

Spectrum, multi-element selectivity and elemental response of a linear sulfur emitter in flame photometry[☆]

Walter A. Aue* and Xun-Yun Sun

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

(First received August 14th, 1992; revised manuscript received November 24th, 1992)

ABSTRACT

Although the luminescence from sulfur compounds in the flame photometric detector (FPD) is dominated by the S₂ main-system bands (of about quadratic response), it contains as well a *linear* emitter whose “spectrum” could be recorded in the 600 to 850 nm region. In this region sulfur chemiluminescence is a first-order process and varies, if at all, by a factor of less than two in elemental response (sulfur equivalency) among several structurally diverse compounds. The single-channel selectivity of linear sulfur against other FPD-active elements—B, C and H, Sn, Pb, N, P, As, Se, Cr, Mn, Fe, Ru and Os—was measured for a band at *ca.* 750 nm (as well as for a wider 600 to 850 nm range), and was compared with the selectivity of S₂ for its commonly monitored band at 394 nm (as well as for the total 300–850 nm photomultiplier range). The IUPAC detection limit ($S/\sigma = 3$) of linear sulfur is $2 \cdot 10^{-13}$ mol S/s and its linear range spans four orders of magnitude. Overall, the new linear mode seems preferable to the conventional quadratic one; and it appears competitive with other methodologies of organosulfur detection. A speculative discussion of inter-element selectivity, mainly as it relates to spectral features, is appended, at the reviewer’s request.

INTRODUCTION

During a study of response ratios in a dual-channel flame photometric detector (FPD) we chanced upon a linear sulfur emitter [1]. Since it attracted some interest, a more detailed assessment of its spectral and analytical properties appears warranted.

Such an assessment poses a few experimental questions: What is the spectrum of the linear emission? Can it be attributed to one or more of the many known sulfur systems? And—given that the search for the linear spectrum is successful—can that knowledge be used to improve selectivity *vis-à-vis* other elements that luminesce in the FPD? Indeed, what are the interelemental selectivities at some well-chosen and typical conditions? How do

they compare with similar selectivities for S₂? Do structurally different compounds produce *different* responses per gram of sulfur? If so, how large is the effect in the linear as compared to the conventional (quadratic) mode? Finally, when most of the above questions have been answered, which analytical mode is likely to emerge as the “better” one for the flame photometry of sulfur compounds? And if that is to be the linear mode, how would it compare with other methods of linear sulfur detection in chromatographic effluents?

The first question—as any first question about a newly recognized emitter—must obviously be directed at its spectrum and, subsequently, its chemical nature. Two aspects make the quest for the linear sulfur spectrum particularly difficult.

On one hand—and common to all elements responding in the FPD—the spectrum of the emitter has to be determined under typical operating conditions. Otherwise, analytical relevance may be lost [2,3]. That means making do with the low spectral

* Corresponding author.

* Part of Ph.D. Thesis of X.-Y. S.

resolution imposed by a feeble luminescence; it also means remaining within the linear (or, in the case of S_2 , quadratic) range of analyte concentration.

On the other hand—and peculiar to sulfur—the S_2 bands arise from a *second-order* reaction [4,5]. Hence they tend to overwhelm any first-order luminescence at those high analyte concentrations that (see above) have to be used for spectral assignments. The S_2 main system stretches from the ultraviolet to the red [5,6] and is extremely prominent in the feeble, cool, and hydrogen-rich flame of the FPD. Optimizing the conditions for the competitive linear emission detracts but little from that prominence. Still, the need is urgent to define if not the chemical nature so at least the spectral distribution of the linear emitter in order to optimize analytical performance.

Analytical performance also motivates the second question of this study, *i.e.* how selective linear sulfur behaves *vis-à-vis* other important FPD elements, and how those selectivities compare with similar data from quadratic sulfur. *Linear* sulfur behaviour allows response relationships to other elements to be described by single numbers (selectivity ratios), which remain valid as long as both elements stay within their respective linear ranges. Quadratic sulfur behaviour does not lend itself to so simple a description: full calibration curves would be required for a complete picture. Yet, even an approximate indication of relative response intensities might prove valuable for the analyst.

That brings up the question under what conditions selectivity ratios should be measured to be of maximum analytical value. Quadratic sulfur response is traditionally determined using a 394 nm interference filter [7,8]. In some of our own work (*e.g.* ref. 9) we have preferred to use the FPD “open”, *i.e.* free of spectral discrimination beyond the response profile of the photomultiplier tube. Recently we compared some main-group [3] and transition [10] elements on that basis. In this study we shall use the open mode again for quadratic sulfur, but only as an appurtenance to the traditional measurement at 394 nm.

A spectrally “open” measurement is not possible for linear sulfur (the S_2 bands would overwhelm it at the required high analyte concentration) but it is possible to measure a relatively large part of the spectrum, *i.e.* the region transmitted by a 600 nm

long-pass (cut-on) filter. To narrow that range down to one band (belonging to the linear sulfur emitter, one hopes), a filter centered at 750 nm is used. As in measurements dealing with quadratic sulfur, the obvious analytical trade-off should occur between selectivity and sensitivity. In order to be fair to both methods of sulfur determination, each is individually optimized. In particular, the quadratic sulfur mode uses the quartz chimney, the linear mode does not. Also, the detector flows differ significantly.

The last major question about the analytical performance of sulfur in the flame photometric detector is one of long standing: Do the molecular surroundings of sulfur in analyte molecules influence its response? Differently put: Does one nanogram of sulfur always produce the same luminescent intensity regardless of the type of functional group that carries it into the flame? Can the response of sulfur compounds be represented solely by the amount of sulfur they contain? Is there (at least in theory) just *one* calibration curve for *all* sulfur compounds?

