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Quenching in the flame photometric detector[☆]

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ABSTRACT

The conventional, roughly *quadratic* sulphur response mode in the flame photometric detector (FPD) is subject to severe quenching by co-eluting hydrocarbons. This interference is greatly reduced in a new, *linear* sulfur response mode, which tolerates an about twentyfold larger amount of quencher. Under these conditions, the response of a variety of elements is quenched to a similar extent as that of sulphur; *i.e.* the amount of quencher needed to halve response typically varies by a factor no greater than three between sulphur and any of the other five elements tested (Fe, Sn, P, Mn and Cr). It is therefore possible to speculate that linear sulfur is not quenched by a mechanism *sui generis*, but that it is simply subject to the same general quenching process(es) as other FPD analytes. The extent of quenching for all tested elements is largely *independent* of analyte concentration —provided the latter remains within linear range.

INTRODUCTION

Hydrocarbons quench the response of sulphur in the flame photometric detector (FPD) [1]. This effect is troublesome to analytical chemists, particularly those concerned with petroleum products, air pollutants, pesticide residues and food aromas. Considerable effort has therefore been expended to elucidate the quenching mechanism (ref. 2 and studies cited therein). Its most common description assumes collisional deactivation of electronically excited S₂ by CH compounds or their fragments [3].

In contrast, there exists to our knowledge no major study of quenching effects involving elements other than sulphur. This is surprising because the FPD responds to some twenty [4,5] of them: beyond sulphur, the detector is routinely used for analytes containing phosphorus or tin in many laboratories, and applications involving several more elements have been reported. In fact, the impression the reader may easily gain

from the literature is that the quenching of sulphur luminescence is unique in extent and kind. The rather sporadic nature of references to the quenching of *other* elements only serves to reinforce this impression.

Currently, quenching mechanisms for sulphur remain speculative and quenching data for other elements sparse, so that any further information should be welcome. In particular, analysts might want to predict the effects of peak overlap in *multi-element* samples. For analyzing such samples, the FPD conditions are typically chosen for optimum response of the most important element, and that is usually sulphur. Given that conditions are tailor-made for sulphur, does quenching then affect other elements? If so, to what extent?

That question arose for us during recent attempts to assess the analytical merits and demerits of a new FPD sulphur emitter (see Note added in proof), *i.e.* during a comparison of the new with the established FPD method for determining sulphur compounds. Briefly, the new mode monitors the red, the old the violet region of the visible electromagnetic spectrum; the new

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mode is linear in response, the old (roughly) quadratic. Response linearity strongly favors the former; sensitivity and selectivity weakly the latter [6]. Beyond these essential analytical criteria, however, it may be the *quenching* effects that could tip the balance in favor of using one or the other. Quenching data could also prove important to photometry in the absence of chromatographic resolution, as in certain types of sensors.

Experimental answers will therefore be sought in this study to a series of fairly obvious but also fairly important analytical questions: Is the response of sulphur in the linear mode *less* or *more* susceptible to quenching than in the quadratic mode? What happens to the response of *other* FPD-active elements under the quenching conditions of the linear sulphur mode? Under these conditions, does sulphur really behave *different* from other elements? What is the *extent* of quenching an analyst should expect when using the linear mode? Is it dependent on the *amount* of analyte?

EXPERIMENTAL

The instrument, an ancient Shimadzu GC-4BMPF with dual-channel flame photometric detector, and its operating conditions were essentially the same as described earlier [6] for the linear and quadratic response modes of sulphur. Briefly, the linear sulphur mode employed flows of 500 ml hydrogen and 40 ml air per minute, a 600-nm longpass filter and no quartz chimney; the quadratic (*i.e.* traditional) mode used 50 ml hydrogen and 40 ml air, a 500-nm shortpass filter and the commercial quartz chimney. Both modes were fed sulphur analyte by 26 ml/min nitrogen from a 100 × 0.3 cm I.D. borosilicate column packed with OV-101 on Chromosorb W, 100–120 mesh; and both channels were monitored by Hamamatsu R-374 photomultiplier tubes of nominal range 180 to 850 nm and maximum response at 420 nm.

