

Gas chromatographic detection of organometallic compounds by reactive-flow photometry

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Abstract

The response of the reactive flow detector (RFD) toward organometallic compounds of several transition metals has been explored, and several of its strong elemental responses have been characterized in detail. The RFDs minimum detectable flow (measured in picograms of metal per second at $S/N_{p-t-p} = 2$) is 0.1 for ruthenium, 3 for chromium, 10 for manganese, 5 for nickel, 15 for iron, and 2 for osmium. Typically, the linearity of response spans four orders of magnitude, with atomic selectivity of metal versus carbon ranging from 2 to 3 orders. Response quenching by co-eluting hydrocarbons is not observed. As a demonstration experiment, the common analysis of methylcyclopentadienyl manganese tricarbonyl (MMT) in gasoline is carried out on an RFD system modified for dual-channel operation. The results show that dual-channel operation of the RFD can increase the native elemental selectivity of manganese over carbon by a factor of 100, in accordance with earlier results obtained on a special version of the flame photometric detector (FPD). Significant differences exist between the optical spectra of carbon flame species resulting from various combustion modes carried out in the RFD capillary, and also between conventional FPD and typical RFD spectra. Consideration of these spectral differences suggests that the virtual absence of C_2^* in the reactive flow may be the primary reason why analyte response quenching by hydrocarbons, while prominent in the FPD, is not observed in the RFD.

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1. Introduction

Chemiluminescence detectors are often used in gas chromatography due to the selectivity and sensitivity they provide for the analysis of hetero-atomic compounds [1–4]. For instance, many analytical applications of recent years have employed such methods for the analysis of sulfur and nitrogen containing analytes [5–9].

One of the most widely used chemiluminescent devices is the flame photometric detector (FPD) [2–4,10–12]. The FPD is well known as a relatively inexpensive and reliable detector for the sensitive and selective analysis of compounds containing sulfur, phosphorus, and tin [13–15]. What is perhaps less well known is that the FPD also responds to many other elements. For instance, earlier studies by our Dalhousie group have demonstrated that the FPD provides useful analytical response for a number of transition metals and main-group elements [16–21]. Despite its utility, however, a major disadvantage of the FPD is the quenching of analyte luminescence that occurs

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in the presence of co-eluting hydrocarbons. This quenching seriously hampers the quantitative analysis of samples containing complex volatile matrices [22,23].

The reactive flow detector (RFD) is a unique type of chemiluminescent device, which has been introduced only a few years ago. Its photometric signal is based on the in situ emission from a luminescent, fuel-rich hydrogen/air “premixture”, which is flowing through a glass capillary during the detection process [24]. Studies have shown that the RFD responds sensitively and selectively to sulfur, phosphorus, and tin containing analytes, and that it displays spectral features and analytical figures-of-merit similar to those found in the traditional FPD for these elements [24,25]. In addition, the RFD offers some unusual advantages, such as the electric and acoustic signals [26,27] that accompany its luminescent response. The most notable and practical difference existing between the RFD and the FPD, however, is that the RFD does not exhibit any of the FPDs hydrocarbon-induced quenching [28]. This can greatly facilitate the analysis of samples containing complex hydrocarbon matrices, and indicates that the RFD may become a useful alternative to the FPD for measuring gas chromatographic effluents containing sulfur, phosphorus, and/or tin. While further research in this area would be clearly beneficial, no report has yet dealt with RFD responses, or their absence, toward the numerous other elements that are known to respond well in the FPD.

Given both the similarities and dissimilarities that exist between the RFD and the FPD, it would thus be useful to examine whether the RFD is indeed capable of measuring other elements, particularly the various transition metals that have been observed to respond strongly in the FPD. Were the RFD to perform in a manner similar to that of the FPD, it would then become worthwhile to characterize, optimize, define and compare such responses in greater detail. This paper therefore presents an investigation of the reactive-flow response toward selected transition metals in order to assess the potential of the RFD to determine organometallic compounds separated by gas chromatography. In an effort to further elucidate the operating mechanism of this unique device, some new spectrochemical experiments, as well as comparisons between RFD and FPD behavior, will also be discussed.