In the conventional FPD determination of sulfur via the S_2 bands, the situation is complicated by the much discussed experimental evidence that the exponent “ n ” of the correlation between the amount and the luminescence of sulfur—in other words the slope of the log/log calibration curve—varies from about 1 to about 2.3. (Note, however, that *most* compounds are reported having n values around the “theoretical” 2.0, *i.e.* between about 1.8 and 2.2 [4]). If n varies, then the determination of response on a “per gram sulfur” basis will depend on the amounts in which these compounds are injected for the measurement. The convenient but hypothetical assumption of a truly quadratic sulfur response has allowed “response corrections” to be used in a variety of literature studies; those notwithstanding, the question of sulfur equivalency (and exponent variability) still remains to be settled to everybody’s satisfaction [4]. (Note that the term “quadratic”, as used in this and other papers from our group, indicates a simple square function ($n = 2$); it is *not* derived from the “quadratic equation” with its additional constant and linear terms.)

A further complication arises from the fact that slowly eluting sulfur (or selenium or tellurium) residues from column and detector “linearize” the

lowest part of the calibration curve [11]. The variability of n among most calibration curves, and its frequent approach to unity in their lower regions, are probably the dominating causes for discrepancies found in the literature. However, the questionable purity of some purchased sulfur compounds or their tendency to sorb on metal surfaces and prematurely decompose, as well as the different levels of quenching wrought by variable concentrations of hydrocarbonaceous and other species originating both from the analyte itself and from the (temperature-dependent) column bleed, all add to the experimental difficulties involved in deciding whether the response of sulfur in the FPD does or does not depend on molecular structure.

Yet, a structure-independent sulfur response would obviously be of great analytical value. The experimental difficulties encountered in defining sulfur equivalency are greatly reduced when, instead of the S₂ band, a linear emitter is monitored. Then n is unity and, of course, does not vary—though compound purity and premature decomposition, as well as internal and external quenching, still may. If only for its analytical utility, a simple investigation of the structure–response relationship of sulfur compounds is therefore clearly called for.

TABLE I

AMOUNTS OF COMPOUNDS USED FOR DETERMINING SELECTIVITY RATIOS

Group	Element	Compound ^a	Formula	Amount injected (ng)			
				Quadratic		Linear	
				394 nm	Open	600 nm long pass	750 nm wideband
3A	B	<i>o</i> -Carborane	1,2-H ₂ C ₂ B ₁₀ H ₁₀	50	50	2000	2000
4A	C	Dodecane	<i>n</i> -C ₁₂ H ₂₆	2000	2000	1000	3000
4A	Sn	Tetraethyltin	(<i>n</i> -C ₄ H ₉) ₄ Sn	0.5	0.5	2	100
4A	Pb	Tetraethyllead	(C ₂ H ₅) ₄ Pb	200	200	2	10
5A	N	Tributylamine	(<i>n</i> -C ₄ H ₉) ₃ N	2000	2000	1000	5000
5A	P	Tributylphosphite	(<i>n</i> -C ₄ H ₉ O) ₃ P	20	20	5	20
5A	As	Triphenylarsine	(C ₆ H ₅) ₃ As	50	50	2	10
6A	Se	Diphenylselenide	(C ₆ H ₅) ₂ Se	5	5	100	1000
6B	Cr	Chromiumhexacarbonyl	(CO) ₆ Cr	50	50	1	10
7B	Mn	MMT ^b	C ₅ H ₄ CH ₃ Mn(CO) ₃	30	30	2	10
8B	Fe	Ferrocene	(C ₅ H ₅) ₂ Fe	20	20	2	10
8B	Ru	Ruthenocene	(C ₅ H ₅) ₂ Ru	1	0.2	3	30
8B	Os	Osmocene	(C ₅ H ₅) ₂ Os	5	2	3	3
6A	S	Thianaphthene	C ₈ H ₆ S	3	3	3	10

^a All compounds except last one tested against thianaphthene.

^b MMT = Methylcyclopentadienyl manganese tricarbonyl.

EXPERIMENTAL

An 18-year old and somewhat worn Shimadzu Model 4 (GC-4BMPF) gas chromatograph with dual-channel FPD was used for this study with a 4-year old packed column (100 × 0.3 cm I.D. borosilicate, 5% OV-101 on Chromosorb W, 100–120 mesh) under a nitrogen flow of 20 ml/min. The two photomultipliers were conventional Hamamatsu R-374 tubes (nominal range 180 to 850 nm, maximum yield at 420 nm).

The “linear” sulfur mode used flows of 500 ml/min hydrogen and 40 ml/min air, a 600-nm long-pass or a 750-nm wideband filter (the latter of bandpass 40 nm), and no quartz chimney. The “quadratic” (conventional) sulfur mode used flows of 50 ml/min hydrogen and 40 ml/min air, a 394-nm interference filter (of bandpass 11 nm), or no filter at all. Also, the commercial quartz chimney was kept in place.

(Note that optimal conditions may vary considerably from detector to detector: for instance, the linear-sulfur mode in our much younger but detector-wise quite similar model 8 single-channel Shimadzu GC-FPD worked best with 100–200 ml/min hydrogen, 20–30 ml/min air, and a 620 or 640 nm

long-pass filter [12]. FPDs from other manufacturers could be expected to show even greater variation in optimum settings.)