Methane was added to the hydrogen supply line (which joins the column effluent in the detector before entering the flame), and its concentration or rate of introduction was calculated in parts per million (ppm, v/v) of the total

gas flow (hydrogen + air + nitrogen) for spectroscopic or mechanistic, and in microgram carbon per second for chromatographic or analytical purposes. The flow of methane was established and measured by either injecting methane into an exponential dilution flask (purged by part of the constant hydrogen stream), or by inserting a bubble flow meter with low-flow valve into the methane supply line.

(The use of an in-line bubble flow meter, though not conventional, is convenient and, judging from basic principles, reasonably precise and accurate. It eliminates the derivative role of the conventional rotameter, whose accuracy depends on that of the bubble flow meter with which it was initially calibrated. For reasons of safety as well as for ease of calculation, there must be no appreciable resistance to the hydrogen–methane flow, *i.e.* the methane pressure in the graduated tube of the bubble flow meter must be close to atmospheric. Note that the procedure introduces trace amounts of water vapor from the soap solution. However, this does not compromise the performance of an FPD. Also, the contribution of the partial pressure of water to the measurement is small enough to be neglected in the calculation.)

Chemicals were obtained from conventional commercial sources and were used as received for preparing solutions in (usually) acetone. Calibration curves, particularly in the case of sulfur, were established by injecting the *smallest* amount first. Injections were routinely performed in duplicate. As a rule, differences between corresponding peaks represented only the typical variability of syringe injection (*i.e.* the error bars from a larger number of injections would have been too short to show up to any significant extent in the graphs).

RESULTS AND DISCUSSION

Any quantitative definition of quenching effects in the new linear sulphur mode needs to include a comparison with the established quadratic mode, preferably carried out on the same instrument. Fig. 1 shows in full symbols the quenching curve (the relative fractional response) of 8 ng bis(*tert.*-butyl)disulphide against

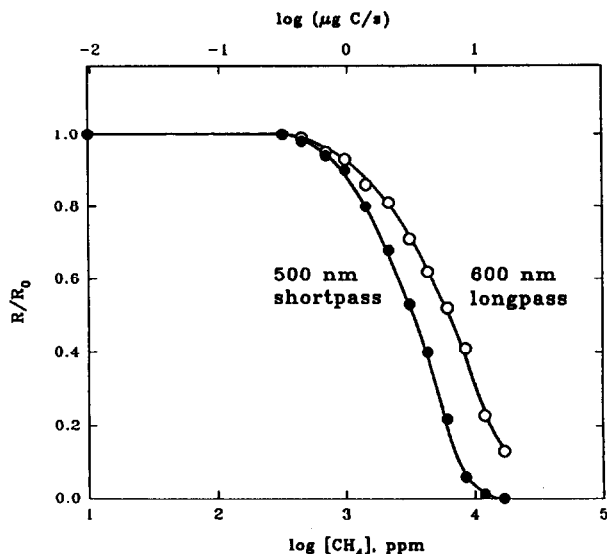


Fig. 1. Quenching of sulphur in the quadratic mode. Analyte: 8 ng of bis(*tert.*-butyl)disulphide; Quencher: methane introduced from an exponential dilution flask into the hydrogen line. R = Quenched response; R_0 = unquenched response. See Experimental for conditions of the quadratic mode.

the methane concentration at the detector flow conditions of the quadratic mode, and with almost all of the S_2 luminescence admitted by the 500-nm shortpass filter. (Essentially the same curve, though at lower sensitivity, can be obtained with the traditional 394-nm interference filter.) The approximate shape and position of this curve is well known (see Fig. 12 of ref. 7), although the *conventional* measurement uses an overlapping peak rather than, as here, a constant background of the quencher.

Given the (in a semilog plot) sigmoid shape of the curve, a measure of quenching intensity may be reasonably and conveniently taken at its halfheight, *i.e.* at the point where quenching has reduced a peak to 50% of its original size and where R/R_0 equals 1/2. This occurs in Fig. 1 for the quadratic mode at a methane concentration (calculated on the total gas flow) of about $3.7 \cdot 10^3$ ppm (v/v), or a carbon flow of $3.4 \mu\text{g/s}$. (The former unit has been chosen for comparison with the spectrochemical, the latter for comparison with the chromatographic literature. While “microgram of carbon per second” is the measure most often used in the literature to

describe FPD quenching effects, it should not be taken to imply independence of chemical structure; that is, the effect of different quenchers should not be automatically equated with the flow of carbon they introduce into the flame.) Methane has played the role of a quenching standard several times before, for instance when it was introduced *through* the column to mimic stationary phase bleed [8].

