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Quenching-free reactive-flow photometry☆

Kevin B. Thurbide, Walter A. Aue*

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada

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Abstract

The reactive-flow detector (RFD) behaves in many aspects like the typical flame photometric detector (FPD) for gas chromatography, thereby strongly suggesting that it, too, may be subject to severe, analytically deleterious quenching effects by hydrocarbons. However, tests carried out with compounds of the prominent FPD analytes sulfur, phosphorus, tin and manganese demonstrate —for *all* their emitting species— that the quenching of chemiluminescence by hydrocarbons does *not* occur in the RFD. A mechanistic hypothesis involving the oxygen atom is put forth in an attempt to rationalize this important difference between conventional flame and reactive flow.

1. Introduction

The reactive-flow detector (RFD) is a simple device that monitors the chemiluminescence of gas chromatographic peaks containing sulfur or phosphorus in a glowing column ("reactive flow") of premixed hydrogen–air gas [1]. The reactive flow is tolerant of solvent peaks, stable vis-a-vis moderate changes in composition, and persistent over any desired length of time. Interestingly, though, it is not self-sustaining: the reactive flow must have continuous access to a conventional flame. Reactive flows are easily generated inside borosilicate or quartz capillaries of various lengths and diameters.

The properties of the RFD, as far as investigated, suggest that it is a close cousin in behaviour and performance to the popular flame photometric detector (FPD) [2–26]. This is certainly true of its response to S and P, in particular its sensitivity, selectivity, and linearity (or non-linearity). The only pronounced difference found so far between the two detectors relates to their behavior vis-a-vis two test hydrocarbons: the RFD responds with roughly equal intensity to naphthalene and *n*-dodecane; the FPD, as is well known, responds much stronger to aromatics than to aliphatics.

A second possible difference, also relating to carbon behavior, may have manifested itself in our earlier pursuit of detection limits: in an attempt to elute sulfur and phosphorus peaks as early and as sharp as possible, we allowed them to ride up on the solvent tail (Fig. 3 in Ref. [1]). This is a practice ill suited to the FPD: there, the solvent tail can severely quench analyte response.

Quenching by co-eluting hydrocarbons is one —if not the— major drawback of the FPD [2–26]. Given the prominence and importance of this detector, it is not surprising that many

* Corresponding author.

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attempts should have been made to elucidate and, more importantly, to eliminate its quenching behavior. Not all such efforts have been entirely successful. Perhaps this was not solely the fault of the FPD: quenching effects are known to affect even typical high-energy, thermal emission sources —although less so than they do affect typical low-energy, chemiluminescent systems. The quenching effect, e.g. that of carbon on phosphorus, has been known for more than a century: as P.T. Gilbert relays it in his labor-of-love monograph, E. Mulder found in the 1860s "that a single drop of ether in the hydrogen generator quenches the green (i.e. HPO) spectrum" [27].

Clearly, if the RFD is to have any chance of being accepted by the *analytical* community, it must be less, not more, susceptible to quenching than the FPD. The FPD has so far been shown to respond in an analytically interesting manner to some twenty elements. The ones whose behavior vis-a-vis co-eluting hydrocarbons has been checked (S, Fe, Sn, P, Mn and Cr) were all quenched to a fairly similar degree. This was taken to suggest "that hydrocarbons may quench the exciting flame rather than the excited analyte" [23].

(Note that, to our knowledge, only the *analytically* interesting quenchers have so far been investigated: this means carbon compounds in GC–FPD and carbon and nitrogen compounds in LC–FPD [25,26]. Also, the tin luminescence on quartz can be quenched by phosphorus or by large amounts of tin itself [28].)

Presuming, perhaps wrongly so, that hydrocarbonaceous quenching mechanisms are similar or identical [23] for most or all of the FPD-active elements, we decided to select only a few examples for testing in the RFD. Our selection considered both the analytical relevance and the spectroscopic variety of the emitting species.

Sulfur and phosphorus are obvious candidates for the test, given their history [20] as well as their industrial, environmental and biochemical importance. Both are prominent analytes in present-day analytical laboratories; both produce *molecular* emitters (and perhaps some underlying, very feeble continua). The green HPO* yields a linear calibration curve, the blue S_2^* a roughly quadratic one [2,3,21,29]. Sulfur response can also be linear if the red HSO* [30,31] is sampled. Tin, a main-group metal, is the most sensitive element in the FPD in the form of its blue surface luminescence, i.e. a *continuum* of spectroscopically unknown origin [32,33]; its weaker emitters are the greenish SnOH* and the red SnH*. Organotins are often monitored by the FPD in the residue analysis of fungicides, antifouling compounds, polymer stabilizers, etc. [34]. The transition metal manganese produces, in addition to a somewhat less prominent continuum, strong *atomic* Mn* emission. Its FPD response can be used to determine the common gasoline antiknock additive MMT ([35], cf. [36,37]).