For spectral measurements, one of the FPD channels was replaced by a Jarrell-Ash Model 82-415 quarter-meter monochromator with a 1180 grooves/mm grating blazed for 500 nm, and equipped with the same Hamamatsu R-374 photomultiplier tube as the regular FPD channel. When necessary, an order-sorting filter was inserted. Spectral measurements were conducted either by automatic scanning of a constant stream of carbonyl sulfide introduced into the flame via the hydrogen line; or by small manual advances of the wavelength drive after each of a larger number of injections of di-*tert.*-butyldisulfide.

All analytes were used "as received". Table I charts them according to FPD-active element and lists the amounts in which the compounds were injected for the determination of selectivity ratios. (Knowing the injected amounts is important only for elements whose response is *non-linear*; all others were injected well within their linear ranges.)

RESULTS AND DISCUSSION

Sulfur spectrum

There is little doubt that the emission monitored for the linear sulfur mode is *not* the commonly observed S_2 main system [6]. We feel obliged to make this point here because, under particular circumstances, S_2 can indeed produce a linear calibration curve. For instance, a sulfur-containing analyte will respond linearly when superimposed on a massive sulfur background [11]. Also, the S_2 emission will become linear if all (or a constant percentage) of analyte sulfur is converted to S_2^+ [5,13]. And, though highly unlikely, it is nevertheless theoretically possible that S_2 could be produced by two different mechanisms: one with second-order, the other with first-order characteristics. Furthermore, beyond the strong, ubiquitous S_2 main system ($B^3\Sigma_u^- - X^3\Sigma_g^-$, 240–711 nm), there also occur (in different sources) three weak, overlapping S_2 systems in the far red and infrared [6]. Much of the remote possibility that main-system S_2 should be responsible for the observed effect can be ruled out by simultaneously observing both quadratic and linear behaviour. Experimentally this is easily achieved by using *both* chan-

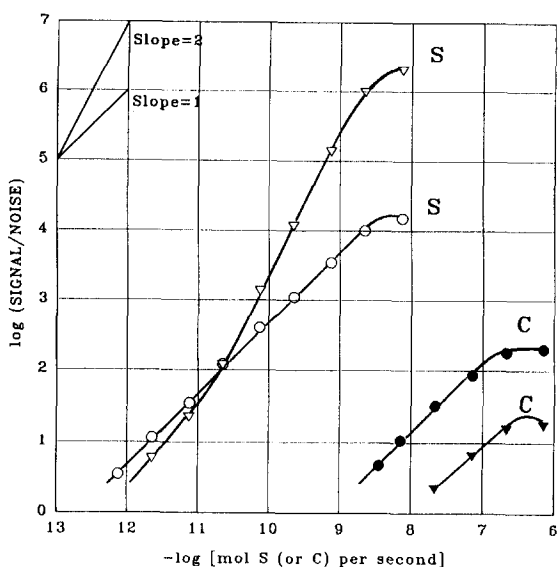


Fig. 1. Calibration curves of thianaphthene ("S", open symbols) and dodecane ("C", closed symbols) in a dual-channel FPD. The flow conditions are those of the "linear mode" (see Experimental). \circ , \bullet = Channel 1, 600-nm longpass filter; ∇ , \blacktriangledown = Channel 2, 394-nm (11 nm bandpass) filter.

nels of the dual-channel FPD. The results of such an experiment are plotted in Fig. 1.

Fig. 1 shows the familiar quadratic response of sulfur and, measured from the very same analyte peaks in the second FPD channel, the new linear response. The flow conditions for this experiment are those that favor the linear (but do not prevent the quadratic) emission: primarily a high hydrogen flow in the absence of the conventional quartz chimney. One channel monitors the commonly used S_2 band at 394 nm; the other the red plus adjoining infrared region from about 600 to 850 nm. (Also shown in Fig. 1 are the calibration curves of a standard alkane, which we shall discuss later in the context of selectivity ratios).

The response measured with the conventional 394-nm interference filter displays the typical behaviour attributed to S_2 : a mostly quadratic (slope 2) calibration curve with an almost linear (slope 1) section at its base. In contrast, the response simultaneously measured with a 600-nm longpass filter is purely linear. It spans about four orders of magnitude (depending on the definition used for detecta-

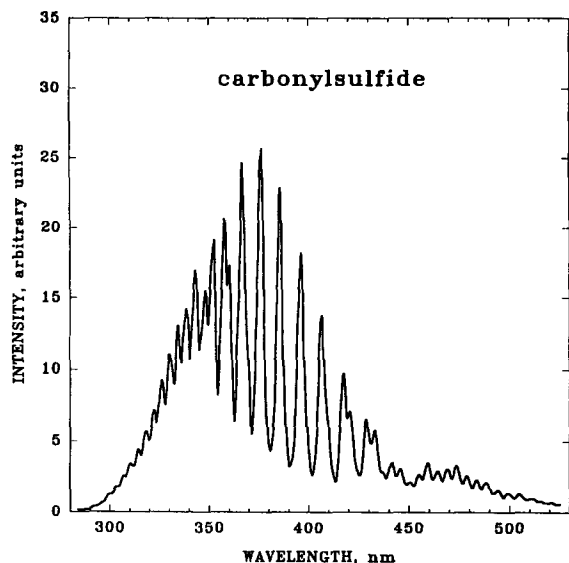


Fig. 2. S_2 luminescence (obtained from continuous introduction of COS) in the “quadratic mode” (see Experimental for conditions). Bandpass *ca.* 6.7 nm.

bility) and bends off, likely for good spectrochemical reasons, at the same analyte level as the S_2 emission. Under this set of conditions, the *linear* response is the stronger of the two in the low-concentration range.