Fig. 1 also includes a measurement of the red region with a 600-nm longpass filter (empty symbols). The two curves were determined off the selfsame peaks, hence are exactly comparable. (In this and other studies, we made as much use as possible of *both* FPD channels, on the assumption that a second set of data from an optically different range would provide confirmation, serve as a back-up, and/or supply additional information—and, if it did none of these, could be easily discarded.) The 600+ nm region contains the spur of the S_2 bands plus the bands of the linear emitter, though at the flow conditions of the quadratic mode. It is nevertheless obvious that the linear emitter appears less susceptible to quenching than S_2^* . The effect is not large, about a factor of 2 at halfheight. The corresponding data for a tenfold amount of analyte—80 ng bis(*tert.*-butyl)disulphide—are very similar and, consequently, are not shown here.

(Despite the exiguity of the effect when measured by the difference in quencher concentration for equal fractional quenching, it can appear dramatic when measured by the ratio of relative peak heights for an equal—and very heavy—quencher concentration. This is demonstrated in Fig. 2—note its logarithmic ordinate!—where the ratio of two peaks changes more than a hundredfold due to the presence of the quencher. Although rare, such cases do occur in analytical practice.)

It is against this background of quenching intensity in the conventional quadratic mode, that the new linear mode has to be assessed. Peaks obtained at the conditions of the linear mode (high hydrogen, no quartz chimney) are monitored by, again, *two* photomultiplier channels. The first channel, equipped with a 600-nm longpass filter, truly represents the *linear* mode:

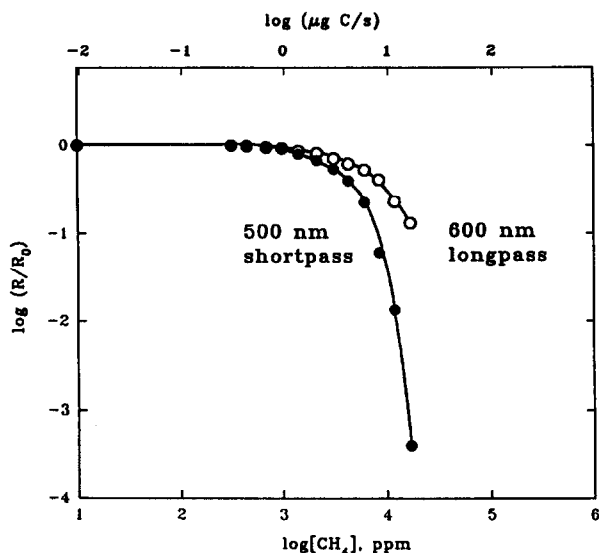


Fig. 2. Extreme quenching of sulphur in the quadratic mode. Similar to Fig. 1 but with logarithmic ordinate.

the calibration curves are purely first order. The second channel is "open" (filterless), *i.e.* it can potentially accept radiation over the full 180–850-nm range of the photomultiplier tube. Calibration curves for sulphur in this channel are approximately quadratic: though weakened by the flow conditions, the S_2 bands still dominate.

Yet, the main role of the open channel is not to pick up all the emissions of sulphur, but all the emissions of those other five elements. Those elements we consider typical of a wider variety of analytically significant FPD analytes, and we include them here to widen the experimental base for a general discussion of quenching. Nevertheless we must note that, strictly speaking, the particular numbers measured depend to some extent on the particular instrument, the particular flow conditions, and the particular combinations of analyte and quencher (as is the case in almost all studies involving flame photometric and other selective GC detectors). Still, we expect the general results and trends of this study to remain valid beyond their experimental origin, *i.e.* we expect them to apply, *mutatis mutandis*, to most GC-*FPD* systems.