2. Experimental

The design of the RFD has been fully documented [24]. Briefly, the device creates a stable, luminescent gas column (~35 mm in length) by the low-temperature (ca. 200 °C) reaction of a fuel-rich hydrogen/air premixture that flows through a quartz or borosilicate glass capillary (35 mm × 1.8 mm i.d.). The emission is sampled midway down the capillary via a quartz rod (150 mm × 6 mm i.d.) that guides the light to a photomultiplier tube (R-268 with wavelength range 300–650 nm; Hamamatsu, Bridgewater, NJ, USA). For dual-channel experiments, an identical light guide assembly is installed at the same height but at a right angle to the one mentioned earlier. At the base of the capillary, the fuel gases are joined by the helium effluent from the gas chromatographic column.

Separations are performed on a Shimadzu GC-8A or a Varian 3700 gas chromatograph. Both of these instruments are adapted to accept the RFD housing as described previously [24], and each employs an EC-5 [(5% phenyl)-95% methylpolysiloxane] megabore column (30 m × 0.53 mm i.d.; 1.00 μm thickness; Alltech, Deerfield, IL, USA) that delivers its effluents to the base of the RFD capillary. Chromium hexacarbonyl, methylcyclopentadienyl manganese tricarbonyl (MMT), ferrocene, nickelocene, ruthenocene, bis-(pentamethylcyclopentadienyl) osmium, dodecane, and naphthalene are used as obtained from Aldrich. Carbon spectra are acquired using an Oriel model 7155 variable interference filter monochromator (15 nm bandpass). The analyte response (from 1 μg injections) is recorded at each of several wavelengths, following manual advances of the wavelength drive. Unless otherwise specified, typical gas flows are about 5 ml/min helium through the chromatographic column, 50 ml/min of hydrogen and 60 ml/min of air through the reactive-flow capillary, and 150 ml/min of air through the detector housing. Further conditions used for optimizing response, and for other experimental variations, are outlined in the text.

3. Results and discussion

3.1. Response characteristics

The transition metals examined in this study included chromium, manganese, iron, nickel, osmium,

and ruthenium, all of which are known to respond strongly in the FPD. Each element was introduced into the RFD as a metallocene (except for chromium, which was introduced in its hexacarbonyl form). The individual response of each compound in the RFD was assessed under various conditions, and several trial runs were carried out in order to establish and confirm the analytical characteristics of emissions observed in the reactive flow.

Initial efforts were made to investigate how RFD response toward the individual metals changed with the range of gas supply rates that are capable of yielding a stable reactive flow (i.e. hydrogen flows between 40 and 160 ml/min and corresponding air flows between 40 and 100 ml/min). Over this test range, the response of all the different analytes decreased by over 50% as the gas flow was increased. While the individual rates of decrease varied slightly, all of the examined elements attained their signal-to-noise maxima at relatively low flow settings (around 60 ml/min each of hydrogen and air). Table 1 presents the optimum gas flow settings for each element in the RFD. These conditions, and the corresponding trends in response, resemble those noted previously for the main-group elements sulfur, phosphorus [24], and tin [25] in the RFD. As can be seen from Table 1, the optimal response for transition metals in the FPD also occurs under a set of common conditions, albeit at an overall much larger flow of hydrogen than in the RFD [20]. It should be noted, however, that while flow variations in the RFD are restricted to ranges that produce

a stable luminescent column, flow variations in the FPD can cover a much wider range (e.g. such high settings as 600 ml/min of hydrogen and 300 ml/min of air are easily attainable).

Prior to this study, tin was the only metal examined in the RFD and also the only element to exhibit two response maxima there: one at lower, one at higher gas flow rates [25]. The second maximum is reported in parentheses in Table 1. This surprising behavior is apparently linked to the unique quartz surface emission observed for tin compounds. Not surprisingly, then, none of the metals investigated here displayed an obvious second response maximum, despite the potential contact between the reactive flow and the surface of its quartz enclosure. In accord with this view are certain visual observations of the reactive flow, in which the investigated transition metals were seen to emit light from the inner volume rather than from the inner surface of the capillary.