While the calibration curves of Fig. 1 establish the likely presence of an emitter other than S_2 , the most direct evidence for this emitter would be its spectrum. However, that is difficult to obtain in the presence of S_2 . Fig. 2 displays these repeatedly shown bands as they appear in our FPD under “conventional” (see Experimental) conditions. This spectrum makes it clear why the linear sulfur emission has remained hidden for so long: on the chosen intensity scale, no further emissions appear beyond 520 nm (except for the S_2 bands in second order, of course).

Even without the quartz chimney, at a higher hydrogen flow, and with an order-sorting filter, it is difficult if not impossible to recognize and define the linear emitter. Fig. 3 shows the crucial region—on the top in automatic scanning, on the bottom in manual injection mode. The latter was used for a spectrally confirmative replication, for a clearer definition of possible continua, and for the circumvention of any conceivable background features. The

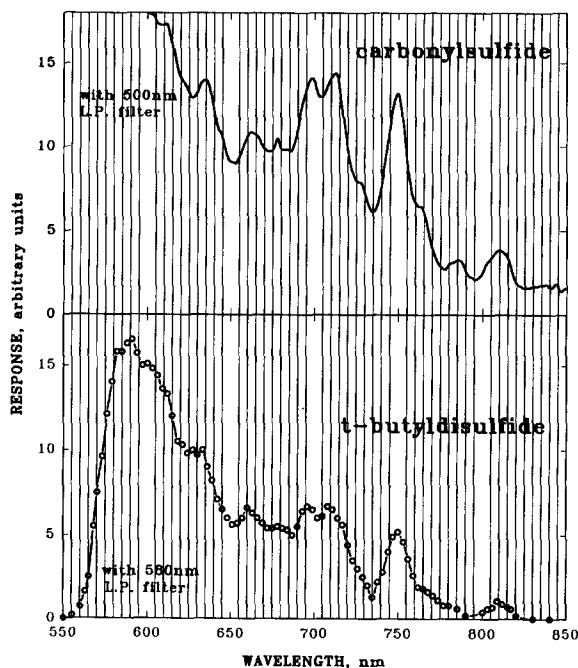


Fig. 3. Luminescence obtained by continuous introduction of COS (above) and repeated injection of (*tert.*- C_4H_9) $_2S_2$ (below) in the “linear mode” (see Experimental for conditions). Bandpass *ca.* 6.7 nm; 500-nm (above) and 580-nm (below) longpass (L.P.) filters are used for order sorting.

automatic mode represents conventional spectroscopic procedure; the manual approach mimics chromatographic practice. Fortunately, the two produce very similar spectra.

The emitter they represent remains unknown; none of the common emission systems of sulfur [6] could be unambiguously assigned to it. (Note, however, that the 0,0i and 0,0ii heads of the “infrared and far red” S_2 systems lie at 751, 743, 710 and 698 nm [6], *i.e.* quite close to the position of the protuberances shown in Fig. 3.) The spectra of Fig. 3 must also include some outliers of the main-system S_2 bands and, for this and other reasons, even the spectral distribution of the new linear emission remains vague. A 600-nm cut-on filter will produce a purely linear calibration curve; a 550-nm cut-on filter will come close to that. The most pronounced—though, response-wise, not very important—feature of Fig. 3 is the band located at *ca.* 750 nm. That it belongs to a linear sulfur emitter is supported by the fact that, as seen through a 750-nm filter of 40

nm bandpass, the band yields *linear* calibration curves for sulfur analytes. The same is the case for the "doublet" at *ca.* 700 nm, as seen through a filter of 70 nm bandpass.

Sulfur selectivity

With the 750-nm wideband filter just mentioned, sensitivity should be clearly lower but selectivity generally higher than with, say, a 600 nm cut-on filter. To determine the selectivity of sulfur against other FPD-active elements in the "linear" mode is interesting and indeed necessary; we have done that for both optical conditions. Note, however, that all selectivity ratios are *single-channel* values. Improvements of one to three orders of magnitude can be easily achieved by *dual-channel* differential operation [10]. It is furthermore possible to use the CONDAC algorithm [3] for obtaining apparent specificity for linear sulfur (as well as for any other FPD-active element).

It is also interesting, as well as conducive to an assessment of the two techniques, to determine the selectivity ratios of sulfur against other FPD-active elements in the *quadratic* mode, and to compare these numbers with those of the linear mode. To remain analytically relevant, such a comparison needs to be carried out with each mode under its own, individually *S/N*-optimized conditions. Yet the comparison will still be restricted in application: it applies only to *one* level of sulfur (see Table I). Higher sulfur levels increase, lower sulfur levels decrease the single-value selectivity ratios in the quadratic mode. (Very rough estimates of the selectivity ratios at higher or lower levels of sulfur can be obtained by assuming response to be proportional to the square of the sulfur concentration; however, as previously discussed, the exponential factor often differs from the ideal value of 2 and, furthermore, often approaches 1 in the low concentration range of the "quadratic" calibration curve.)

TABLE II

MOLAR SELECTIVITY OF SULFUR AGAINST OTHER ELEMENTS IN TWO FPD RESPONSE MODES

The selectivity of sulfur against element X, $S_{S/X}$, is calculated as

$$S_{S/X} = \frac{R_{(S)}}{R_{(X)}} \cdot \frac{\text{mol X/s}}{\text{mol S/s}}$$

where $R_{(S)}$ is the peak height response at unit attenuation of thianaphthene, and $R_{(X)}$ is the same for a compound of element X (see injection amounts from Table I); while mol X/s and mol S/s are the molar flows per second at peak apex of element X and sulfur.