Fig. 3 shows the quenching curves for sulphur measured under the flow conditions of the linear mode. The methane levels for peak halfheight

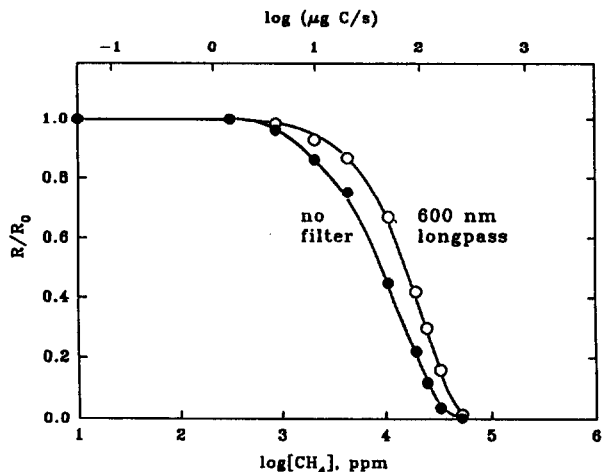


Fig. 3. Quenching of sulphur in the linear mode. Analyte: 50 ng of thianaphthene. See Experimental for conditions of the linear mode.

are about $9.6 \cdot 10^3$ ppm and $1.6 \cdot 10^4$ ppm for the open and >600-nm channels, respectively. The corresponding carbon flows are 43 and 73 $\mu\text{g C/s}$. Again, the difference between the two optical channels amounts to roughly a factor of 2.

Much more important than the comparison of the two optical channels is, however, the comparison of the quadratic with the linear mode under individually optimized conditions (*i.e.* the 500-nm shortpass curve in Fig. 1 vs. the 600-nm longpass curve in Fig. 3). The result is quite interesting: the linear mode can tolerate a methane flow that is, in flame ppm, roughly 4.4 times and, in $\mu\text{g C/s}$, 22 times larger than in the quadratic mode (the numbers are measured at a 50% reduction in peak height, but remain fairly constant over the whole analytically interesting quenching range). The former number represents the spectrochemically and kinetically relevant one in that it addresses the flame composition; the latter, however, represents the chromatographically and analytically important one in that it predicts the relative intensity of quenching by an overlapping peak (or a heavy column bleed). That the linear mode shows an approximately twentyfold greater tolerance of quenching than the quadratic mode may prove decisive for the *FPD*'s most common task, the

determination of sulphur compounds in complex hydrocarbon matrices.

A look at the absolute quenching intensities for sulphur reveals a surprising fact: it seems that these numbers are not all that different from the numbers that characterize the extent to which the luminescence of other elements is quenched. The literature, as mentioned before, contains some isolated descriptions of quenching beyond sulphur and, in our own work, we have occasionally measured (though never closely studied) the quenching characteristics of one or the other transition metal. To wit, the flame concentrations of methane that caused a 50% reduction of peaks containing Fe [9], Ru [10] and Mn [11], were $4.8 \cdot 10^3$, $1.6 \cdot 10^3$ and $3.5 \cdot 10^3$ ppm (v/v), respectively. That is quite close to, say, the $3.7 \cdot 10^3$ ppm measured for sulphur in the quadratic mode. However, these earlier measurements were taken at significantly different flow conditions (hydrogen range 300 to 370, air range 60 to 80, total nitrogen range 44 to 55 ml/min, *i.e.* at generally higher air flows hence higher temperatures). A direct comparison of these old data with the new ones could thus prove misleading.

What is obviously needed for a valid comparison is to examine *all* elements at approximately the *same* conditions (“approximately” because different temperatures for the chromatographic separation, hence slightly different column flows and bleed levels, as well as temporally, qualitatively, and quantitatively variable memory effects of the chromatographic system, can never be completely ruled out). The one common set of conditions that we shall apply to *all* elements of this study will obviously be that of the linear sulphur mode.