The four elements S, P, Sn and Mn thus represent a good cross-section of chemically important, spectrally disparate, and analytically meaningful test species. Suitably volatile and stable compounds of these elements (the "analytes") will therefore be co-chromatographed with hydrocarbons of a similar retention time (the "quenchers"), in a technique familiar from the literature. The hydrocarbon concentration is to be varied, up to the point where it will temporarily expel the reactive flow from the capillary [1]. The constancy of the analyte's peak height —over several orders of quencher concentration— will then offer a highly sensitive and analytically relevant measure of the detector's resistance to quenching.

2. Experimental

The RFD has been described in Ref. [1]. Briefly, this simple detector, built on the remains of an old Tracor 550 flame ionization detector (FID), monitors the emission of a luminescent, H_2-rich premixed hydrogen–air column, which is enveloped by a glass capillary carrying a regular air-rich hydrogen flame on top. The glowing column in this first prototype is of 3.5 cm length and 1.8 mm diameter; its central section is sampled by a 1/4 in. (1 in. = 2.54 cm) diameter glass image conduit (Edmund Scientific, 101 E.

Gloucester Pike, Barrington, NJ 08007-1368, USA; item 38307) and a Hamamatsu (360 Foothill Road, Bridgewater, NJ 08807-0910, USA) R-268 or R-374 photomultiplier tube of nominal range 300 to 650 nm, or 185 to 850 nm, respectively.

The typical flows are 12 ml/min nitrogen through the 2 m × 1.8 mm I.D. borosilicate column packed with 10% Apiezon L on Chromosorb W, 45–60 mesh (roughly 350–250 μm in particle diameter) used to separate the compounds; ca. 40 ml/min hydrogen and 60 ml/min air premixed to establish the hydrogen-rich reactive flow; and approximately 150 ml/min air introduced into the detector housing to maintain the air-rich, FID-type flame on top of the capillary. Other conditions are similarly conventional and/or conform to precedent [1].

3. Results and discussion

By fortunate circumstance and low chromatographic resolution, pairs of analyte and quencher that would co-elute on the existing Apiezon L column [1] were not hard to find. The pairs used were thianaphthene and naphthalene for sulfur, tris(pentafluorophenyl) phosphine and *n*-hexadecane for phosphorus, tetra-*n*-butyl stannane and *n*-hexadecane for tin, and methylcyclopentadienylmanganese tricarbonyl and *n*-dodecane for manganese. Fig. 1 shows the reassuringly consistent results, which are expressed there as fractional analyte response versus the (logarithmic amount of) quencher. Clearly, the co-eluting quencher exerts no influence on the analyte's response in any of the four cases.

Experimentally, the quenchers were also chromatographed by and for themselves; their quencher-without-analyte signals serving as background checks on the measured quencher-with-analyte peaks. This was done to ascertain that the peak of the quencher (i.e. its own luminescence) was indeed small enough not to interfere with that of the "quenched" analyte. (For one data point of Fig. 1, the quencher peak did indeed turn out a bit too large and had to be deducted.) Quencher amounts between about 10

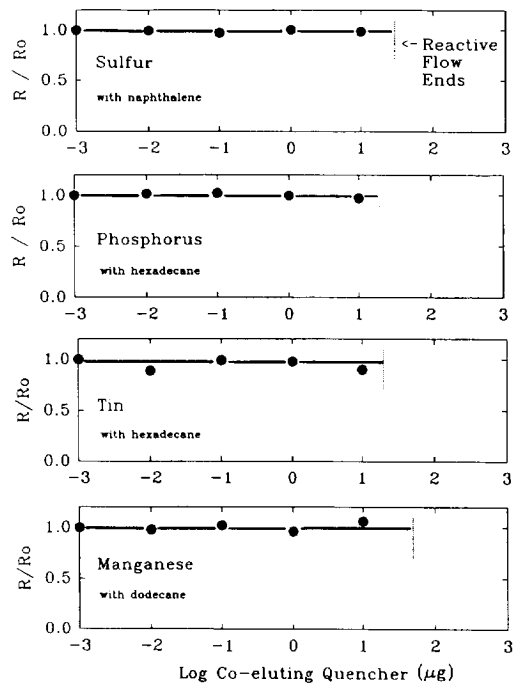

Fig. 1. RFD response in the presence of co-eluting hydrocarbons as indicated. Analytes: 50 ng thianaphthene (benzo[*b*]thiophene), 500 ng tris(pentafluorophenyl) phosphorus, 1 ng tetra-*n*-butyl tin and 500 ng methylcyclopentadienylmanganese tricarbonyl (MMT).

and 100 μg —and above, of course— cause the luminescent column of the reactive flow to temporarily abandon the capillary (i.e. withdraw from purview of the image conduit): this event therefore defines the upper limit of the RFD's operational range.

