

Constancy of spectral response ratios in the flame photometric detector

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Abstract

The response ratio of a chromatographic peak in two optically different channels of the flame photometric detector depends little if at all on the size of the peak (analyte concentration), as long as the latter remains within the linear range of both calibration curves. However, if *wide* wavelength ranges are monitored for analytes with *multiple* emitters of a *different* kinetic order (non-linear calibration curves), response ratios may become subject to variation. Such variation may also occur if multiple-emitter luminescence is variably quenched and/or if the linear range of the analyte is exceeded. These effects are demonstrated with compounds of Cr, Fe, Mn, P, Sn and, particularly, S. In contrast, if *narrow* ranges of properly selected wavelengths can be monitored—so that a *single* emitter predominates—the constancy of response ratios will be maintained even if heavy levels of a quencher and/or multiple emitters of different kinetic orders are present in the flame. For instance, the response ratios of sulfur remain constant under these circumstances both in the conventional quadratic and the novel linear response mode.

1. Introduction

Recent developments have significantly broadened the role of the flame photometric detector (FPD). Once limited to sulfur and phosphorus [1,2], it is now known to respond to some twenty elements [3]; once restricted to gaseous inputs, it is now used with such techniques as micro-HPLC [4] and supercritical fluid chromatography [5]. For the well responding elements, it performs superior to other types of instrumentation [6]. In its two-channel configura-

tion it can produce chromatograms that are nominally specific (*i.e.*, of apparent infinite selectivity) for *any* luminescing element [7].

Such chromatograms are based on the response ratio (RR) of the selected element in the two FPD channels. This, however, is not the only role RRs can play. They can also serve in elemental recognition and confirmation, as well as in the subtraction of carbon matrix components [8,9] and of other types of interfering peaks. Differently expressed, RRs provide an additional, chemical dimension for chromatograms [10]. This dimension is not restricted to the FPD: any detector with two or more channels that produce synchronous peaks (or peaks of equal or at least adjustable dispersion) could be

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used (*cf.* ref. 11). The obvious condition for profitable use of additional dimensions is their “orthogonality”, *i.e.* the ability of different channels to extract significantly and sufficiently different chemical (or physical) information from the analyte.

If RR values are to play these important roles consistently and reliably in the analytical laboratory, they have to be invariant in analyte as well as quencher concentrations. (A quencher, in the narrow sense of the FPD, is a substance that reduces the luminescence of the analyte peak; a process that occurs, for instance, in the well known depression of sulfur response by co-eluting hydrocarbons [2,12–21]. In the wider context of spectroscopic flames, or of detection in general, other species or processes may perform roles similar to that of the typical FPD quencher). It is not possible to ensure the complete absence of quenchers in the FPD: column bleed, hydrocarbonaceous fragments from the analyte molecules themselves, and residual contamination from irreversibly absorbed and/or decomposed compounds are almost always present.

Although RR values in the FPD have proven to be fairly constant, exceptions have emerged [10]. Yet, no study has so far followed RR behavior over the full range of analyte and quencher concentrations. This neglect may have been justified for elements with only one emitter. For elements with multiple emitters, however—in particular when contained in multi-element samples and monitored over spectral ranges wide enough to allow optical access to *all* luminescing species—the constancy of RR values has to be ascertained before the various methods that depend on it [7–10] can be used in full confidence.

Why would the presence of more than one emitter—in other words of multiple spectra—change the constancy of RR values? The most obvious case occurs when the emitters follow different kinetic orders. The classic example here is again that of sulfur, which produces both second-order [1,12] and first-order [22] emitters. When these are simultaneously observed (*e.g.* when there is inadequate or no wavelength discrimination between the two emitters) the spectrum of the former dominates at high, that

of the latter at low analyte concentrations. The spectral mix, hence the RR value, thus *changes* with concentration.

Most FPD-active elements produce solely first-order (linear) emitters. If all emitters of a particular element are linear, its spectral mix—and, in consequence, its RR value—should remain constant over the whole linear response range of analyte concentration. However, the calibration curves for the different emitters may not all start to deviate from linearity at the same concentration. Or the different emitters may be influenced by a quencher in a different way or to a different extent. *Beyond* linear range, then, and/or in the presence of variable concentrations of a quencher, RR values could lose their constancy (and with it their analytical *raison d'être*).

Other factors exist as well that could alter the spectral mix of multiple emitters: temperature (column bleed), detector memory (system contamination), long-term repeatability of flow settings, etc. However, these factors are neither consistently reproducible nor meaningfully reportable, and they do not lend themselves to the same kind of systematic investigation as the straightforward variations of analyte and quencher levels. This study will therefore be restricted to the latter.

One further variable needs to be considered here: the optical ranges in which the luminescence is to be monitored. If both FPD channels are limited to one and the same emitter, the presence of others should not matter. However, such restrictive conditions are sometimes unattainable, sometimes undesirable. Extensive band systems or continua may overlap the primary emission of interest; or a survey-type analysis may call for a spectrally wide-open range in order to register *all* FPD-active elements. Also, sensitivity considerations may demand broader optical windows.

Clearly, there exist two extreme sets of conditions for dual-channel FPD measurements: broad (“polychromatic”) and narrow (“monochromatic”) spectral windows. Either case (or a combination of the two) may be chosen for good analytical reasons. (Given the 10-nm bandpass typical of a narrow-band interference filter, the

term “monochromatic” is used here rather loosely.)