Fig. 4 shows the quenching data of the chosen five elements, plus sulphur, at the exact conditions of the linear mode. Fig. 5 takes an “open” (filter-less) look at the very same peaks. What is obvious but surprising in these figures is that all curves huddle together, with sulphur right in their middle. No curve is farther away from the sulphur curve than by a factor of two (Fig. 5) or three (Fig. 4) in quencher concentration. If all elements and both figures are combined, the strongest quenching curve turns out to be no

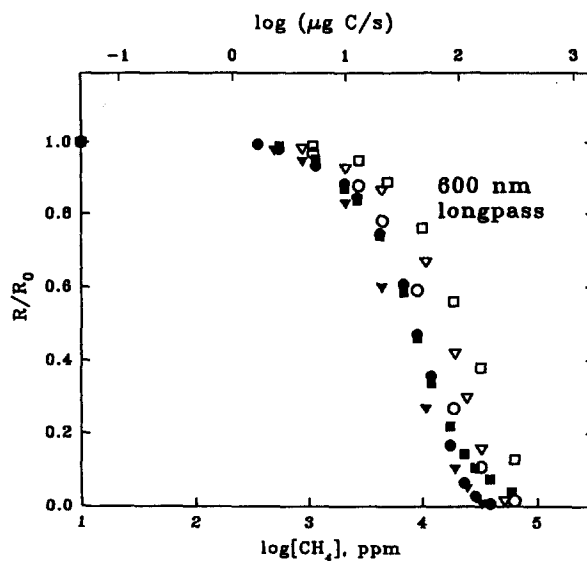


Fig. 4. Quenching of six elements in the linear-sulphur mode. Optical filter: 600 nm longpass. Curves omitted for clarity. \circ = Ferrocene; \bullet = *n*-tetrabutyltin; ∇ = thianaphthene; \blacktriangledown = triethylphosphite; \square = cyclopentadienyl manganese tricarbonyl; \blacksquare = benzene chromium tricarbonyl.

farther away from the weakest than by a factor of four. This suggests that the behavior of all elements tested in this mode is so far similar and, hence, that the behavior of *sulphur is not unique*.

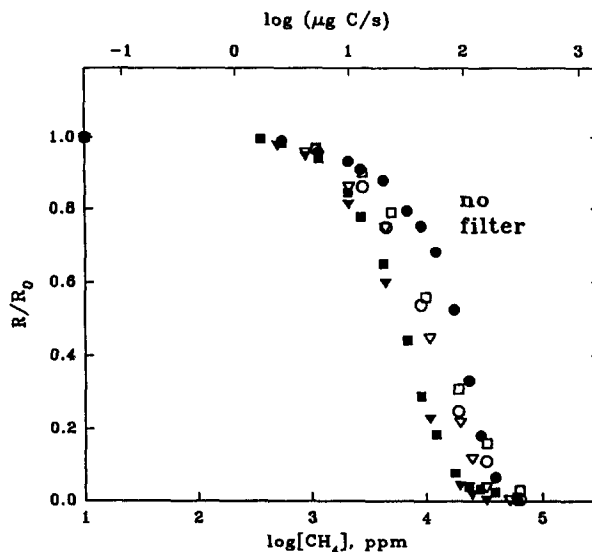


Fig. 5. Quenching of six elements in the open mode. Simultaneous measurements from the experiment shown in Fig. 4, but as seen by the second, filter-less FPD channel. Symbols as in Fig. 4.

Stark speculation may compare the narrow spread of data in Figs. 4 and 5 with—to pick an example for the sake of argument—a listing of Stern–Volmer rate constants for the quenching of singlet oxygen, which includes numbers varying over more than eight orders of magnitude [12]. Such a comparison is not to imply that collisional deactivation of the emitter can be safely excluded as the dominant quenching mechanism: one could, for instance, hypothesize that the FPD system (with similarly wide-spaced differences assumed at the molecular level) could be governed overall by a *diffusional* quenching constant. The far-flung analogy merely suggests the viability of other mechanistic scenarios. The most obvious alternative scenario: the quencher deactivates high-energy flame species that, directly or indirectly, are supplying luminescence energy. This type of mechanism, when used to rationalize the closeness of the quenching curves, also suggests that the various elements undergo common—or at least kinetically interconnected—energy-transfer processes leading to excitation. In this context it is interesting to note that the atomic emissions of several transition elements in the FPD conformed to an apparent upper limit (3.6 V) for the excited state [5]. All this suggests, oversimplified, that *hydrocarbons may quench the exciting flame rather than the excited analyte*. The concept of physical or chemical quenching of high-energy flame species has been mentioned several times before in the sulphur-FPD literature, although it is usually discounted there in favor of the direct collisional deactivation of the excited emitter [2,3,13].