Using the specific optimal gas supply rates from Table 1, the analytical response characteristics for each metal in the RFD were individually measured. The results of these calibrations are presented in Table 2, while the chromatographic elution pattern and peak shapes are documented in Fig. 1. For inclusion in

Table 1
Optimum gas flows (ml/min) in the RFD and the FPD

Element	RFD ^a		FPD ^b	
	H ₂	Air	H ₂	Air
Ru	50	50	300	80
Cr	58	55	300	55
Mn	50	50	300	55
Ni	70	65	300	55
Fe	60	55	300	60
Os	58	55	300	60
S	40	60	50	40
P	40	60	140	60
Sn	33 (90)	50 (75)	140	60

^a Data obtained from this study except for S, P [24], and Sn [25].

^b Data obtained from [20] except for S [22], P, and Sn [31].

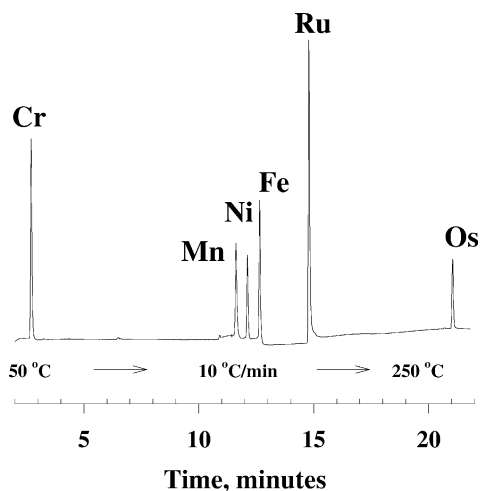


Fig. 1. RFD chromatogram of organometallic model compounds obtained under common conditions of 50 ml/min hydrogen and 60 ml/min air. The analytes, in order of elution, are chromium hexacarbonyl (100 ng), MMT (100 ng), nickelocene (100 ng), ferrocene (100 ng), ruthenocene (50 ng), and bis-(pentamethylcyclopentadienyl) osmium (100 ng).

Table 2
Response characteristics of various metals in the RFD and the FPD^a

Element	Detection limit (pg/s) ^b		Linearity ^c		Selectivity ^d	
	RFD	FPD ^e	RFD	FPD	RFD	FPD
Ru	0.1	0.1	1×10^4	4×10^4	4×10^3	4×10^5
Cr	3	3	2×10^4	1×10^4	3×10^2	1×10^3
Mn	10	3	2×10^4	2×10^4	9×10^1	1×10^4
Ni	5	0.6	1×10^4	2×10^4	1×10^2	1×10^4
Fe	15	3	2×10^4	1×10^4	1×10^2	2×10^4
Os	2	40	1×10^4	1×10^3	1×10^3	1×10^2

^a Each tested under conditions as given in Table 1.

^b Defined as the signal-to-noise (peak to peak) ratio equal to 2.

^c Linear slope with correlation coefficient >0.99; range of compound injected (1 ng to 50 µg for all; except ruthenocene 50 pg to 500 µg).

^d Elemental metal flow (g/s) vs. elemental carbon flow (g/s), the latter in the form of dodecane and naphthalene, in amounts that provide equivalent response within the linear dynamic range.

^e FPD references as given in Table 1.

Table 2, the RFD detection limits are measured as elemental flows in picograms per second at the conventional signal-to-noise ratio of 2, with noise determined as the “peak-to-peak” variation of the baseline over an interval of at least 10 analyte base widths. Thus determined detection limits are 0.1 for ruthenium, 3 for chromium, 10 for manganese, 5 for nickel, 15 for iron, and 2 for osmium. Compared with the detection limits obtained for the same elements in a conventional FPD (whose literature data are also included in Table 2), the RFD detection limits for ruthenium and chromium are similar [18,20]; those for manganese, nickel, and iron are somewhat higher [16,17,20]; and that of osmium is lower [19]. (For a comparison with non-conventional FPD systems, the reader may want to consult performance data from the “pulsed” [29] and “small stoichiometric flame” [30] versions of this detector). Similar to the behavior of most metals in the FPD, the linearity of each metal response in the RFD spans about four orders of magnitude.