Typical optical combinations of the polychromatic variety could comprise an open (filterless) channel plus one equipped with a short-pass (SP) or longpass (LP) filter, or two channels fitted with overlapping SP and LP filters. Both channels would carry wide-range (UV-sensitive, red extended) photomultiplier tubes. In contrast, the typical case of the monochromatic (really: bichromatic) variety would rely on two channels both fitted with narrow-band interference filters (and appropriate photomultiplier tubes).

In general, the polychromatic mode is more sensitive and offers simultaneous detection/determination for most or all FPD-active analytes; the bichromatic mode is better suited to monitoring one element only. Although the latter mode is more likely to display the desired constancy of the two-channel response ratios, the former is in even greater need of investigation because it represents—in our opinion, at least—a scenario that is analytically the more important, spectroscopically the more interesting, and technically the more demanding of the two. If RRs are wont to vary, they are more likely to do so when probed at a multitude (rather than at just a pair) of wavelengths.

Checking for the constancy of RR values could, however, become an endless task. For instance: what detector conditions should be chosen? Individually optimized conditions for each element? If so, should they be optimized for sensitivity, or selectivity, or RR constancy? And, if optimized for selectivity: selectivity against which element? Or, in contrast, should one common condition be selected that could fit all elements equally well (or badly)? Or a common condition that would be close to optimal for one (important) element while still allowing others to respond? Good analytical reasons could be found for pursuing each one of these alternatives. Each on its own would, however, require considerable experimental effort.

Since sulfur is the most important analyte in the FPD, and since we have recently described in detail a new linear mode for its detection/determination [22], it seems reasonable for us to use its conditions for all elements. Also, only the

most important and/or representative of the twenty-some elements that respond in the FPD will be scrutinized: the main-group elements [7] sulfur, phosphorus and tin; and the transition metals [6] chromium, manganese and iron. We shall start with the broadest optical windows possible, but narrow them down severely as soon as the RR values start to show signs of diversion.

2. Experimental

All experiments were carried out on a 1974 Model Shimadzu GC-4BMPF gas chromatograph with dual-channel FPD. The conditions, unless otherwise indicated, were those of the linear sulfur mode described earlier [22], *i.e.* 500 ml hydrogen and 40 ml air per minute, with the quartz chimney removed. The FPD was situated under an efficient exhaust duct for safety reasons. The nitrogen flow through the 1-m 5% OV-101 packed column was usually between 20 and 26 ml/min. The column temperature was chosen such that analytes would elute at a retention time of about 2 min, with σ values of approximately 5 s. Both FPD channels carried Hamamatsu R-374 phototubes (nominal range 180 to 850 nm, maximum response at 420 nm). Optical filters were used as needed; they are described in the captions to the figures. Methane, serving as quencher, was usually added through an in-line bubble flow meter to the hydrogen supply (which mixes with the column effluent before emerging around the central air jet). In one case (Fig. 4), methane was added to the hydrogen supply line via an exponential dilution flask. (Both methods yield essentially the same result; however, the exponential dilution flask does so with greater speed, the bubble flow meter with greater accuracy.)

3. Results and discussion

Fig. 1 shows the dependence of response ratios on analyte concentration through very wide spectral windows, one completely open, the

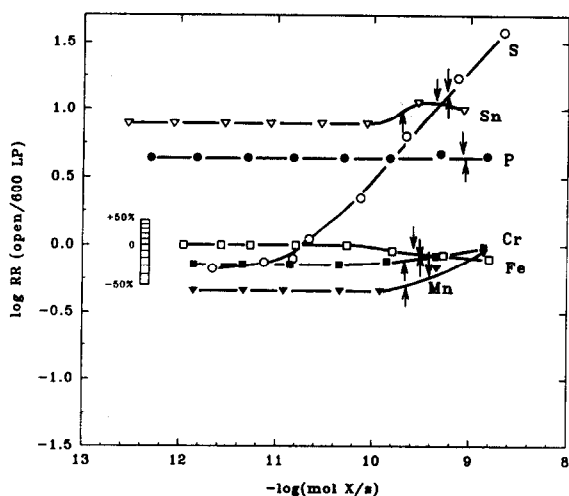


Fig. 1. Dependence of response ratios on analyte concentration for six test elements through and beyond their linear response range in the absence of a quencher. First channel: filterless; second channel: 600-nm longpass (600 LP) filter. Flow conditions are those of the linear sulfur mode. Downward and upward pointing arrows indicate the end of the linear calibration range in the first and second channel, respectively. \circ = Thianaphthene ($X = S$); \square = ferrocene (Fe); ∇ = tetra-*n*-butyltin (Sn); \bullet = diphenylmethylphosphine (P); \blacksquare = chromium hexacarbonyl (Cr); \blacktriangledown = MMT (Mn).

other open to wavelengths above *ca.* 600 nm. The measurement starts at some convenient concentration at which the baseline noise no longer influences the measurement—inconstancy occurs at high, not low analyte levels!—and stretches deliberately beyond the analytical range of the six test elements. The conventional calibration curves themselves are not shown here, but the upper ends of their linear ranges (defined by a 10% deviation from linearity) are indicated in Fig. 1 by arrows: pointing down for the open (filterless) channel, pointing up for the 600 nm longpass-filter channel. (In the case of sulfur, the down arrow marks the end of the *quadratic* range.) A percent deviation scale is put in place for the iron curve; it can, of course, be shifted up or down to serve *any* element.

