviously restricted to conditions at which the reactive flow can exist. Within the stability region of the reactive flow, then, photometric responses for sulfur and phosphorus compounds that had been found strong at relatively low hydrogen and air flow-rates, fell off dramatically at relatively high flow-rates [1].

As shown in Fig. 2, the reactive-flow luminescence of a carbon compound (*n*-dodecane) follows a similar path. So, roughly but still surprisingly, does the flame ionization current. This “(RFD)FID” response is superimposed in Fig. 2 on the photometric RFD profile (which was obtained, simultaneously and gratuitously, by the RFD–FID functioning in the dual-channel mode for which it was designed). Though far from being perfect, the similarity of the two chemically and physically disparate channels is striking. But why *do* the two responses follow similar trends?

Chemiionization and chemiluminescence are

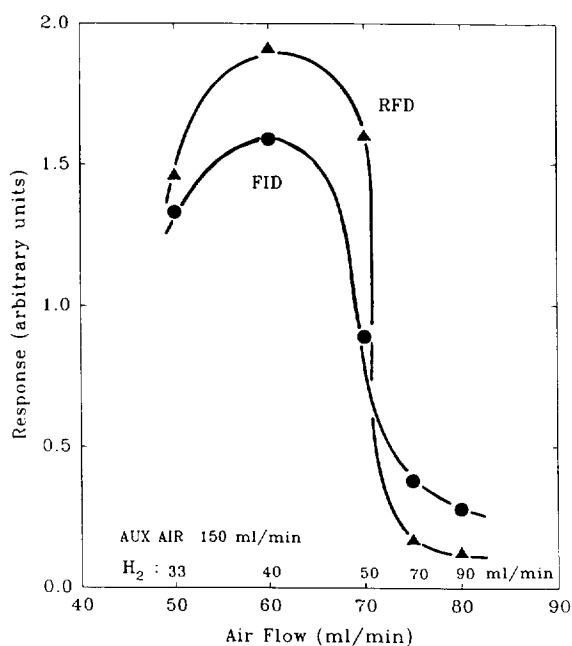


Fig. 2. Simultaneous optical (“RFD”) and electrical (“FID”) responses from 0.10- μ g injections of *n*-dodecane within stability range of reactive flow.

known to correlate frequently in flames [e.g. 4,24]—although the reason for this correlation, more often than not, remains obscure. However, the present case is clearly different in its nature: the chemiionization is observed in the flame, the chemiluminescence in the reactive flow. The RFD–FID thus seems to separate optical from electrical responses: at typical operating conditions, the flame shows only insignificant luminescence compared to the reactive flow; conversely, the reactive flow shows only negligible ionization compared to the flame.

The latter does make sense, at least to a degree. If the chemiionization needs CH (or a similar reactant) to function, and if its product is CHO^+ (or a similar oxygenated product not subject to further chemiionization), then the virtual absence of ionization in the reactive flow indicates that it is possible for CH (or a similar species, or a precursor) to be passed on in sufficient amounts to the flame, there to produce typical FID response. (Note that we speculated, in a study of carbon-based quenching, that the

reactive flow contained negligible concentrations at most of the presumed second reactant in the chemiionization reaction, the oxygen atom [2].)

A certain amount of congruity between the RFD and the FID response profiles could also have been expected from the fact that the conventional FID, as has been known since its inception, displays a characteristic carbon response *maximum* at relatively low hydrogen flows. It is, however, not known to what extent, or even to what products (H_2O vs. H_2O_2 , for example) premixed hydrogen and air (i.e. oxygen) combine in the reactive flow, and whether the extent and/or the products change with different flow-rates and compositions. What is obvious from Fig. 2 is that the reactive-flow mixture is hydrogen-richer at high than at low flow-rates. At the same time, high flow-rates deliver more —though also more diluted— oxygen.

3.2. Single and double flames vs. the reactive flow

The incentive for this comparison came from a (seemingly) simple question: Given that the hydrogen-rich *reactive flow* passes on structures capable of later chemiionization, would a hydrogen-rich *flame* behave likewise? Behavior alike or not alike could have implications analytic (e.g., the feasibility of a dual-flame FPD-FID) or mechanistic (e.g., the distinction between a reactive flow and a flame). The comparison is easy to carry out —although its formal credentials suffer, as most experiments in this area do, from the fact that different phenomena can be obtained and compared only under different flow regimes.