In practical terms, the fact that similar quenching effects can be expected for peaks of different elements provides at least a rule-of-thumb to the analyst. Incidentally, the luminescent *response* of carbon is also subject to the *interference* of carbon: in fact, plain hydrocarbon peaks are somewhat stronger quenched by background methane than are peaks containing iron [9] or manganese [11].

If the extent of interference is to be estimated for analytical purposes, a crucial criterion is whether quenching does or does not depend on the amount of analyte (in the presence of a constant amount of quencher). Farwell and

Barinaga [2] have stated that, “as with nearly every aspect of the FPD sulfur response, confusion and contradiction are associated with the concept of quenching”. This applies here as well [e.g. refs. 3 and 13]; no doubt because of the very different systems and conditions that are traditionally reported under the FPD heading.

The experimental question is thus whether the calibration curve measured in the presence of a quencher is linear and, if so, whether its linear range is comparable to that of the regular calibration curve measured in the quencher's absence. Further, whether any parallelism of the two curves occurs not only through but also beyond their respective linear ranges.

Fig. 6 shows conventional log–log calibration curves for sulphur—with vs. without methane, and for the full spectrum vs. for just its linear portion. The full-spectrum runs illustrate the difficulties a quadratic emitter brings to photometric analysis: although the general shapes of the two calibration curves appear reasonably

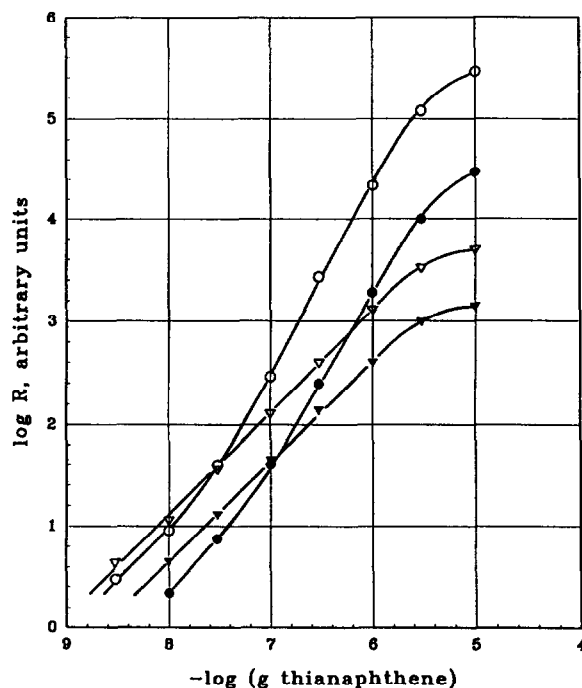


Fig. 6. Calibration curves of a sulphur compound with and without quenching in two optical modes. \circ = No filter, no CH_4 ; \bullet = no filter, with CH_4 ; ∇ = 600-nm longpass filter, no CH_4 ; \blacktriangledown = 600-nm longpass filter, with CH_4 .

congruent, their response ratio fluctuates wildly. This is not surprising since (a) at least two emitters of different kinetics contribute luminescence in commensurately different proportions, and (b) the lower end of the calibration curve is, in addition, subject to the linearizing effects of contaminant background sulphur.

In contrast, the runs using the 600-nm cut-on filter, *i.e.* the quenched and unquenched calibration curves of the *linear* mode, appear nicely parallel, at least until their upper bend-off. They resemble in their linearity the quenched and unquenched calibration curves of other elements. As an example, Fig. 7 displays the corresponding set of curves for the second-most important element in the FPD, phosphorus. Again, overt differences in ratio between quenched and unquenched calibration occur only when the linear range is about to end.