With the exception of sulfur—whose behavior will be discussed later—the RR values are *constant* over the *linear* concentration range. Their deviations in that region do not normally exceed the random error of measuring peak

heights on a recorder chart. Only when the calibration curves approach or exceed the upper ends of their linear ranges do the RR values begin to diverge from their former constancy. Thus, as a rule of thumb, *spectral response ratios are independent of analyte concentration within linear range.*

For the apparently constant RR ranges—*i.e.* for the first four to six points of all curves except that of sulfur in Fig. 1—the relative standard deviation was measured as approximately 2%; it never exceeded 4%. (The same is true for Fig. 2.) This deviation is typical of the manual peak height measurements used in this study. If a worst-case 4% R.S.D. is assumed, and the condition is further imposed that each curve must be at least 6 standard deviations away from the next (*i.e.* a 99.7% correct assignment in the case of a normal error distribution), the +1.5 to –1.5 log RR range shown in Fig. 1 could accommodate 30 curves. (Log RR values higher than +1.5 or lower than –1.5 can obviously be measured, but such measurements are subject to increasingly wide error bands if carried out at trace levels of analyte.) It is, of course, statistically highly improbable that 30 curves could thus be stacked into the given space merely by the judicious choice of two wavelength regions. It is, however, equally obvious that a few more elements could be safely added to Fig. 1 (that is, under an—in this context—*incidental* spectral regime).

Thus, if the response ratios of other FPD-active elements should turn out to be as independent of analyte concentration as those of Fig. 1 (a reasonable assumption for linear emitters), most if not all of them could fit into a convenient range of RR values without overlapping—*i.e.* they could be safely used for recognition and confirmation of elemental composition [10], as well as for generation of element-specific [3,7] or otherwise computer-adjudicated [9] chromatograms. *One* chromatographic run could therefore identify, at least in theory, *all* FPD-active elements.

What, however, happens to RRs under *quenching* conditions? To answer that question, the standard quencher methane was introduced at arbitrary but constant levels; levels that re-

duced the analyte peaks to between 60 and 30% of their original height. Calibration curves were measured in the presence of methane in open and > 600 nm channels. Table 1 lists for illustration and later reference the experimental flows of methane and the percent quenching they caused in the two channels; Fig. 2 shows the variation of response ratios as plots of log RR vs. molar analyte flow. These results are very similar to those displayed in Fig. 1 in that the *response ratios can be considered constant under constant quenching conditions over the linear range of the calibration curve*. This occurs even though the percentage of quenching often differs significantly between the two channels.

The only and obvious exception to the claimed constancy of RR values in Figs. 1 and 2 is provided by the case of sulfur. This should come as no surprise: under the flow conditions of the linear sulfur mode, but with the optical channel wide open, the linear (HSO) sulfur emission dominates at low, the quadratic (S₂) sulfur emission at medium and high concentrations. The former is situated mainly in the red [22], the latter in the near ultraviolet and violet (with considerable extensions to the blue, the green, and beyond). The "open/600 LP" RR values for the two (pure) emissions are hence very different. Since one follows first-order but the other (roughly) second-order kinetics, the composite luminescence strays over much of Figs. 1 and 2. If *constant* RR values are required, optical

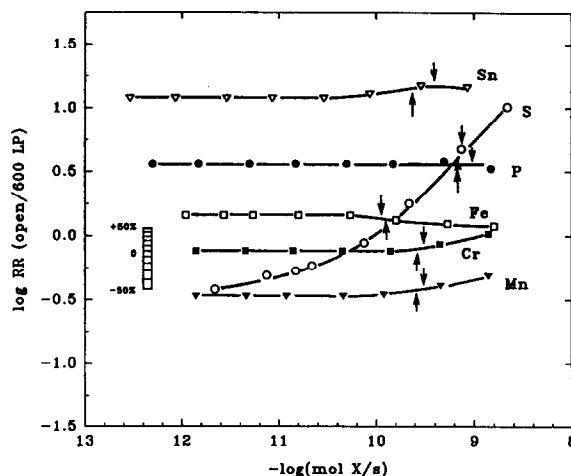


Fig. 2. Dependence of response ratios on analyte concentration in the presence of a quencher (methane). Conditions are similar to those in Fig. 1. The added constant flows of methane range from 2.0 to 8.0 ml/min, the quenching from about 30 to about 60% (see Table 1). Symbols as in Fig. 1.

conditions will have to be chosen such that *one* spectrum predominates over the entire analyte concentration range. We shall return to this problem later.

While Figs. 1 and 2 agree that RRs (that of sulfur excepted) are constant, they disagree on some (not all) of their *absolute* values. An overlay of the two figures points to particularly obvious discrepancies in the cases of tin and manganese. Given the absence of severe inter-experimental changes in flow settings, detector

Table 1
Experimental methane flows vs. resulting quenching for various elements in two detector channels

Analyte	Methane (ml/min)	Quenching (%)	
		Open	600 nm longpass filter
Thianaphthene	8.0	28	31
Diphenylmethylphosphine	4.3	39	50
Ferrocene	6.2	44	30
Chromiumhexacarbonyl	2.0	50	52
Tetra- <i>n</i> -butyltin	3.3	58	36
Methylcyclopentadienyl manganese tricarbonyl	4.0	32	45

contamination, etc., what basic explanation could be advanced for this behavior?

The most probable explanation is that both of these elements respond via more than one emitter. Although their spectra have not yet been measured at the flow conditions of the linear sulfur mode, their emissions at individually optimized settings have: tin produces the SnOH and SnH bands as well as a blue surface luminescence on quartz [23]; manganese yields two strong atomic lines, a sizable continuum [8], and perhaps some molecular bands. These features should be present here as well. Although the quenching mechanisms are unknown for these (as well as for all other) emitters, their relative quenching efficiencies could be expected to differ. But any such difference could cause significant differences in spectral distribution between the (partially) quenched and the unquenched luminescence, and hence lead to a significant change in RR value.