Group	Element (X)	Quadratic sulfur mode ^a		Linear sulfur mode ^b	
		394 nm	Open ^c	600 nm long pass	750 nm wideband
3A	B	$6 \cdot 10^2$	$2 \cdot 10^2$	$3 \cdot 10^3$	$> 10^4$
4A	C	$2 \cdot 10^4$	$2 \cdot 10^4$	$1 \cdot 10^{3d}$	$6 \cdot 10^{3d}$
4A	Sn	0.1	0.05	0.03	0.7
4A	Pb	$2 \cdot 10^2$	$4 \cdot 10^1$	0.07	0.1
5A	N	$7 \cdot 10^2$	$1 \cdot 10^2$	$1 \cdot 10^{2d}$	$1 \cdot 10^{2d}$
5A	P	$1 \cdot 10^1$	0.1	0.2	0.5
5A	As	3	4	0.05	0.1
6A	Se	8	6	7	$5 \cdot 10^1$
6B	Cr	$3 \cdot 10^1$	2	0.05	0.1
7B	Mn	$2 \cdot 10^1$	7	0.08	0.2
8B	Fe	5	5	0.09	0.2
8B	Ru	0.4	0.09	0.2	1
8B	Os	6	0.3	0.08	0.1

^a 50 ml/min H₂, 40 ml/min air and 22 ml/min carrier N₂; with quartz chimney; Hamamatsu R-374 photomultiplier tube.

^b 500 ml/min H₂, 40 ml/min air and 22 ml/min carrier N₂; without quartz chimney; Hamamatsu R-374 photomultiplier tube.

^c No optical filter used.

^d Inverted peak.

Although the quadratic sulfur mode has been in use around the world for several decades, published information on sulfur selectivity ratios is largely restricted to the selectivity of sulfur *versus* carbon (really: *versus* the particular hydrocarbon that serves as a carbon standard in the selectivity ratio measurement). Recently, selectivity ratios of sulfur against various other elements were reported [3], but these values pertain to open (filter-less) operation at a generalized (as opposed to a sulfur-optimized) set of conditions. Thus the values of Table II may be helpful to users not only of the linear but also of the quadratic sulfur mode.

With the above caveats in mind, we can now examine the compilation of experimentally determined selectivity ratios in Table II—first for each mode on its own, then for the two modes in comparison. Those of the conventional quadratic mode show the expected higher selectivity conferred by the 394-nm narrow-band interference filter (*versus* open, *i.e.* filter-less operation) in all but three cases. However, the increase in selectivity—which comes at some decrease in sensitivity—is small (a factor of 5 on average). This is in agreement with earlier data on the generally minor improvement interference filters bring to FPD selectivity [3,9,10].

For obvious reasons the linear sulfur mode cannot be run “open”, *i.e.* it cannot be observed unless a filter cuts off most of the S₂ bands. Still, analogous comments can be made about the comparison of the nominal 730–770 nm range monitored through the 750-nm wideband interference filter, with the much wider 600–850 nm range admitted by the 600-nm longpass filter and the red-extended R-374 photomultiplier tube. Not surprisingly, the increase in selectivity owing solely to optical discrimination is smaller in the linear than in the quadratic mode.

Perhaps more important than these *intramodal* relationships is the *intermodal* confrontation of linear with quadratic sulfur. The linear mode shows selectivity ratios that are better in three, about equal in two, and worse in eight cases. This seems reasonable if one considers the decidedly greater intensity of the S₂ emission overall. At higher sulfur levels than those used for Table II, the selectivity ratios of the quadratic mode would increase, tilting the comparison still further in its favor. An advantage of the linear mode, on the other hand, is that

the response of hydrocarbons is generally negative (peaks are inverted), thereby providing a qualitative distinction between compounds that contain sulfur and those that contain only carbon and hydrogen. (It may be noted that in the comparison with selenium, the S/Se selectivity ratios depend strongly not only on the injected amount of sulfur but also on the injected amount of the—similarly quadratic—selenium analyte.)

Sulfur equivalency

Another seeming advantage of the linear mode is the very minor (if at all existing) dependence of the response of sulfur on the structure of its compounds. Obviously, any intrinsic dependence of organosulfur peak size on analyte concentration or retention time (as it occurs strongly and predictably in the quadratic mode) can be ruled out. Differences observed between the sensitivities of various compounds are thus directly attributable to differences in photon yield per sulfur atom (absent impurity, degradation and quenching effects, of course).

Fig. 4 shows the linear calibration curves of seven disparate sulfur compounds, plotted on a “peak area vs. gram sulfur” basis. The responses vary (*i.e.* they differ vertically in the graph) by a factor of less

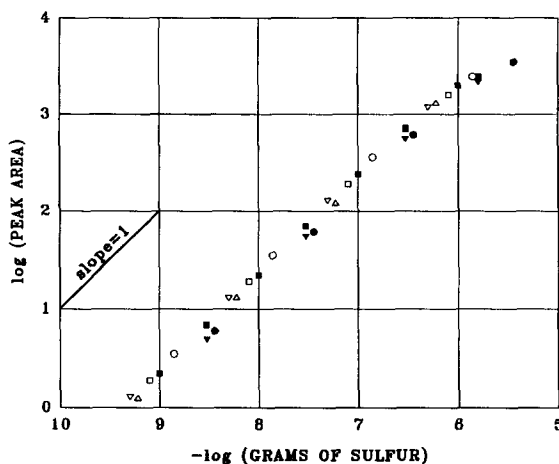


Fig. 4. Calibration curves for seven sulfur compounds in the “linear mode”. ○ = Thianaphthene; △ = *n*-octylsulfide; ■ = *n*-hexylsulfide; □ = dibenzothiophene; ▼ = 1-dodecanethiol; ▽ = phenylsulfide; ● = di-*tert.*-butyldisulfide. Conditions: 600-nm longpass filter; R-374 photomultiplier tube; 500 ml/min H₂, 40 ml/min air; no chimney.