Yet, conventional calibration curves still appear too tolerant of small differences in ratio. Also, several more elements need to be brought into the picture. Therefore we have plotted the ratio of the calibration curves (the fractional quenching) *versus* the flow of the FPD-active element X in $\log[\text{mol X/s}]$; and we have also

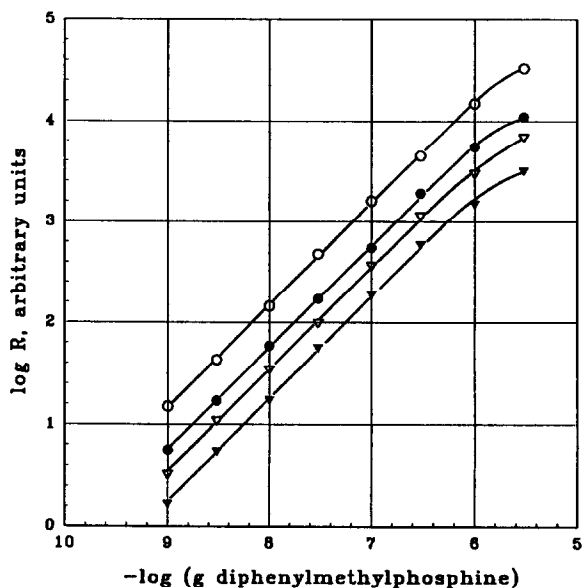


Fig. 7. Calibration curves of a phosphorus compound with and without quenching in two optical modes. The conditions are those characteristic of the linear-sulphur mode as used in Fig. 6. Symbols as in Fig. 6.

included arrows to point to the upper (-10%) end of the linear (or, in two cases involving sulphur, quadratic) response range of the unquenched curves. Fig. 8 shows this for the 600-nm longpass filter (*i.e.* the linear sulfur mode), Fig. 9 for the corresponding filter-less operation. The choice of the individual quenching level of methane was arbitrary for each analyte; however, we aimed for a general range of 40 to 70% peak reduction so that any change in the relative quenching intensity would show up clearly in the figures for later analytical and mechanistic interpretation. The analytical interpretation, for one, turned out to be pleasantly unambiguous.

Fig. 8 establishes that *fractional quenching is generally independent of analyte concentration* over most of the linear range (of the unquenched calibration curves). Even beyond the linear range, however, most deviations from this rule are relatively minor. Linear sulphur is certainly well-behaved in this regard. The only major deviation is that of iron, perhaps because of multiple emitters [9]. No experimental effort was made to extend the horizontal lines all the way back to the detection limit, but then, no devia-

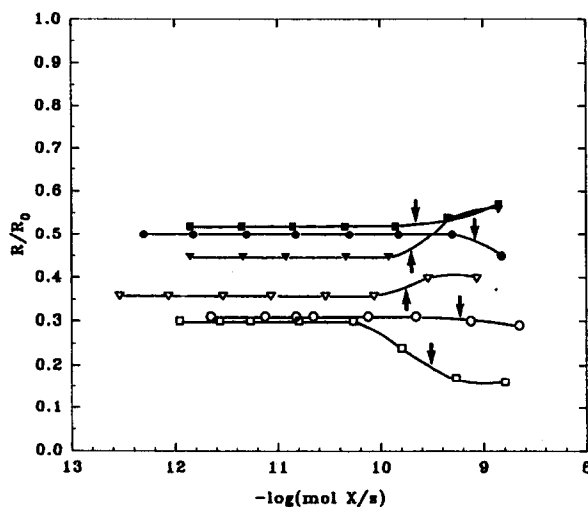


Fig. 8. Fractional response of six elements under constant quenching conditions in the linear-sulphur mode. X = FPD-active element. The arrows mark the upper end of the linear range (10% deviation) as taken from the unquenched calibration curve. \circ = Thianaphthene; \square = ferrocene; ∇ = tetrabutyltin; \bullet = diphenylmethylphosphine; \blacksquare = chromium hexacarbonyl; \blacktriangledown = methylcyclopentadienyl manganese tricarbonyl. 600-nm longpass filter.