The comparison of Figs. 1 and 2, while pointing to a problem, fails to define its full extent. In Fig. 2 the quencher is present at an (arbitrarily chosen) constant level. What about varying levels of the quencher? What about varying levels of the analyte? The intuitive expectation about the quencher is, of course, that higher levels should lead to larger RR discrepancies; while the empirical expectation about the analyte is that higher levels (with the quencher concentration remaining constant) should make little or no difference. (The latter presumes that the analyte remains within the linear range of both calibration curves and, more importantly, that percent quenching is inherently independent of analyte concentration. That view is shared by most but by no means all researchers in the field [2,5,12–17], owing perhaps to the many different FPD conditions under which quenching phenomena can and have been observed.)

Fig. 3 shows the response ratios of various elements challenged by increasing levels of quencher, all at the same detector conditions. The response ratios remain constant (within 10%) until the open-mode peak is quenched by more than approximately 20% for Sn, S and Mn; 30% for Cr; 70% for P; and 90% for Fe. (Due to the

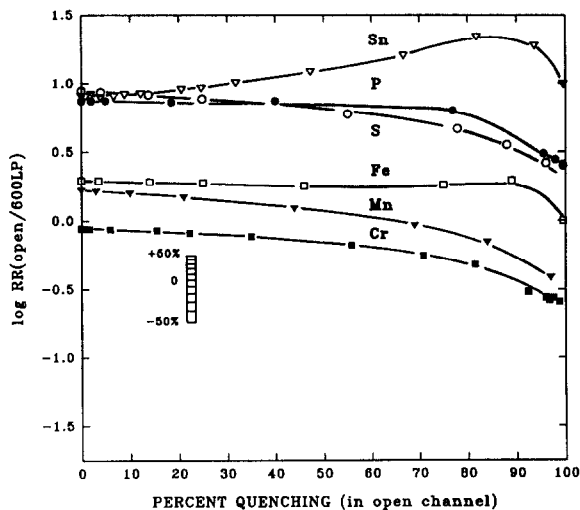


Fig. 3. Dependence of response ratios on percent quenching. Quenching percentages on the x axis are those of the filterless ("open") channel. The optical conditions are the same as in Figs. 1 and 2. However, flow conditions may have slightly changed due to time (and resetting of flows) between the two experimental series, and different test compounds were used for Mn and Cr. O = Thianaphthene; □ = ferrocene; ∇ = tetra-*n*-butyltin; ● = diphenylmethylphosphine; ■ = benzenechromium tricarbonyl; ▼ = cyclopentadienylmanganesetricarbonyl.

poor measurement conditions at quenching efficiencies higher than 90%, data points in that region are less reliable, though analytically also less interesting.)

The quenching of FPD peaks can be traced not only to the co-elution of hydrocarbonaceous components [12–21] of the sample—including the solvent tail—but also to column bleed [17] and other types of contaminants. Usually the latter are persistent in nature but also relatively low in concentration and small in effect. Often that effect is already included in the calibration curves and hence would not be separately recognized by the analyst.

Note that the data points describe the response ratio in two different optical channels of the *same* eluting peak, hence refer to the *same* quencher concentration. However, the extent of quenching as measured in the two channels may strongly differ. A choice has therefore to be made which channel to use for the—analytically important—"percent quenching"

efficiency shown on the abscissa. The open (= filterless) channel is chosen because it represents the most general and the most widely applicable of optical conditions.

It may be asked how the same quencher concentration can lead to apparently different percentages of quenching (compare Table 1) on two different optical channels. A variety of circumstances can cause such an effect.

First, and by far most likely, the analyte may produce two or more different emitters that are (directly or indirectly) quenched to different extents. Second, a single emitter may be excited by two or more processes of energy transfer (as an example only: 4.5 eV from H + H and 5.2 eV from H + OH) in which (a) the same emitter reaches different upper vibrational (in the case of atoms: electronic) levels and (b) the relative concentration of the radicals responsible (in this example: H and OH) is influenced by the concentration of the quencher. Third, different excited states of even the same emitter may be quenched to different degrees. Fourth, emissions may be present that originate from species other than the analyte, and are subject to quenching by a different mechanism and to a different extent. The always present OH or the usually present CH provide cases in point. Fifth, the ubiquitous—and often slowly changing—FPD background (baseline luminescence) may also be quenched differently at different wavelengths. For instance, the analyte itself could be draining the excitation energy of ambient emissions. Several more scenarios, or combinations thereof, appear possible. In general, such effects are likely to be exacerbated if FPD conditions change (by temperature programming, premature sample decomposition, etc.) and/or if different emitters follow different kinetic orders.