The experiment starts with pure hydrogen (plus nitrogen from the column) flowing through the capillary and burning in an FID-type flame on top. Increasing amounts of air are then premixed into the capillary flow. Visually at least, the increasing amounts of air fed into the capillary appear, at some point, to cause the “inner cone” of the air-rich flame to extend downwards, fill the capillary evenly with the “reactive flow”, then contract into a second

flame burning at the restriction. The resulting double-flame arrangement is, in fact, reminiscent of the Smithells separator [29] and its modern descendants [22,30,31]. Three reactive-flow/flame regimes are thus successively entered by increasing the influx of premixed air starting from zero: the air-rich flame on top is first being fed by pure hydrogen and intact analyte; then by the effluent of the adjacent hydrogen-rich reactive flow; then by the effluent of the hydrogen-rich flame burning way below it. This simple increase of premixed air thus tests the important transfer of electrical response properties. Here the experiment was carried out for two different levels of (additional) nitrogen flow, and for both aromatic and aliphatic test compounds.

Fig. 3 shows the interesting results. Higher (additional) nitrogen flows shift the curves to higher ion yields. This could have been predicted by analogy to the conventional FID. If, as is

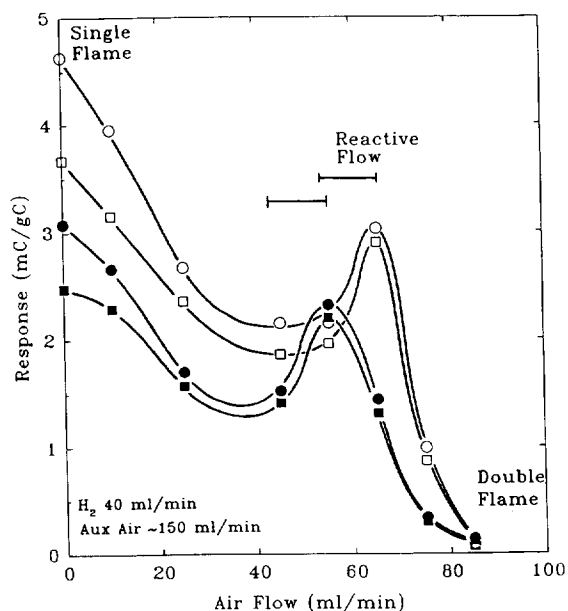


Fig. 3. Ionization response profiles for 0.10- μ g injections of *n*-dodecane (circles) and naphthalene (squares), without (filled symbols) or with (empty symbols) 40 ml/min of additional nitrogen in premix. Left side: air-rich flame on top of capillary without reactive flow; middle: air-rich flame on top with adjacent reactive flow; right side: air-rich flame on top without reactive flow but with hydrogen-rich flame at the bottom restriction.

common today, the conventional FID is fed by a capillary column, nitrogen is routinely added: not just for preserving chromatographic resolution but also for increasing detector response [5]. A similar effect pertains here, except that the different jet dimension and the (for an FID) high hydrogen flow-rate slightly distort the familiar picture. The constant flow of hydrogen used, 40 ml/min, is convenient for accessing the reactive-flow regime, yet it is far too high for conventional FID operation. To wit, the response maximum of the conventional-FID analogue —i.e. of a single, air-rich hydrogen diffusion flame burning on the same capillary as the RFD-FID, but without the additional nitrogen and oxygen of the premixed air— occurs at 18 ml/min hydrogen. This response maximum is more than twice as intense as the response obtained under the same conditions, but in the “FID-only” mode at 40 ml/min hydrogen.

Considering the circumstances, the overall response intensity shown in Fig. 3 is reasonable compared to the roughly 15 mC/g effective carbon that a top commercial FID will yield. No doubt the FID performance of the RFD-FID could be further improved, for instance by forcing the auxiliary air closer to the top flame, by polarizing the jet itself, etc. [c.f. 3]. However, comparative response is neither the most important nor the most interesting feature of Fig. 3.