In terms of metal selectivity against carbon (on a mole element/mole carbon basis), the RFDs performance for osmium and chromium differs by no more than a factor of 10 from the corresponding selectivity for these metals in the FPD, while that of ruthenium, nickel, iron, and manganese is lower by about a factor of 100 [16–20]. These “native selectivity” data were collected in the absence of any optical filter or other wavelength discriminating device (except for the spectral sensitivity profile of the photomultiplier tube). This procedure was chosen both for easiest

data reproducibility in other labs, and for highest analyte sensitivity in our own. As has been shown previously for the RFD [24], and as is also true for the FPD, a suitable interference filter can moderately improve the analyte’s selectivity over carbon, but it does so at a corresponding increase in the detection limit [31]. Thus, if otherwise acceptable, improvements of the RFDs native selectivity can usually be obtained from single-channel optical filters. Greater improvements still can be expected from certain dual-channel, computer-aided methods of generating virtual chromatograms, which have earlier been shown to greatly increase selectivities for various elements in FPD-based analyses [21].

3.2. RFD selectivity in dual-channel mode

In order to demonstrate the applicability of such a dual-channel approach for improving selectivity in the RFD, a sample of premium unleaded gasoline containing 30 ppm by weight of the anti-knock additive MMT was used. This type of sample was chosen because it contains large amounts of various hydrocarbons but only a small amount of the manganese compound. Manganese presents a particular challenge in this regard since its selectivity over carbon (i.e. its mole Mn/mole C response) is lower in the RFD than that of the other elements studied. Fig. 2 shows the chromatograms resulting from an injection of undiluted gasoline as seen (a) through a single, filterless channel (channel 1, “open”); (b) through a single channel

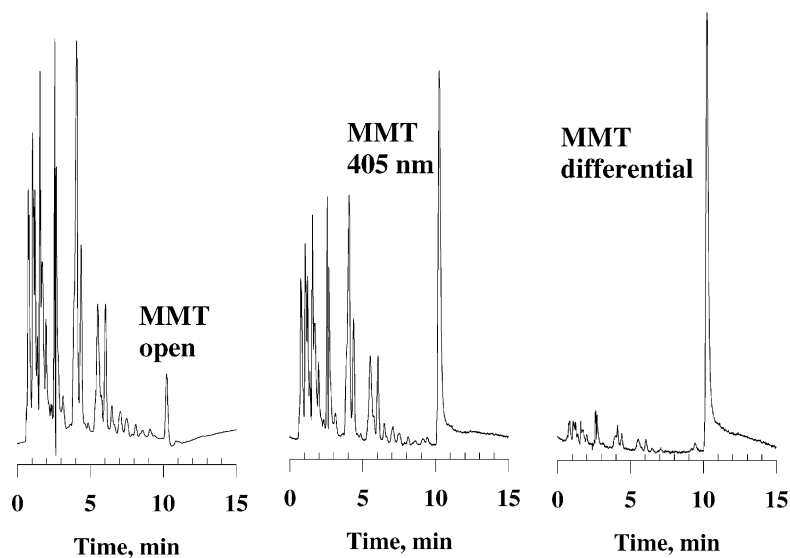


Fig. 2. Dual-channel RFD chromatograms of premium unleaded gasoline. Left trace: open channel. Middle trace: 405 nm interference filter (11 nm bandpass) channel. Right trace: differential chromatogram of the 405 nm channel minus the open channel, after background removal and amplitude matching of the carbon signal.

containing a 405 nm interference filter (channel 2, “405 nm”); and (c) through a dual-channel arrangement with appropriate computer processing (channels 1–2, “differential”) [17,32]. The filter, which makes use of a prominent Mn emission line, increases the manganese/carbon selectivity in a single channel by a factor of 9.6. The increase is similar to the improvement of 7.3 found previously for a corresponding FPD-based analysis [17]. In the dual-channel mode, manganese selectivity over carbon is increased by a factor of 108. In this case the computer tracks the difference between the two channels (after roughly equalizing their response to carbon). Such a procedure had been shown earlier to dramatically reduce the intensity of hydrocarbon to analyte signals in the FPD [17,33].