An example of the degree to which two emitters of a different kinetic order can influence the response ratio is shown in Fig. 4. It is presented here not only to illustrate a particular problem—which will later be explored and rectified—but also to address, at least in passing, the most prominent mode of the most prominent FPD analyte. The analyte is (of course) sulfur, but the detector flow conditions

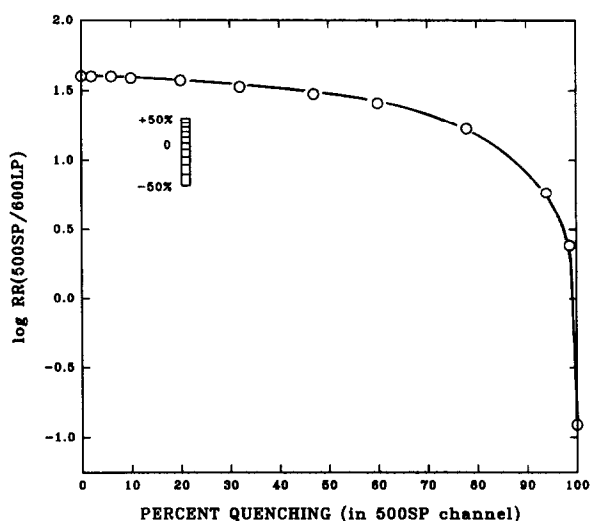


Fig. 4. Dependence of sulfur response on percent quenching at conditions of the quadratic mode. Analyte: 8 ng bis(*tert.*-butyl)disulfide. Flows in ml/min: hydrogen (total) 50, air 40, nitrogen (column) 26. This measurement series uses the commercial quartz chimney and introduces methane (the quencher) into the hydrogen flow via an exponential dilution flask. 500SP = 500-nm shortpass filter.

chosen here are not those of the new linear mode [22] as used for Figs. 1–3, but those of the conventional quadratic mode [2,12]. The 500-nm shortpass filter admits almost all of the quadratic S_2 emission while the 600-nm longpass filter accepts mainly the linear sulfur emitter (though the latter under less than ideal circumstances). The two emitters are influenced to different degrees by the presence of the quencher, resulting in a dramatic effect: the response ratio displayed in Fig. 4 varies by more than two orders of magnitude! A similarly dramatic variation of the response ratio occurs when the concentration of the analyte—rather than that of the quencher—is changed. In fact, it was a comparable experiment that provided the first clue to the presence of a linear sulfur emitter in the FPD [10].

Clearly, it should be demanding as well as rewarding to change the optical conditions such that—in the ideal case—only two transitions off the same excited state are sampled and that, therefore, the response ratios do remain constant *regardless* of quencher and analyte concentra-

tions. Only then could the analyst who is exclusively interested in, say, sulfur, draw conclusions about the presence or absence of that element in chromatographic peaks without having to be mindful of sample composition, peak height correlation and detector contamination. (At the same time, the analyst interested in a broad range of elements may well prefer the widest optical conditions for an all-inclusive though conceivably precarious and possibly preliminary look at the elemental composition of peaks contained in a complex sample.)

If previous thoughts about multiple spectra and/or excitation modes are any guide, the best chance for obtaining constant response ratios for sulfur in the quadratic mode seems to lie in monitoring, through narrow-band interference filters, two strong bands of the dominant S_2 system—preferably two bands that originate from the same upper vibrational level ($\nu' = 0$ is, of course, the most likely candidate). We happened to have available two 11-nm bandpass interference filters of wavelengths 394 and 405 nm, which fitted well to the S_2 transitions at 393.89 nm (0,9) and 404.56 nm (0,10) [24]. While these filters do not represent the *ideal* choice and do not exclude *all* interference from CH, they are still suited to the task.

Fig. 5 shows the outcome of the experimental variation of quencher and analyte concentrations. To set the conditions as demanding as possible, the experimental variation of analyte was carried out in the presence of a constant level of methane, and was driven beyond the quadratic range of the analyte. (Here, as in some later figures, the solid line is drawn deliberately at slope zero. The degree to which individual data points deviate from this ideal RR constancy can thus be judged. In contrast, linear or non-linear regression lines would show a slight slope for the whole group, thereby minimizing individual deviations.) The 394/405 nm response ratio for sulfur in the quadratic mode is now practically non-variant, despite the fact that the percentage of peak quenching, and the amount of analyte injected, vary over extremely wide ranges.

This strongly suggests that the same emitter is

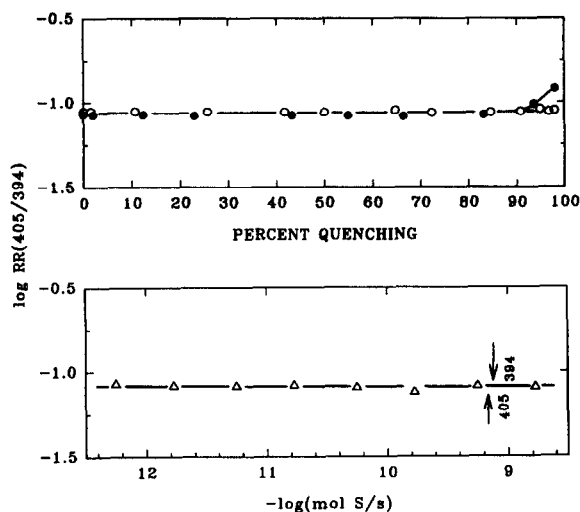


Fig. 5. Constancy of response ratios for quadratic sulfur (S_2) at different quenching intensities and analyte levels. Interference filters: 394 and 405 nm, both of 11 nm bandpass. Commercial quartz chimney around flame. Analyte: 20 ng (open circles) and 300 ng (full circles) of thianaphthene. Gas flows in ml/min: hydrogen 50, air 40, nitrogen (column) 20; methane variable (upper plot), or equivalent to a 60% reduction in peak height on both channels (lower plot).

being monitored—predominantly if not exclusively—in the two channels. A further indication to that effect arises from a comparison of the quenching percentages for analyte peaks appearing simultaneously in the two channels. The percentages are not just directly proportional (which would be sufficient to ensure the constancy of response ratios) but they are practically identical. Identical quenching percentages for quadratic sulfur concur with the findings of Sugiyama *et al.* [13], who characterized the decrease in S_2 emission as “independent of wavelength and almost uniform over the whole wavelength range”.