Of much greater interest is the response maximum that is located roughly in the reactive-flow region. (The region where full reactive flow exists —as judged by a (when doped) clearly visible, stable, full-length glowing column— is marked on Fig. 3. Less stable and/or partial glowing columns persist on both sides of this range.) Save for this local maximum, the response curves of Fig. 3 might have descended monotonically from single flame to double flame. So whence the maximum?

The answer —for now but a speculative one— is that the maximum is indeed associated with the reactive flow; and that this is so because the reactive flow “assists” in producing and/or conveying into the flame the carbon-based species on which chemiionization depends. Thus, al-

though operation of the FID mode at the reactive-flow maximum does not quite match the best ion yield of the pure diffusion flame, perhaps conditions and dimensions *could* be found at which the presence of a reactive flow may rival conventional FID response. (No such effort is, however, underway or planned in our labs.)

3.3. Response correlations

Table 1 presents three types of response for various types of compounds, including some typical FID and FPD analytes. The same set of flow conditions —selected to give good *photometric* response— was imposed on *all* compounds. While repeatedly injecting a particular test compound, the reactive flow under the FID was switched on and off by switching on and off the premix air stream. Any comparison between the two FID modes with and without a prelude reactive flow was thus imperfect, since the (in the case of the reactive flow even unknown) composition of the gas entering the FID flame changed during switch-overs. However, this was as close to a valid comparison as we could come.

That the reactive-flow was indeed “on” when supposed to be, was affirmed by the presence of proper photometric response. (The latter also provided some interesting comparisons of its own. Note, however, the exceptional case of tin: for purpose of a consistent experimental protocol, and as judged by analogy with the complicated spectral mix of *FPD* emitters [32], the injected amounts of the two stannanes may have exceeded the linear photometric range.)

The FID responses are given in “mC/g C”, i.e. in mC peak area per gram of carbon injected; for the obvious purpose of comparison with other absolute or relative response data. Given the extent to which both vary in the conventional-FID literature [e.g. 4,25–27], the absolute numbers of Table 1 for FID-only response (i.e. with the reactive flow turned off) do not present much of a surprise.

Of somewhat greater interest is the comparison between the responses of single compounds with the reactive flow turned off and on. (Note that while the absolute response value of a

Table 1
Response of different compounds in three detector modes

Compound	FID response		RFD response
	RF off	RF on	
Dodecane	3.3	1.5	$4.1 \cdot 10^9$ (C)
Naphthalene	2.3	1.2	$3.2 \cdot 10^9$ (C)
Ethyl decanoate	2.3	1.2	$4.0 \cdot 10^9$ (C)
<i>p</i> -Methylbenzophenone	2.2	0.95	$4.1 \cdot 10^9$ (C)
1,3,5-Trioxane	0.39	0.06	$1.7 \cdot 10^9$ (C)
1,4-Dioxane	0.55	0.12	$1.9 \cdot 10^9$ (C)
Pyrazine	0.44	0.22	$3.3 \cdot 10^{10}$ (N)
Pyridine	0.61	0.32	$3.0 \cdot 10^{10}$ (N)
Thianaphthene	2.0	1.0	$3.6 \cdot 10^{13}$ (S)
Di- <i>tert.</i> -butyldisulfide	3.0	1.2	$4.5 \cdot 10^{13}$ (S)
Di- <i>n</i> -hexylsulfide	1.6	0.97	$2.1 \cdot 10^{13}$ (S)
Methylcyclopentadienyl manganese tricarbonyl	1.6	0.57	$9.7 \cdot 10^{12}$ (Mn)
Tetramethyltin	0.87	0.58	$1.1 \cdot 10^{14}$ (Sn)
Tetra- <i>n</i> -butyltin	1.8	1.0	$1.9 \cdot 10^{14}$ (Sn)
Tris(pentafluorophenyl) phosphine	3.0	1.2	$1.1 \cdot 10^{14}$ (P)

All compounds injected in 100-ng amounts, except 1 μ g for the two oxanes. Electrical responses for reactive flow ("RF") off or on are given in mC/g carbon injected; optical responses are given in arbitrary (but internally consistent) peak height units per gram of the element shown in parentheses. Flows in ml/min: premix H₂ 40, air 60, column nitrogen 12; auxiliary air 150. Optical channel filterless, with R-268 photomultiplier tube at -800 V.

compound can be compromised by on-column decomposition or sample impurity, its response *ratio*—in the absence versus the presence of the reactive flow—can not.) To strengthen the following argument, the ionization data of Table 1 are replotted in Fig. 4, with elemental symbols included.