In the absence of optical filters, the peak heights of Fig. 1 may represent more than one major emitting species per element (the likely numbers are 1 for P, 2 for S and Mn, and 3 for Sn). To check separately for each one of these (and perhaps for some as yet unrecognized ones) would be a difficult and daunting task. Fortunately it proved unnecessary. With the usual FPD interference filter removed, all emissions within optical range of image conduit and photomultiplier tube are being recorded —and with it the quenching of any emitting species. Since no peak was ever quenched, it is safe to assume that

all emitting species of *each* particular element are indeed immune to quenching in the RFD.

It would be surprising if the clear result of Fig. 1 —no quenching anytime in the RFD— were not to hold for other elements and quenchers as well. We refrain, therefore, from extending the series of tested elements beyond the prominent FPD foursome of S, P, Sn and Mn. Yet there remains one aspect that, though subject to prediction by analogy, still needs verification by experiment. It concerns the analyte concentration.

The four analytes whose behavior is depicted in Fig. 1 were for obvious reasons injected in large and constant amounts. If this had been the FPD, the fact that the amounts were large and constant would not have made any difference: fractional quenching in the FPD depends only on the concentration of the quencher, not on the concentration of the analyte (cf. [23,24] and references cited therein). Since the RFD has shown itself to differ from the FPD's quenching behavior, however, similarity in regard to analyte concentration can not be presumed. Rather, it must be established.

Experimentally that calls for investigating the behavior of *small* amounts of analyte. Yet this is difficult to achieve within the framework of Fig. 1, since the peak of the quencher is then likely to overpower the peak of the analyte. For this reason we resort here to a type of FPD experiment —often carried out unwittingly, rarely carried out deliberately [7]— in which a small analyte peak rides on the tail of a large quencher (solvent) peak. Obviously, the more prominent the tail the more pronounced the quenching.

Fig. 2 shows one typical experiment from a series of tests that comprise various elements but produce invariably the same result. The amount of analyte is now much closer to the detection limit. As suggested by the earlier Fig. 1, the solvent tail exerts no visible influence on the analyte peak: the latter retains its normal height. We are therefore pleased to conclude that quenching does *not* occur in the RFD to any significant extent, no matter what the analyte (or quencher) concentration.

From an analytical viewpoint that conclusion is welcome indeed. Quenching has presented a major problem for the FPD, particularly since this detector is often used to determine trace analytes contained in hydrocarbonaceous matrices. The most typical cases involve sulfur compounds in natural gas and oil; however, thiophosphate pesticides, organotin biocides or polymer additives, and a variety of other heteroorganic species found in environmental or biological systems have (or might yet be) proven important as well.

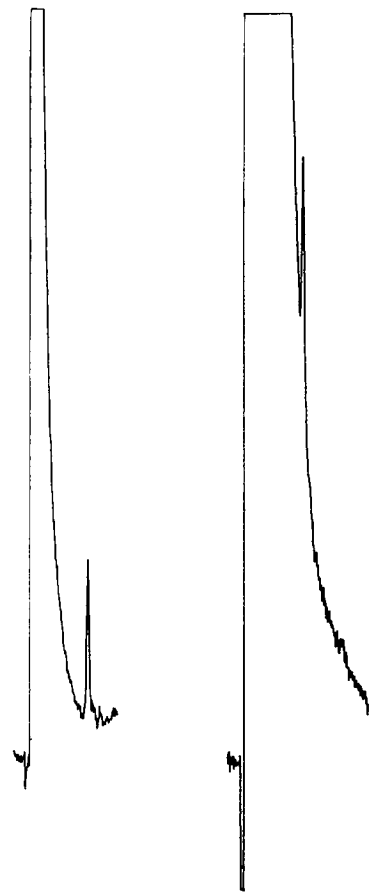

Fig. 2. RFD response of a trace sulfur peak on and off the solvent tail. The amount of injected analyte (1 ng thianaphthene) is precisely the same; however, the amount of solvent (acetone) has been increased 12 times for the second chromatogram by drawing additional acetone into the syringe prior to injection. The enhanced dip preceding the second solvent peak is due to the increased pressure surge caused by the sudden evaporation of a larger amount of acetone.