(It may be parenthetically noted that the use of response ratios—which are highly sensitive to small changes in relative emission intensities—and of huge experimental variations in quencher and analyte concentrations could offer a second, more discerning look at sulfur luminescence. Our first attempt of establishing response ratio constancy for the S_2 system used an available 340/394 nm interference filter combination, and

resulted in RR values that were by far not as constant as those shown in Fig. 5 [25]. Whether this was related to the different S_2 upper vibrational levels in the 340 nm region [24], or to the presence and/or reactions of other emitters, has not been determined.)

As with varying quencher concentrations, the 394/405 nm S_2 response ratio remains constant in the face of a strongly varying *analyte* concentration as well. It does so over the whole quadratic range of the calibration curves (whose upper ends are marked in Fig. 5 by two arrows) and, reassuringly, even beyond.

Yet, to modify the behavior of *quadratic* sulfur was not the main objective of this study. More important to us was the behavior of sulfur's response ratio under the flow conditions of the *linear* mode [22]. As Figs. 1, 2 and 3 demonstrate, response ratios can become grossly unstable under latitudinarian monitoring. The main emissions of the linear mode appear to be the 0,0 and 1,1 bands at 696 and 711 nm, and the 0,1 band at 749 nm, of the $^2A'-^2A''$ transition of HSO [26]. Therefore, the available combination of a 700-nm wideband filter (of 70 nm bandpass) and a 750-nm wideband filter (of 40 nm bandpass) was chosen. When observed only through these spectral windows, linear sulfur turned out to be well behaved indeed. This is demonstrated in Fig. 6 by a response ratio that remains constant in the face of large variations in quencher and analyte.

The quencher-variation data of Fig. 6 were obtained with two, relatively high levels of analyte (where the challenge from S_2 emissions is the most acute). Still, the RR values remain constant even under severe quenching conditions, quite unlike those of the otherwise comparable sulfur curve of Fig. 3.

The analyte-variation data of Fig. 6 were obtained at a constant methane level (equivalent to 47% quenching). Again, the constancy of the RR value—quite unlike that of the otherwise comparable sulfur curve in Fig. 2—is maintained over a wide range of analyte concentrations. Furthermore, the RR values of the two plots are identical, thereby lending further credence to their overall constancy, and hence to the suppo-

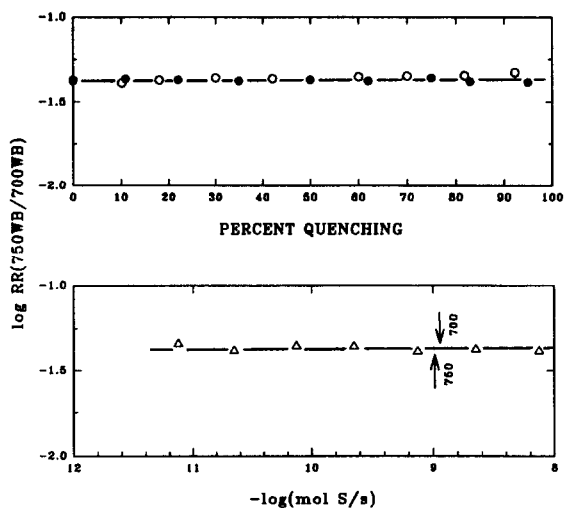


Fig. 6. Constancy of response ratios for linear sulfur (HSO) at different quenching intensities and analyte levels. Interference filters: 700 nm wideband (bandpass 70 nm) (700WB), 750 nm wideband (bandpass 40 nm) (750WB). Analyte: 100 ng (open circles) and 1000 ng (full circles) of thianaphthene. Conditions are those of the linear sulfur mode as defined in the Experimental section. Methane flow: variable in upper plot; equivalent to a 47% peak height reduction in both channels in lower plot. Arrows indicate the upper ends ($\sim 10\%$) of the linear calibration curves.

sition that the *same single* emitter is being monitored on the two channels.

Sulfur, the most prominent FPD element to determine (and the most difficult one to determine well) thus produces constant RR values in both the conventional quadratic and the novel linear mode. Under carefully selected optical conditions, then, either mode is capable of providing constant, hence diagnostic response ratios. This means that various computer-manipulated chromatographies [7–10] can detect sulfur reliably, even in the case of ill-defined hydrocarbonaceous sample matrices.

This successfully concludes the study of sulfur. However, the FPD responds not only to sulfur but (so far) to some twenty other elements as well. Sulfur, while outstanding in its prominence as FPD analyte, does differ from all other elements of this study in its kinetic behavior. Thus it may be worthwhile to consider, by way of example and however briefly, a couple of selected elements that (a) show particularly

strong RR deviations in Fig. 3, (b) differ considerably in their (constant-range) RR values between Figs. 1 and 2, (c) are known to produce multiple emitters, and (d) hold proven or potential significance as analytes in the FPD. The elements selected by these criteria are tin and manganese.

Organotins have been the target of many environmental analyses [27], quite a few of which made use of the FPD (*e.g.* ref. 28). Authentic FPD spectra are available [23]. In contrast, organomanganese compounds have only recently been suggested as FPD analytes [8]. Yet, future use of the FPD seems likely for determining manganese in industrial and environmental samples. Also, a suitable spectrum, from the common gasoline additive methylcyclopentadienylmanganese tricarbonyl (MMT), has been measured in the FPD [8].

So far, the same detector conditions —*i.e.* conditions optimized for linear sulfur detection— have been used for all elements. This appears reasonable for multi-element analysis with sulfur as the prime target, but makes little sense for single-element determinations of tin or manganese. Clearly, compounds of these two metals are best observed at their own, individually optimized conditions.