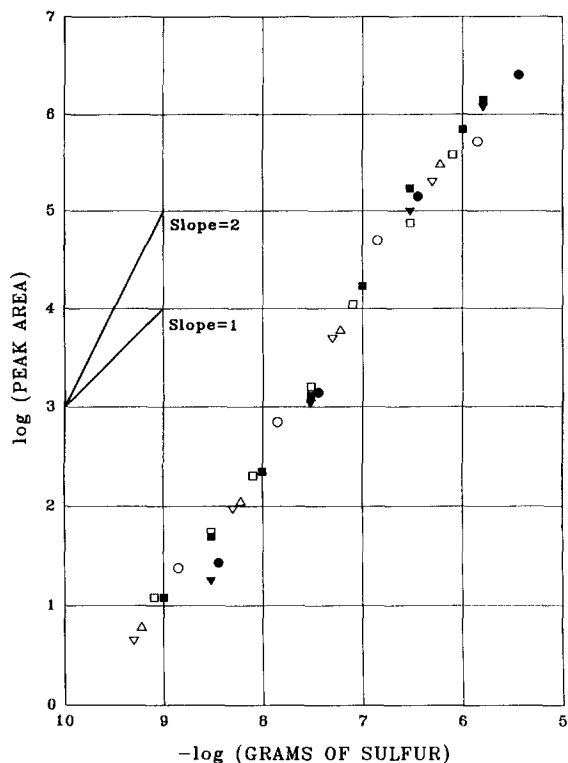


Fig. 5. Calibration curves for seven sulfur compounds in the "quadratic mode". Symbols as in Fig. 4. Conditions: 394-nm interference filter; R-374 photomultiplier tube; 50 ml/min H_2 ; 40 ml/min air; with chimney.

than two, over an analyte concentration range of more than three orders of magnitude. Given (a) the experimental error band (injection, flow and temperature control, etc.) for each individual sulfur compound; (b) the always possible and often present perturbations caused by premature decomposition, irreversible absorption, or lacking purity of the analyte; and (c) the likely quenching that occurs internally (by analyte carbon) or externally (by column bleed and/or co-eluting compounds); a factor of two seems small enough for sulfur response to be considered *independent* of molecular structure. A similar factor of two is, for instance, apparent in the two newest instrumental contenders for linear organosulfur determination; each of which is nevertheless considered "a specific detector for sulfur present in different molecular forms" [14]. For purposes of analytical response estimates, therefore, a rough

sulfur equivalency can be assumed for the linear mode. Note, however, that the range of compounds tested in this study is limited, and that its present conclusion should remain open to future re-evaluation.

What about sulfur equivalency in the *quadratic* mode? Fig. 5 exhibits the "quadratic" calibration curves of the compounds used for producing the earlier Fig. 4. *Response* among the seven analytes varies here by a factor of just less than five. That seems clearly more than the factor of two for the linear mode. However, while analytically relevant, this comparison is not fair. A quadratic emitter will, per definition, respond to any structure-related difference in the *second* power. Hence, a mechanistically fairer approach will use the *square root* of the response or, more simply, the *amount* of sulfur involved. If this is done, the variation in sulfur equivalency of the quadratic mode that may be attributed to *structural* factors is only slightly larger than a factor of two, *i.e.* it appears to correspond to the like variation of the linear mode.

If such narrow variation should prove typical of a more extensive and variegated future roster of sulfur compounds, it would suggest that the *quadratic* mode may be independent of molecular structure as well. (Note that this study is unable to identify the linear emitter, and that the literature remains uncertain even about the basics of the quadratic response mechanism [4,5,15]. It could, for instance, be possible that both modes start from the same species, *e.g.* H_2S , S, etc. Ergo, if the linear mode is really structure-independent, so could be the quadratic one.) Sulfur equivalency in the quadratic mode was indeed credibly claimed a long time ago [16], but evidence to the contrary has since amassed [4] and appears to have been accepted.

Sulfur performance

Minimum detectable flows of linear sulfur can be read off the (extrapolated) calibration curve of Fig. 1, since the ordinate is based on signal/noise measurements (where noise is the peak-to-peak baseline fluctuation, with drift and outliers excluded). The detectability measurement most common to chromatography calls for $S/N = 2$ (*i.e.* $\log [S/N] = +0.3$ on our scale); while the IUPAC-recommended detection limit of $S/\sigma = 3$ (where σ is the standard variation of the baseline noise) lies for our experi-

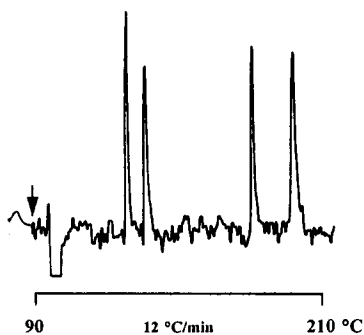


Fig. 6. Temperature-programmed separation of four sulfur compounds near their detection limit in the "linear mode". In order of elution: 3 ng di-*tert.*-butyldisulfide, 3 ng benzo[*b*]thiophene (thianaphthene), 4 ng diphenylsulfide, 4 ng dibenzothiophene.

ments at approximately $S/N = 0.5$ (*i.e.* $\log [S/N] = -0.3$ [2]). The detection limits for the optimized linear mode are larger by about a factor of five than those for the optimized quadratic mode. {For the quadratic sulfur mode in various FPDs, Dressler [8] cites a range of minimum detectabilities ($S/N = 2$) of $2 \cdot 10^{-12}$ to $5 \cdot 10^{-11}$ g S/s}. The detection limits for the linear mode are also larger, by about an order of magnitude, than those reported about a side-by-side comparison of the Hewlett-Packard atomic emission detector (AED) and the Sievers Research sulfur chemiluminescence detector (SCD) [14].