In this graph, the FID response as fed by the reactive flow appears to be a more or less constant fraction of the FID response as fed by the intact analyte. (The line is drawn at exactly slope 1/2, though for no obvious kinetic reason.) It does not seem to matter whether the compounds are hydrocarbons, hetero-organics or organometallics; whether they contain this or that hetero-element; whether they are relatively stable or unstable thermally or chemically; and whether they yield weak or strong photometric response. (The latter may be irrelevant to the discussion, except that strong RFD response

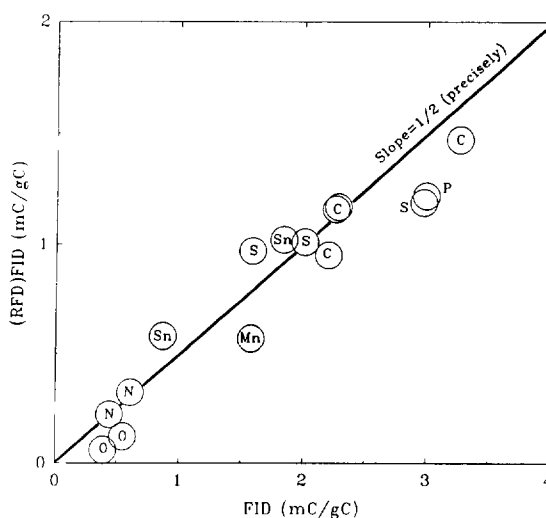


Fig. 4. Ionization efficiency for different types of compounds with (ordinate) or without (abscissa) passage through reactive flow. Line drawn at slope = 1/2. Data obtained by switching reactive flow on and off between injections.

from mono-, di- or triatomic emitters presupposes a significant extent of structural damage to the precursor analyte.)

Fig. 4 succeeds in suggesting a general relationship between the respective sets of data and, by extension, between the respective degradation mechanisms of the reactive flow and the air-rich flame. (One rare type of exception will be discussed later.) The flame atop the RFD can hence be considered to behave like a conventional FID flame; thereby offering a new, practically simultaneous and, by all evidence, chemically orthogonal response channel. This should make the RFD–FID a convenient and sensitive system for response ratio studies and correlation chromatograms [11–15], and perhaps even for exploring flame degradation mechanisms.

Although luminescence was monitored only because the photometric channel was already in place, and because it was able to provide unambiguous information on the presence or absence of the reactive flow, it is still interesting to look at some of the gratuitously obtained *RFD* information. Of the four carbon compounds listed at the top of Table 1, three yield very similar responses per gram carbon, with only naphthalene being slightly lower. This is interesting because, in the *FPD*, naphthalene responds significantly stronger than *n*-dodecane [33]. This would agree with a scenario in which all carbon compounds in the reactive flow would produce the same, single-carbon, hydrogen-containing luminescer—say CH—with roughly similar efficiency.

Clearly, however, many more compounds would have to be run before such a relationship could be proposed with confidence. Since the absolute responses—as opposed to the response ratios—are subject to bias from, e.g., impure standards and premature decomposition (causes of bias that are too laborious to check and control for too trivial an analyte, or for too trifling an answer), the measured numbers should *not* be used to draw conclusions on whether the RFD response is or is not element-specific.

An apparent exception to the more or less constant ratio of (RFD)FID and FID-only re-

sponses appears to be the behavior of two compounds that were included here simply because interesting FID data had already been collected on one of them. Blades [34] used 1,3,5-trioxane as an indicator of thermal decomposition (pyrolysis having been suggested earlier as a possible FID degradation scheme). This because the thermal decomposition of trioxane yields methanal: as it happens, the former yields significant, the latter insignificant response in the conventional FID.