While the use of a filter in dual-channel experiments can be expected to degrade the detection limit, the effect appears minimal here since the signal-to-noise ratios of the manganese peak in the open and filtered channels of Fig. 2 differ by only a factor of 2. As far as signal integration is concerned, and for its own interest, it is worth noting that the manganese peak in the 405 nm channel exhibits tailing, most likely from the chromatographic process, which is also transferred by way of subtraction to the differential chromatogram.

However, this feature is not observed in the open channel, where the manganese peak elutes upon, and appears to interact with, the sizable background luminescence that is believed to originate mainly from the surface of the quartz capillary. As is well known, this type of surface can emit an intense glow under certain conditions. Such a glow can be reduced by injections of tetraethyl lead (an efficient scavenger of radicals) [24]. While it is not known whether MMT and tetraethyl lead, both of which serve as anti-knock additives in gasoline, engage also in the same type of surface interaction, it is clear that the background component speculated to contribute to the perturbation in the open channel of Fig. 2 is not visible in the 405 nm channel. In effect, then, analyte luminescence appears to decrease in the open channel due to a concomitant reduction of the background luminescence (i.e. peak tailing appears diminished through a simultaneous and commensurate dip of the baseline).

3.3. Mechanism

As in the above case of manganese, the other elements examined in this study also responded fairly similarly in RFD and FPD. In fact, of all the elements

studied in the RFD to date, none responded excessively stronger or weaker than it did in the FPD. This is perhaps not surprising, given the fact that the respective chemiluminescent spectra in the two detectors are very similar [32].

These findings suggest that both detectors operate via a similar excitation mechanism. Previously, the RFD had been found to have an upper excitation energy limit of 4.4 eV, which is in excellent agreement with the hydrogen radical recombination energy of 4.5 eV [32]. While the maximum energy found thus far for the FPD is still around 3.6 eV, the hydrogen radical recombination reaction is nevertheless considered the prime contributor to FPD analyte excitation [20]. Therefore, if both of these detectors do indeed operate through the same excitation mechanism and elicit the same type of response from various chemiluminescent elements, the immediate question arises why the RFD is not subject to the same detrimental type of analyte response quenching that is well known to interfere with quantitation in the FPD.

Based on an earlier study of several FPD-active elements, it has been suggested that quenching in the FPD originates from hydrocarbons ‘quenching the exciting flame, rather than the excited analyte’, presumably by scavenging key flame-propagating species such as hydrogen and oxygen radicals [22]. In contrast, the reactive flow may propagate via peroxide species, and it has been postulated to contain much lower concentrations of oxygen radicals [28]. In accordance with this scenario it was suggested that, if analyte emission quenching were to occur through the initial scavenging of oxygen radicals by hydrocarbon fragments, it should be much less prevalent in the RFD.

Due to its simple design, the glass capillary burner of the RFD can accommodate several modes of combustion other than that of its primary emission source, the reactive flow. The actualization of these modes is directly dependent upon the supply of air. When only hydrogen flows through the capillary and all air flows around it, i.e. through the detector housing, the RFD burner will support an (air-rich or hydrogen-rich) diffusion flame similar to that of an FPD. If all air is instead premixed with the hydrogen flow through the capillary, the RFD burner can support a premixed flame. If air is introduced through both the burner and the detector housing, the capillary is able to develop the reactive flow that provides the typical RFD emis-

sion. If the premix air flow is still further increased, the reactive flow is extinguished and a second flame appears at the bottom restriction of the capillary, similar to the ‘split-flame’ of a Smithell’s separator [24]. Thus the RFD capillary is capable of several modes of combustion, all of which can be produced and controlled by simply varying the introduction of air.

Before this study, it was reported that no discernable amount of quenching could be observed in either the reactive flow or the split-flame, even though the latter is thought to arise from the accumulation of oxygen radicals in the system [28]. However, since the split-flame temporarily ejects from the capillary in the presence of excess hydrocarbon, it was suggested that this event might have precluded the observation of any quenching effects. In contrast to typical RFD behavior, quenching now became clearly visible through the introduction of premixed and diffusion flame modes, which mimic the behavior of the FPD. Thus there must exist a significant chemical difference between quenching and non-quenching systems, a difference that could be used to distinguish these various combustion modes and influence the onset and/or extent of quenching.