A more practical, visual assessment of detectability can be provided by the actual chromatography of some sulfur compounds near their detection limit in a temperature-programmed separation. Such a chromatography is shown in Fig. 6. (Note that it uses a 1-m packed column; capillary columns should do much better.)

The linear range of the new sulfur mode is approximately 4 orders of magnitude (depending on the definition used for the detection limit). For comparison, the linearity of the SCD is generally four, that of the AED five orders of magnitude [14]. As shown in Fig. 4, the linear sulfur response in the FPD is independent of analyte structure within a factor of 2, similar to the behaviour of SCD and AED [14]. Remember, however, that our study sampled only seven different sulfur analytes.

As far as we can tell, the linear sulfur response in our FPD has remained approximately constant since we started investigating it a year or so ago. However, we did not carry out special studies of

long-term (or short-term) reproducibility; in part owing to the reputation—well deserved, in our opinion—of the FPD as a reliable and stable workhorse. (One might add that it is also inexpensive compared to some of the newer instrumentation: our recently purchased gas chromatograph with single-channel FPD came at < US\$ 10 000.)

Preliminary experiments indicate that the linear sulfur mode suffers significantly less from quenching by co-eluting hydrocarbons than does the quadratic mode. However, the problem of quenching is a complex one and will be dealt with in a separate manuscript; we mention it here only because it can constitute a major factor in evaluating detector performance.

A much-cited review of sulfur determination in the FPD concludes that further research into the S_2 mode should be encouraged, but that "the development of a simple and sensitive sulfur-selective detector with a linear response should receive even higher priority" [4]. The new linear sulfur mode may well meet those requirements. Although its sensitivity is at present somewhat lower than that of the quadratic mode, that disadvantage may be more than compensated by its other advantages, in particular its uncompromised linearity.

NOTE ADDED IN REVISION

One of the reviewers of this manuscript requested that we "provide some discussion with regard to the selectivities [of the linear sulfur mode], since some of these markedly differ from the quadratic mode." We are pleased to oblige, although to do so will force us to rely heavily on speculation.

There are several problems to bear in mind when discussing the selectivity ratios of Table II. That their values depend on the *amount* of sulfur (or selenium) in the quadratic mode has already been mentioned. The problems of comparing kinetically different emitters and vastly different linear ranges are persuasively illustrated by Fig. 1. Selectivity ratios (in logarithmic, *i.e.* order-of-magnitude form) are represented by the horizontal (or vertical) distances between two corresponding log-log calibration curves. Obviously, they are constant only if measured exclusively between two *straight* lines of the *same* slope.

The next problem concerns absolute signal inten-

sity: sulfur response is considerably more intense in the quadratic than in the linear mode. Furthermore, the two modes differ strongly in their flow conditions, hence also in flame and excitation characteristics. This applies not only to sulfur, but also to all the other elements with which sulfur is being compared. At present there exists no logical framework that would be capable of predicting whether an element will chemiluminesce, or to what extent and where in which type of a flame. Theories of chemiluminescent flame excitation, few as they are, are often derived by necessity from experimental hindsight and speculative analogy.

The numerical values of selectivity ratios depend on the sometimes arbitrary choice of conditions at which they are measured. In the present case the conditions are based on the *maximum S/N ratio* for sulfur in the two modes, with further choices based on their characteristic spectral distributions (the bands at 394 and 750 nm). Yet, if one were to base the conditions on the *maximum selectivity ratio* for pairs of sulfur with each of the other elements, the flow conditions and related spectral distributions of *both* elements would have to be taken into account. For instance, the origin, shape and behaviour of spectral features of the “other” element would have to be considered as well: it is far easier to improve selectivity by focussing on, say, the element with the strong atomic line or the one whose response varies conspicuously with changes in flow, than on the one with the prominent continuum or the one whose response ignores changes in flow. Not that we propose to carry out *selectivity* optimization (except, perhaps, for the “important” sample that cannot be dealt with by any other means), but mentioning it helps us to draw attention to the many parameters and choices that hide behind those deceptively simple numbers known as selectivity ratios.

It is obvious from the above considerations that what is mainly left to speculate on is the effect of spectral distributions on selectivity ratios. The spectrum of quadratic sulfur (S_2) is well known; the “spectrum” of linear sulfur has been measured (Fig. 3). However, the spectra of other elements have not; at least not, as demanded by the present context, *at the conditions of the linear sulfur mode*. FPD spectra are difficult to determine under analytically relevant conditions, particularly when the emitters are weak. Also, FPD spectra can change drastically with

flame conditions. It is therefore not surprising that uncritical reference to literature spectra measured under different conditions —sometimes conditions in the FPD that yield the highest *S/N* ratio not for sulfur but for the particular element with which it is being compared, or even conditions in other excitation sources— can prove highly misleading.

To rely on literature spectra thus requires a leap of faith, *i.e.* it implies (sometimes correctly but often in error) that spectral distribution does not change significantly with changes in flow conditions. Yet, with the tenuous nature of this implication being understood, we shall attempt (as requested) to comment on the selectivity of linear sulfur *vis-à-vis* other elements; and further, to compare it to the behaviour of quadratic sulfur as listed in Table II.