While the RFD does not appear to be subject to quenching, it should be noted that its operating range is shorter than that of the FPD: A large amount of hydrocarbon, just like the usual solvent peak, will temporarily expel the reactive flow from the capillary. This occurs in the prototype RFD with amounts of 10 to 100 μg. On the other hand, this much quencher hardly if ever flows from a capillary column: if contained in a single peak it would represent the 1 to 10% component of a 1-μl injection! Furthermore, the glowing column invariably recovers —faster with higher flows, slower with lower ones. Whether different dimensions of the reactive flow —i.e. of the capillary that houses it— would change its operating limit has not been investigated.

A direct comparison of RFD and FPD quenching behavior is difficult because the latter strongly depends on detector construction and operation. Farwell and Barinaga's review [3] mentions that "several tens of nanograms of carbon per second are necessary before hydrocarbons will produce significant reduction in the sulfur response". In our old Shimadzu Model 4 FPD, quenching effects (by a constant stream of methane) became noticeable at roughly 1 μg C/s [23,24]. Quenching is significantly reduced when the column effluent is carried to the detector by the air or oxygen (rather than by the hydrogen) stream (e.g. [13]). There are also differences between different detectors depending on whether their flame is a "pure" diffusion flame or whether, by jet wear or design, their gas streams premix to some degree while ascending toward the reaction zone.

From a mechanistic point of view, the fact that quenching does *not* occur in the reactive flow is certainly interesting. A variety of scenarios may offer plausible causes. We shall describe here only one of these —for the general purpose of citing the literature and starting the discussion; for the particular purpose of justifying its use as our working hypothesis. It should be understood, however, that a kinetic scenario at this early stage of the RFD's development stems from pure imagination, not experiment.

The reactive flow regime may be compositionally related to the well-studied region between the second and third explosion limits of hydrogen–oxygen mixtures, where peroxide chemistry plays a decisive role [38]. If so, it is likely that a radical like the oxygen atom —which characteristically functions as a chain-branching agent— should be nigh absent in the RFD.

Let us for now assume, therefore, that quenching in the FPD is indeed, as has been suggested, a quenching "of the exciting flame rather than of the excited analyte" [23]; and that such quenching occurs via the reaction (or reactions) of the oxygen atom and a simple carbon species (or a pool of simple carbon species) —say reactions like the chemiionization process that is usually considered responsible for the response of the flame ionization detector [39]:

$$CH + O \rightarrow CHO^+ + e^-$$

Such reactions would tend to diminish chain branching, i.e. they would reduce the concentration of those free radicals (H, OH) whose recombination is believed to provide the energy for many of the chemiluminescent processes monitored in the FPD (e.g. [20,40,41]). It is perhaps worthy of note that propane added to H_2–O_2 mixtures depresses the second explosion limit proportional to the oxygen atom concentration (although the authors attributed the effect to the reaction of the hydrocarbon with hydrogen atoms [42]).

In some (unrelated) studies by our group, hydrocarbons introduced into the FPD flame did indeed quench the radical-driven OH emission (experimentally: the $0 \rightarrow 0$ bands at 306–309 nm); and there also appeared to exist some correlation between the quenching of the OH bands and the quenching of several FPD-active elements in the same, methane-doped flame [43]. In contrast, the strong 306+ nm OH emission from the RFD showed no (or only negligible) quenching by one-microgram amounts of typical quenchers and analytes.

A variety of reactions have been considered responsible for the appearance of the OH bands under various conditions [40], e.g.

$$H + OH + OH \rightarrow H_2O + OH^*$$

and

$$O + H \rightarrow OH^*$$

and it thus seems permissible to link the quenching of FPD response by hydrocarbons to a quenching of the radical chain mechanism driving the hydrogen–air *flame*. Whether it is really the oxygen atom that serves as the primary target of carbon species is open to debate: too little is known about the FPD flame (or, for that matter, the RFD glow).

But let us assume —for sake of a model argument— that the crucial link is indeed the oxygen atom. This would explain why the presence of hydrocarbons has little or no influence on the reactive flow: in the RFD that crucial link must be largely missing. (If the reactive flow would increase its rate of oxygen atom formation, it would use the oxygen atom for branched-chain propagation and could thus no longer remain a glowing column. Rather, it would revert to a premixed hydrogen-rich, small flame burning at the bottom of the capillary. Incidentally, such a flame is easy to produce by increasing the air content of the supply gases: once the flame ignites at the bottom, the glow above it *vanishes* [1]. See "Note added in proof".)