One notable difference in response characteristics, which has been documented in earlier comparisons of the RFD with the FPD, concerns the relative abundance of carbon species. In the FPD, carbon compounds are spectrally observed to produce both CH^* and C_2^* [20]. In the RFD, however, CH^* is the predominant product of both aromatics and aliphatics [24]. Hence it would be interesting to know whether the presence or absence of C_2^* could possibly be correlated with the various quenching and non-quenching combustion modes.

In the present study, therefore, and in order to answer this question, carbon spectra were obtained for model aliphatic and aromatic hydrocarbons (*n*-dodecane and naphthalene) under each of the modes described earlier. The results are presented in Fig. 3, along with a schematic view of the location where each spectrum was obtained. As can be seen for both the reactive flow and the split-flame, the predominant spectral feature is centered near 430 nm. This is the well known flame species CH^* [34]. While CH^* is also strongly present in the premixed and diffusion types of flames, additional spectral features can be clearly seen in the region between about 470 and 570 nm.

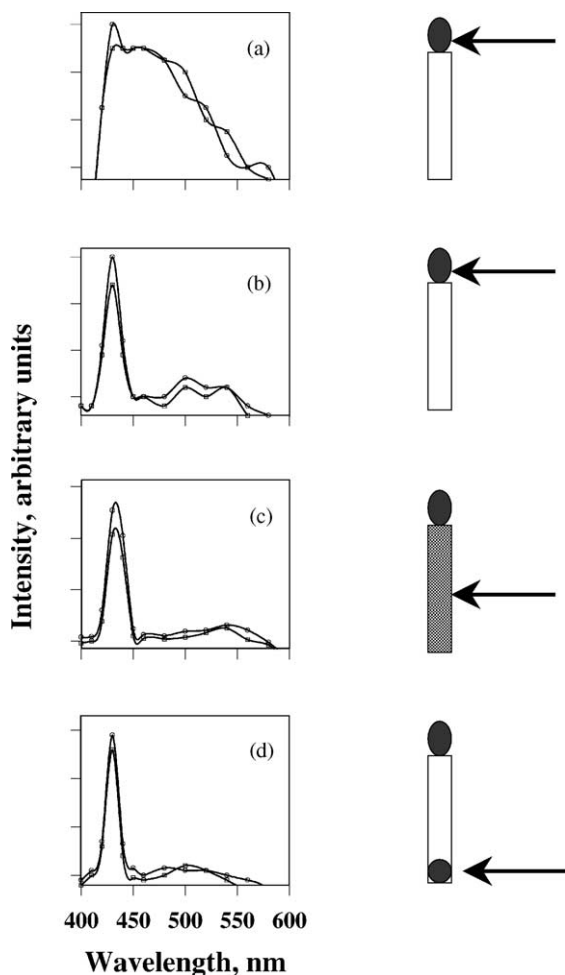
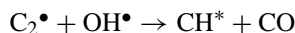


Fig. 3. Carbon spectra of *n*-dodecane (○) and naphthalene (□) in various combustion modes in the RFD set-up, viewed as illustrated at the right. The different modes are as follows (in parentheses: ml/min of hydrogen flow, premix air flow, and detector housing air flow, respectively): (a) a diffusion flame (50, 0, 85), (b) a premixed flame (50, 85, 0), (c) a reactive flow (50, 60, 150), and (d) a split-flame (50, 80, 150). See text for details.

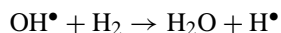
The additional features in this region correspond to those found for C_2^* in flames and, coupled with the CH^* emission, the overall spectra are very similar to those obtained for carbon in the FPD [20,34]. Thus C_2^* was observed only in those flames (of the premixed and diffusion type) where quenching was present. Conversely, in the reactive flow and in the split-flame (where quenching was absent), C_2^* was not observed. This suggests that the flame species C_2^* (based on

the observation of C_2^*) may indeed be involved in, or indicative of, the hydrocarbon-induced quenching of analyte emission as monitored in the premixed and diffusion flame modes of the RFD capillary. By analogy, the same postulated correlation between spectrum and response quenching should apply to the FPD flame.