Similar to Blades' results (which were obtained on a conventional FID), trioxane yielded a low but still sizable response on our setup when the reactive flow was turned off. When the reactive flow was turned on, however, trioxane response dropped to almost zero. Whether the product of the degradation was formaldehyde, and to what degree the degradation was thermal, is unclear. In Blades' study, trioxane disintegrated in a Pyrex tube between 300 and 400°C [34]. In comparison, the reactive flow showed thermocouple temperatures between 200 and 230°C when measured on an opened detector of otherwise ambient temperature [1]. (The temperature under typical RFD–FID operating conditions was not measured but would, of course, be considerably higher.)

In any case, the reactive flow seems unable to convert trioxane carbon into an FID-active species. It is interesting to note in this context that the *photometric* response of trioxane is also reduced (as compared to that of other oxygenates)—although not to the same extent as the electrical response. Such similarity is consistent with the earlier assumption of CH being the predominant emitter. If so, the *same* species (albeit in different locations) would be responsible for *both* the chemiionization and the chemiluminescence responses of carbon compounds.

3.4. Analytical figures of merit: response linearity, baseline noise, and detection limits

Since the reactive flow “modifies” gas chromatographic effluents before they enter the top flame, it may be reasonably asked whether that process could become subject to chemical

exhaustion by a very large analyte influx. Put as a question: Is the (RFD)FID as linear a detector as is the FID?

Fig. 5 shows *n*-dodecane calibration curves for both the “FID” and the “(RFD)FID” ionization responses (as well as for the simultaneous RFD photometric response). The linear ranges for the two ionization channels are similar, thus affirming the conventional FID behavior of the (RFD)FID channel. Naturally the two channels draw closer together when the reactive flow is terminated (expelled) by analyte overload, i.e. when the only difference between the channels is the absence or presence of air in the capillary.

This pivotal process can be observed in a darkened room: the reactive flow appears to leap out of the capillary and enter the top flame, a process also accompanied by characteristic audible emissions [1]). Aside from such subjectively noticeable sights and sounds, the RFD response terminates and the (RFD)FID data deviate most noticeably from the straight when this occurs.

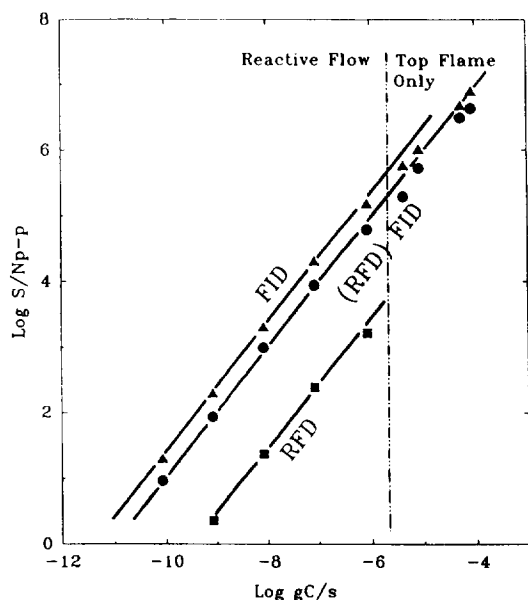


Fig. 5. Ionization response linearity for *n*-dodecane without (“FID”; ▲) and with (“(RFD)FID”; ●) passage through reactive flow, together with optical response (“RFD”; ■). The reactive flow is temporarily expelled by carbon flows higher than about 2 $\mu\text{g/s}$.

(Note that the calibration lines of Fig. 5 are drawn at exactly unity slope to help the viewer assess the degree and extent of deviation from linearity.)

Thus the “linear” FID range (six orders of magnitude plus) is not quite as clean as expected of conventional FID detectors, and the minimum detectable carbon flow is not quite as low. The (RFD)FID line in Fig. 5 yields $2 \cdot 10^{-11}$ g C/s for the $S/N_{p-p} = 2$ definition and (further extrapolated) $5 \cdot 10^{-12}$ g C/s for the $S/\sigma = 3$ definition.