This forces a choice in the case of tin: Although tin's blue surface luminescence on quartz is far more sensitive than either the broad SnOH continuum or the sharp SnH bands [27,28], the latter are still favored by many environmental laboratories. Also, they appear more amenable to accepting the intended spectral probe. The main heads of the (0,0) SnH band's $^4\Sigma^-2\Pi_{1/2}$ and $^4\Sigma^-2\Pi_{3/2}$ components are located at 609.5 and 689.2 nm [24].

The spectral characteristics of manganese are quite different. The predominant FPD emission, at 403 nm, contains most likely one or more of the (usually very strong) atomic lines at 403.076, 403.307 and 403.449 nm. The other prominent emission, at 540 nm, may represent one or both of the (usually very weak) lines at 539.467 and 543.255 nm. All of these lines represent transitions to the ground state, *i.e.* they occur from *different* excited states. Furthermore, both of

these sharp emissions rest on a continuum, of minor intensity at 403 nm, but of major intensity at 540 nm [8]. The present task of achieving constancy for RR values would perhaps be served best by sampling the continuum, or by exploring further manganese emissions in the red and near infrared. However, since the 403-nm lines are the obvious choice for the practical FPD determination of Mn, the decision was made to pair them with the 540-nm emission, despite the latter's uncertain nature and underlying continuum.

Fig. 7 demonstrates the constancy of the tin (SnH) response ratio *vis-a-vis* large variations in quencher and analyte concentrations. The slight slope of the quenching curve for 5 ng of tetra-*n*-butyltin may be due to interference from the strong surface luminescence continuum, which saturates at about the 30-ng level [23]; however, this assumption has not been further investigated. Note that the absolute RR values are essentially identical in the two plots; and that, in stark contrast to the polychromatic tin curves

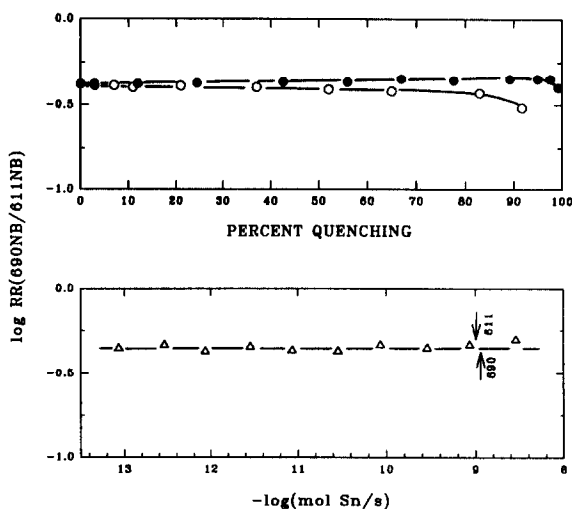


Fig. 7. Constancy of response ratios for tin (SnH) at different quenching intensities and analyte levels. Interference filters: 690 (690NB) and 611 nm (611NB), both of 12 nm bandpass. Analyte: 5 ng (empty circles) and 100 ng (full circles) tetra-*n*-butyltin. Flows in ml/min: hydrogen 300, air 150, carrier nitrogen 20; methane variable in upper plot, or equivalent to a 40% peak height reduction in both channels in lower plot. Arrows indicate the linear-range end of the calibration curves.

shown in Figs. 2 and 3, they are close to invariant. The difference between the two types of behavior may be reasonably attributed to monitoring one *vs.* more than one emitter.

A somewhat different picture emerges from the bichromatic assessment of manganese shown in Fig. 8. Its response ratios, at 10 and 300 ng levels of the injected analyte MMT, stay constant in the analytically more important first half of peak height reduction, but grow then progressively worse. Large and small amounts of manganese are affected to the *same* extent (as is typical of FPD quenching behavior, the above case of tin notwithstanding). The shape of the curve appears consistent with a mechanism in which the continuum that underlies (mainly) the 540-nm emission is quenched significantly less than the two (sets of) atomic lines. However, other spectrochemical rationalizations cannot be excluded at this point. Manganese response through the full range of quenching is, as expected, significantly better under bichromatic than under polychromatic (Fig. 3) conditions.

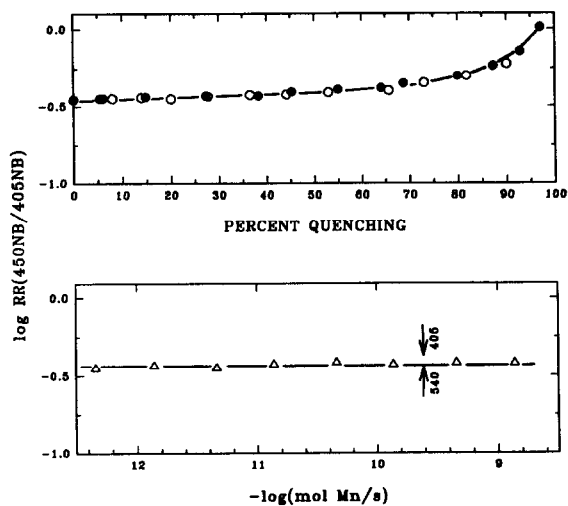


Fig. 8. Response ratios for manganese (Mn) (two emitters?) at different quenching intensities and analyte levels. Interference filters: 450 nm (9 nm bandpass) (450NB) and 405 nm (11 nm bandpass) (405NB). Analyte: 10 ng (empty circles) and 300 ng (full circles) of methylcyclopentadienylmanganese tricarbonyl (MMT). Flows in ml/min: hydrogen 300, air 55, carrier nitrogen 20; methane variable in upper plot, or equivalent to a 47% reduction in peak height on both channels in lower plot.