While a variety of flame reactions are known of species such as C_2^* , one that is likely to be important involves the hydroxide radical



It is strongly believed to be a dominant pathway for CH^* formation in carbon containing flames [35]. Since OH^* is also a key flame species in steps such as the propagation reaction



its removal could easily depress the concentrations of other flame radicals such as hydrogen atoms. This is important, because it is the recombination of hydrogen atoms that is believed to provide the excitation energy for analyte chemiluminescence. Therefore, to quench hydrogen atoms means to “quench the exciting flame”, and hence quench analyte response. While this is not the only pathway by which quenching may occur (for instance, collisional quenching of the excited analyte emitter has long been proposed in the literature [36,37]) the assumed mechanism does agree with the spectra of Fig. 3 and with what is known about the respective properties of RFD and FPD.

For example, when OH^* (i.e. the typical spectral background found in a clean FPD) was monitored, injections of hydrocarbons led to a notable reduction in the observed emission [28]. This implies that OH^* (based on the observation of OH^*) was being removed from the FPD flame either indirectly, through the scavenging of radicals that contribute to its formation; or directly, through its reaction with carbon species in a process similar to the one noted earlier. In contrast, analogous experiments involving the injection of hydrocarbons into the reactive flow of an RFD showed no signs of reducing the dominant OH^* background [28].

While CH^* is indeed the predominant carbon emitter in the typical RFD, it should be noted that some non-typical (i.e. differently constituted) reactive flows may produce significant amounts of C_2^* . For example,

we have produced a reactive flow from a premixture containing 40 ml/min of methane and 45 ml/min of oxygen. It clearly displays, both visually and spectrally, very strong C_2^* emission. This reactive flow with its prominent green background emission failed to show any significant response to several typical RFD/FPD analytes. Similarly, a reactive flow obtained from approximately 40 ml/min each of hydrogen and chlorine in a premixture, where radical production from OH^\bullet does not play a role, also failed to show any significant emission from elements that otherwise respond strongly in the RFD. Furthermore, in related experiments that made use of a platinum-coated capillary, we could not establish a typical hydrogen/air reactive flow within the detector's usual operating range (i.e. hydrogen flows between 40 and 160 ml/min and corresponding air flows between 40 and 100 ml/min) even though a flame would spontaneously ignite at the platinum surface. Together, these findings indicate that when key propagating and energizing species, such as hydrogen radicals, are depleted in the combustion premixture, the RFD emission, and even the reactive flow itself, are compromised.

4. Conclusions

The RFD provides sensitive and selective responses toward organometallic compounds of chromium, manganese, iron, nickel, ruthenium, and osmium. The detection limits for these elements in a typical (i.e. air/hydrogen premixed) RFD vary from about 0.1 to about 15 pg of metal per second. The linearity for each metal response spans approximately four orders of magnitude, with native molar selectivities versus carbon typically ranging between 2 and 3 orders of magnitude. Similar to selectivity studies carried out earlier on the FPD, the RFDs native selectivity of manganese versus carbon can be increased approximately 100 times by using a differential, computer-assisted readout in an intensity-matched dual-channel configuration.

While, analytically and spectrally, the RFD and the FPD elicit similar responses from many elements, the unique absence of analyte emission quenching in the RFD was correlated with the virtual absence of C_2^* in the reactive flow. The well known presence of carbon as both CH^* and C_2^* in the FPD has been dupli-

cated in this study by using related combustion modes, in which quenching then became clearly apparent. In contrast to this FPD-like behavior, only CH^* was observed in the typical (hydrogen/air) RFD combustion mode, in which quenching was clearly absent. This suggests that C_2^\bullet (as based on the observation of C_2^*) may be a key carbon flame species and an indicator for the type of analyte response quenching commonly observed in a conventional FPD.

In addition to beneficial features such as the absence of analyte emission quenching and the capability of auxiliary flame ionization detection [26] in the RFD, the sensitivity that this detector provides for several elements suggests its use as an alternative to the FPD for the chemiluminescent detection of a variety of volatile hetero-organic compounds. While only the typical (air/hydrogen) reactive flow was employed for analyzing these elements, it would be interesting to investigate other potential modes of RFD metal response. For instance, a reactive flow based on oxygen/hydrogen premixtures, though potentially less stable, may produce different elemental emission characteristics and possibly improved RFD response. Such investigations will form the focus of future studies.

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