It is, of course, also possible to imagine scenarios of a different kind. For instance, there could perhaps exist one type of hydrocarbon species that, while responsible for quenching in the FPD, is not formed in the RFD. (This species would again play the role of a missing link, though this time on the quencher side). While we do not give much credence to this particular scenario, it might still be of interest to collect, analyze and compare organic effluents from doped RFD-type glows vs. FPD-type flames (see the extended discussion of glow and flame "reactor" systems in Ref. [1]).

Indeed, most of the above speculations could be easily confirmed or denied by subjecting the technically accommodating RFD system to some fairly obvious and —at least from our point of view— quite promising experiments. Such experiments would, however, exceed the simple chromatographic and analytical objectives of the current study.

It was designed solely to determine whether or not quenching occurs within the operating range of the RFD. The obvious and clear conclusion is that it does not —at least not for the conditions, analytes and quenchers used. This welcome finding removes one of the major impediments to the analysis of photometrically responsive elements in hydrocarbonaceous matrices.

4. Note added in proof

During the setting of this manuscript we happened to investigate, very roughly, the optical emission and analyte quenching properties of the lower part of what may be called a "separated", "double" or "split" flame (compare [1,20] and references cited therein). This system was produced in the RFD by increasing the air supply to an existing reactive flow, thereby collapsing its luminescent column into a hydrogen-rich, premixed flame burning at the bottom (restriction) of the capillary. One result of this investigation happens to be of particular relevance to the present manuscript. Similar to the reactive flow, this lower part of the split flame failed to show any clear evidence of anlyte quenching. When exposed to *exorbitant* concentrations of hydrocarbons, it —again like the reactive flow— withdrew temporarily from the capillary (and left only the upper, air-rich flame burning).

This interesting result does not alter the conclusions and speculations of the main manuscript. It does, however, allow us to consider the RFD's immunity to quenching from an additional viewpoint. First, note that the lower flame, while clearly of the hydrogen-rich variety, contains *more* air than the typical FPD flame (or, for that matter, the reactive flow). It is also *premixed*. Such conditions can, in other systems, drastically lower the extent of analyte quenching (compare, e.g., Ref. [13]).

Second, the expulsion from the capillary of the reactive flow or the lower flame can be considered mechanistically identical or at least chemically analogous to such flow or flame being terminally "quenched", i.e. being extinguished, by the hydrocarbon. This analogy is important

here because, for the FPD, we had earlier suggested, "oversimplified, that *hydrocarbons may quench the exciting flame rather than the excited analyte*" [23]. For spatially and kinetically restricted excitation regimes —that is, for regimes operating within a limited range of conditions as in the RFD capillary— the (imaginary) onset of quenching of the analyte may be preceded and hence pre-empted by the terminal quenching of the reactive flow or the lower flame itself.

(Interestingly, a *regular* hydrogen-rich premixed flame —established for comparison purposes with the same flows as the lower split flame, but made to burn on *top* of a capillary of smaller diameter— *did* show clear quenching effects. This free-burning flame was, however, extinguished by approximately the same load of quencher that would expell the reactive flow or the lower flame from the capillary, i.e. by peaks containing roughly 50 to 80 μg of hydrocarbon.)

The expulsion/extinction of the RFD's excitation medium defines, of course, the end of the detector's operating range. The reactive flow and the lower flame could hence be considered systems that, by their composition and circumstance, are highly resistant to analyte quenching in the first place. If exposed to *overwhelming* loads of organics, however, they simply self-extinguish (and later re-ignite) —thus preventing any quenching of analyte response from ever taking place.

This scenario suggests a correlation between the spatial stability of a reactive flow and its experimental immunity to analyte quenching. Whether this correlation subsumes all kinetics and encompasses all conditions possible in the RFD capillary would still have to be investigated.

An investigation of this sort may also shed further light on the validity of the (here imported) mechanistic premise that, in the typical FPD quenching process, a reduction of the analyte's chemi-excitation rate is caused primarily by a reduction in the concentration of flame-sustaining radicals such as H, OH, etc., whose energy of recombination powers the chemiluminescence. In simpler terms, this premise —which is consistent with, and supported by, the present study— suggests that most if not all response quenching is caused by a general quenching of the *flame* chemistry —here to the point of pre-emptive extinction/expulsion— rather than by processes like collisional deactivation of the excited state, chemical scavenging of its precursor(s), etc., that could be considered a specific quenching of the *analyte* chemistry (cf. [3,23] and references cited therein).

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