Furthermore, the response ratio of manganese is perfectly non-variant over four orders of analyte variation (compare Fig. 2). Here as elsewhere, the full variation of the analyte appears to mount less of a challenge to the constancy of response ratios than the full variation of the quencher.

It should be recognized in this context, though, that a plot of dual-channel response ratios represents an exquisitely sensitive probe of quenching behavior. This becomes obvious by looking at Fig. 9, where raw data from Figs. 6–8 are displayed in the form of conventional quenching curves [29].

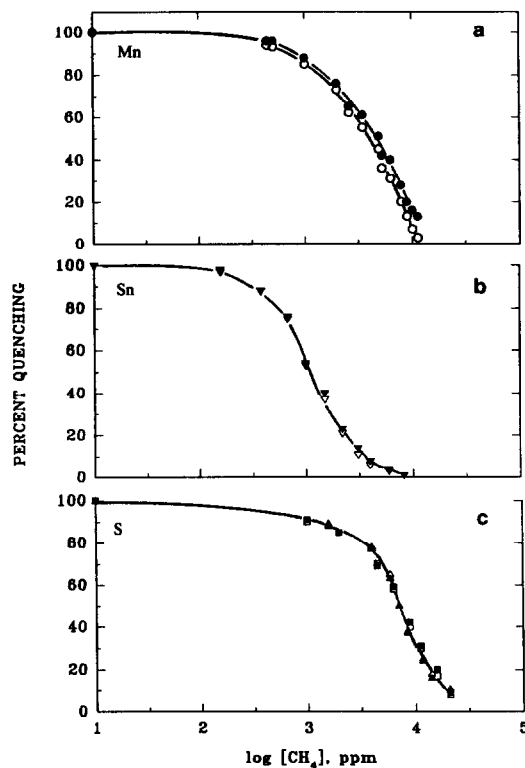


Fig. 9. Percent quenching of manganese, tin and linear sulfur luminescences at individually optimized conditions *vs.* quencher concentration. The abscissa refers to the molar (*i.e.* volume) concentration of methane in the *unburnt* flame gases. Conditions for 300 ng MMT (Mn) are those of Fig. 8; for 100 ng tetra-*n*-butyltin (SnH) those of Fig. 7; and for 100 and 1000 ng thianaphthene (HSO) those of Fig. 6. (a) MMT: 300 ng, ○ = 405 nm, ● = 450 nm. (b) Tetra-*n*-butyltin: 100 ng, ∇ = 611 nm, ▼ = 690 nm. (c) Thianaphthene: □ = 0.1 μg, 700 nm wideband; △ = 0.1 μg, 750 nm wideband; ■ = 1 μg, 700 nm wideband; ▲ = 1 μg, 750 nm wideband.

For manganese (MMT), these typically sigmoid curves portray the fractional quenching of the larger of the two analyte amounts. In contrast to Fig. 8, the small difference in behavior at the two wavelengths is hardly noticeable. (The smaller amount of MMT produces like results.) Similarly, only the larger amount of tin (as tetra-*n*-butyltin) is shown. For tin, no difference is expected from Fig. 7 and none is found. To complete this round of comparisons, the full data set for linear sulfur (the same set as used for Fig. 6) is redrawn in this "kinetic" representation. The latter demonstrates well (a) that the percentage of quenching is independent of analyte concentration, and (b) that the two channels register essentially identical behavior—hence, most likely, the same emitter.

Graphic contrast aside, the main reason for showing the quenching curves of these three key elements at three different sets of conditions is that they exemplify and quantify the typical dependence of "percent quenching"—the particular measure used in this study—on the spectrochemically important molar concentration of the quencher methane in the (unburnt) flame gases.

4. Conclusions

Response ratios from dual-channel detectors offer additional chemical information and can therefore aid the identification or confirmation of chromatographic peaks on the qualitative side, and the suppression of interferences or background features on the quantitative side. The obvious requisite is, however, that they remain non-variant *vis-a-vis* large changes in analyte and/or quencher concentrations.

In the case of the FPD, the most obvious and most effective means for achieving unlimited response ratio constancy is based on the selection of the two monitored wavelength regions. Yet, that selection also determines whether the analysis will scan a wider array of elements or focus on one element only. Polychromatic conditions (wide wavelength ranges) yield constant ratios if the analyte produces a single emitter. If

it produces more than one emitter—a common occurrence—the response ratios will remain constant if all emitters are linear (*i.e.* if their luminescence is first order in analyte) and if they remain within their respective linear calibration ranges. Although such a linear multi-emitter FPD system will tolerate a constant or weakly variable influx of quencher, it will not normally tolerate a strongly variable one.

In contrast, bichromatic conditions (in the ideal case: two transitions off the same excited state, with no other emissions around) may have to be chosen if multiple emitters of different reaction orders are present, if the analyte exceeds linear range, and/or if the concentration of the quencher (usually a co-eluting matrix component) fluctuates excessively among samples.

Possible sets of such bichromatic conditions have been successfully defined for both the quadratic and the linear response mode of the most important FPD element, sulfur. Under these conditions, sulfur response ratios remain constant at any concentration of quencher and analyte. Additional exploratory experiments with tin and manganese suggest that the constancy of response ratios can be achieved not only for sulfur, but also for most if not all elements that are known (or will still be found) to luminesce in the FPD.

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6. References

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