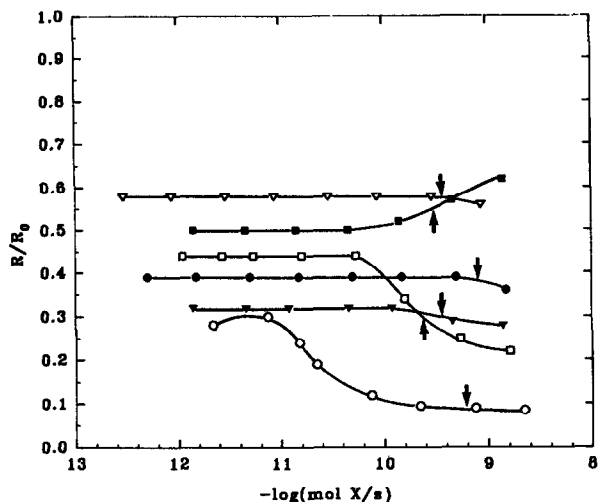


Fig. 9. Fractional response of six elements under constant quenching conditions in the open mode. Simultaneous measurements of the experiment shown in Fig. 8, but as monitored by the second, filter-less FPD channel. Symbols as in Fig. 8.

tions from a constant R/R_0 ratio would be expected to occur at low concentrations, either. That quenching can be considered independent of the amount of analyte (a fact familiar to many analysts working with sulphur, but one that needed confirmation in regard to the *linear* sulphur mode and in regard to other elements) should prove helpful in analytical practice.

Presumably, the assumption of quenching being constant would be more severely tested in a wider optical range. In open mode, more emitters will be seen: tin will emit via SnOH, SnH and the blue surface emission on quartz [14]; some transition metals will radiate via atomic lines, molecular bands and continua [5], etc. It could be argued that this should make no difference as long as all simultaneous emissions, though being affected to different degrees by quenching, do obey first-order kinetics. However, different emitters (of the same element), quenched to different degrees, will likely have different endpoints of linearity. Thus it is to be expected that multiple-emitter systems will exhibit variations of the R/R_0 ratio when the optical conditions are changed, or when the analyte amount exceeds one or more of the different linear ranges. Generally speaking, the extent of deviation from the ideal, *i.e.* constant

R/R_0 ratio should therefore depend on the position and width of the optical window.

This may indeed have been the case for some elements in the optically open configuration of Fig. 9; although no deviation is excessive and, for a case like tin, turns out to be even smaller than in the 600–850-nm region. (Such a case may, for instance, occur if the spectrally open mode would allow the strongest emitter to dominate, while a spectrally more limited mode would curtail its dominance and hence allow another emitter to be noticed as well.) The only roguish curve is that of sulphur—but, as can be ascertained from Fig. 6, that is mostly due to a quadratic joining in with a linear emitter. It would therefore seem that the rule of constant relative quenching could be extended even to very *wide* spectral regions (provided that all monitored emitters respond in linear fashion and remain in linear range).

NOTE ADDED IN PROOF

A prescient comment on “linear sulfur emission” and the “linear sulfur mode” has just appeared in print [15], and we would like to draw the attention of the reader to it. Also, in our earlier reports [6,16,17] we had characterized the linear sulfur emitter—which is of importance in the context of this manuscript—as “unknown”. At the time we were, however, unaware of a particular spectrum that had been obtained some time ago by Schurath *et al.* [18]. The luminescence in question emanated from the system $O_2/O + H_2S + O_3/O_2$ (total pressure 1.3 torr) + 50 mtorr water vapor, and was assigned to the (vibrationally cooled) $^2A' - ^2A''$ electronic transition of HSO [18]. This cited spectrum is remarkably similar to the spectrum of the linear sulfur emitter [6]. In particular, the HSO 0,1 band shows up clearly at 749 nm, as do the (incompletely resolved) 0,0 and 1,1 bands at 696 and 711 nm. The 2,0, 1,0 and 0,2 bands at 634, 663 and 809 nm appear to be present as well [6]. While we cannot exclude the presence of the “infra-red and far red” systems of S_2 —note, for instance, that 0,0 bandheads of the latter are listed at 751 and 710 nm [19]—the resemblance of the recorded spectra and the linearity of the

emission (*i.e.* the linear calibration curve for sulfur analytes) argue strongly against the (presumably second-order) emitter S₂ and for the (presumably first-order) emitter HSO.

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