This (in comparison with modern FID’s) somewhat depressed performance is a consequence of detector construction and conditions. Overall priority had been given to a design that was fast and facile to test and would allow the reactive flow to persist and yield maximum luminescence, rather than to one that would yield maximum ionization. For these reasons, the *relevant* comparison is that between the “(RFD)FID” and the “FID” modes (rather than between the former and a conventional FID). The same applies to signal amplitude and baseline noise.

Baseline noise is important in the RFD–FID because, at a given signal amplitude, it determines the detection limit. Earlier, the photometric RFD noise was found to be fundamental in nature, i.e. determined by the quantum nature of light and matter [1]. Thus it is interesting to check whether electrical (RFD)FID noise is of a similar nature.

In a study of the response of three prominent detectors, namely FPD, ECD and FID, all three displayed, predominantly if not exclusively, *fundamental* noise behavior [35]. The important point here is that, noise-wise, the detectors were essentially as good as they could be: if noise is predominantly or exclusively fundamental in nature, there is little point (for a given time constant) in attempting to suppress it further by developing detector constructions and/or noise filters of increasing complexity and sophistication. Improvement can only be achieved by altering other circumstances, e.g. by increasing a too-low light transmission in the FPD [15] or by decreasing a too-high baseline current in the FID.

If the reactive flow should cause chemical or physical fluctuations, the RFD–FID flame could become excessively noisy. The fundamental, i.e. the minimum electrical noise of the flame can be calculated from counting statistics as the square root of the charges generated, i.e.

$$\text{RMS}_{\text{FID}} = (Ie/t)^{1/2}$$

where RMS is the root-mean-square (the standard deviation for a Gaussian) of the baseline fluctuations and I is the baseline current, both in A; e is the charge of the electron ($1.6 \cdot 10^{-19}$ As); and t is the effective time constant of the acquisition/filter system in s [35].

Table 2 lists the background current, the calculated fundamental, and the measured experimental noise for the (RFD)FID and FID-only modes. The numbers are virtually identical among the two modes. Interestingly, however, the measured and the calculated noise disagree by a factor of more than 2. While this degree of disagreement is still small, and perhaps even within the error range of measuring and calculating noise (the prime consideration here being the time interval over which the measurement is to be carried out), visual inspection of both (RFD)FID and FID traces suggests a noise with some genuinely slower components.

Since *both* electrical modes show the effect (while the photometric mode does not [1]), it can only be attributed to the happenstance construction and condition of our prototype RFD–FID, rather than to some detrimental influence—e.g., fluctuation—of the *reactive flow*. (Interestingly enough, if the *FID*-optimized condition—i.e. 18 ml/min hydrogen with no internal but much auxiliary air—is used, the experimental noise

reduces to the theoretical level.) While we do recognize the symptom, we do not understand the cause.

Within this experimentally restricted study, then, the presence of the reactive flow does not significantly degrade the performance of an FID-type flame in terms of noise. (Its present conditions do, however, degrade performance in terms of signal by about a factor of two.) We had earlier argued, in response to a referee's request, that the presence of the reactive flow should not lead to significant peak broadening [1]. To accommodate a like-minded request by our current referee, we monitored the shape of a sharp, unretained peak: its profile was, in essence, determined by the speed of the recorder pen (giving a 0.8 s width at half height). Thus, no untoward effects should be expected for capillary column effluents.

Given that the RFD–FID is optimized for stability of the reactive flow and for optical, not electrical response, this performance of its FID channel is quite satisfactory. It is, in any case, far better than the ionization performance of conventional FPDs. Furthermore, suitable modifications could still improve (RFD)FID performance. For meeting our particular interests, though—i.e., for obtaining dual channel RFD–FID response ratios and correlation chromatograms—the detector's performance already exceeds our requirements.

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Table 2. FID noise characteristics with and without a preceding reactive flow

	Background current (A)	Fundamental noise (A)	Experimental noise (A)
(RFD)FID	$2.0 \cdot 10^{-12}$	$1.4 \cdot 10^{-15}$	$3.2 \cdot 10^{-15}$
FID	$2.0 \cdot 10^{-12}$	$1.4 \cdot 10^{-15}$	$3.2 \cdot 10^{-15}$

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