In the cases of boron and selenium, the linear sulfur mode shows the much better selectivity, presumably because the dominant FPD spectra (BO/BO_2 [3] and Se_2 [17]) do not stretch beyond 600 nm. A similar though not as clear-cut case can be made for tin. The main spectra relevant to the quadratic sulfur mode (the blue luminescence of tin on quartz, and $SnOH$ [18]) do not extend beyond 600 nm. The dominant FPD spectrum in the red is due to SnH , with its strongest band at 610 and a much weaker one at 690 nm [6,19].

The (inverted) peaks of carbon/hydrogen and nitrogen found under the conditions of the linear sulfur mode represent *decreases* in emission, *i.e.* they are due to a quenching of the background luminescence. The spectral distribution and origin of the luminescent background in the > 600 nm region is unknown and could, furthermore, contain “memory” components both significant in intensity and variable in time. (Some of this background is evident from a comparison of the two spectra of Fig. 3 in the > 800 nm region.) In the quadratic sulfur mode, in contrast, C/H and N peaks represent *increases* in emission. The FPD emission spectra resulting from aliphatics, aromatics, oxygenates [2] and nitrogen compounds [3] have been measured (though not identified) at different conditions. Both stretch, however weakly, beyond 600 nm, and must then obviously dip below the zero intensity level at longer wavelengths. Thus we are dealing with a mixture of emission and quenching spectra in that region, which makes the selectivity ratios of the two

modes neither easily predictable nor directly comparable.

(Parenthetically it may be added that, as Fig. 1 illustrates, measurement of selectivity against carbon, or other elements of weak response and short linear range, can lead to an inappropriately high result if the injected amount of carbon exceeds its linear range. The more appropriate way to increase selectivity ratios is to use a *dual*-channel FPD for annulling the response of carbon, or of other elements, by differential operation [10]; or to have the CONDAC algorithm deny unwanted elements access to the chromatogram [3].)

In the cases of lead, arsenic, chromium, manganese, iron and osmium, the selectivity ratios of the linear sulfur mode are quite noticeably worse than even those of the *open* (filterless) quadratic mode. In part this is due to the considerably higher intensity of the S₂ bands. But it also strongly suggests that the listed elements do produce sizeable emissions between 600 and 850 nm. Indeed, the FPD spectra of chromium [2] and osmium [20] contain strong continua in the far red and near infrared. Also, noteworthy red/infrared emissions emanate from lead under conditions of the linear sulfur mode; these are currently under investigation [21]. We have no like information on the FPD spectra of iron [22] or manganese [23], since these metals were unfortunately measured with a photomultiplier restricted to wavelengths below about 650 nm. The only surprise, in view of the well-known As continuum [ref. 3 and references cited therein], comes from the apparently sizable response of arsenic above 600 nm.

The case of ruthenium, an unusually sensitive element, — seems different from that of the other transition metals. Its dominant features are molecular bands (of RuH?) at 484 and 528 nm, while several (much weaker) atomic lines appear in the 350 to 400 nm range (ref. 24; cf. discussion in ref. 2). We have no spectral information beyond the nominal 650 nm upper limit of the photomultiplier, but the selectivity ratios suggest only minor ruthenium emission activity in that region.

That leaves to the last the case of phosphorus, the second-most important FPD analyte. The selectivity measurement of quadratic sulfur against phosphorus at 394 nm is the highest of the four taken, not surprisingly so in light of the well-documented

S₂ and HPO systems. The major HPO band appears at 526 nm; however, the whole HPO spectrum stretches from 460 to 680 nm [25] and often rests on a “white” continuum with strong components in the green and red [5]. This could account for the unexpectedly poor selectivity ratios of the linear sulfur mode against phosphorus.

Any further discussion of the selectivity ratios of quadratic and linear sulfur against the roster of other FPD-active elements must await the determination of the latter's spectra at the precise conditions of these two analytical modes and, still farther away, a better understanding of the chemistry and excitation/quenching processes in the FPD flame. Until then, the selectivity ratios of Table II are best understood as condition-dependent, empirical data of mainly analytical (as opposed to spectrochemical) value.

Our reviewer also requested that “the detection limit should have numerical values in the text”. Certainly such numbers facilitate comparison with other methods of chromatographic organosulfur analysis. We therefore established separately the minimum detectable quantity of sulfur by using isothermal chromatography of the standard analyte thianaphthene (benzothiophene), and by following the IUPAC-recommended criterion $S/\sigma_N = 3$ via an algorithm that determined σ_N , the standard deviation of the baseline noise, by a least-squares fit to a normal (Gaussian) distribution. The result was $2 \cdot 10^{-13}$ mol sulfur per second. For easy comparison with values arrived by other commonly used definitions, that value translates into $6 \cdot 10^{-12}$ g S/s or $2.5 \cdot 10^{-11}$ g thianaphthene/s; or, at the $S/N_{p-t-p} = 2$ limit (where N_{p-t-p} is the peak-to-peak baseline noise, with drift and spikes excluded), $7 \cdot 10^{-13}$ mol S/s or $2 \cdot 10^{-11}$ g S/s or $1 \cdot 10^{-10}$ g thianaphthene/s. Fig. 7 shows the 2 ng peak of thianaphthene (of 8 s peak width at half height) that was used for this evaluation of sulfur detectability in the linear mode; together with a sizable stretch of baseline fluctuations and their approximation by a Gaussian curve.

ACKNOWLEDGEMENT

This study was supported by NSERC operating grant A-9604. We appreciate the assistance of C. H. Warren and B. Millier in obtaining the Gaussian fit shown in Fig. 7.

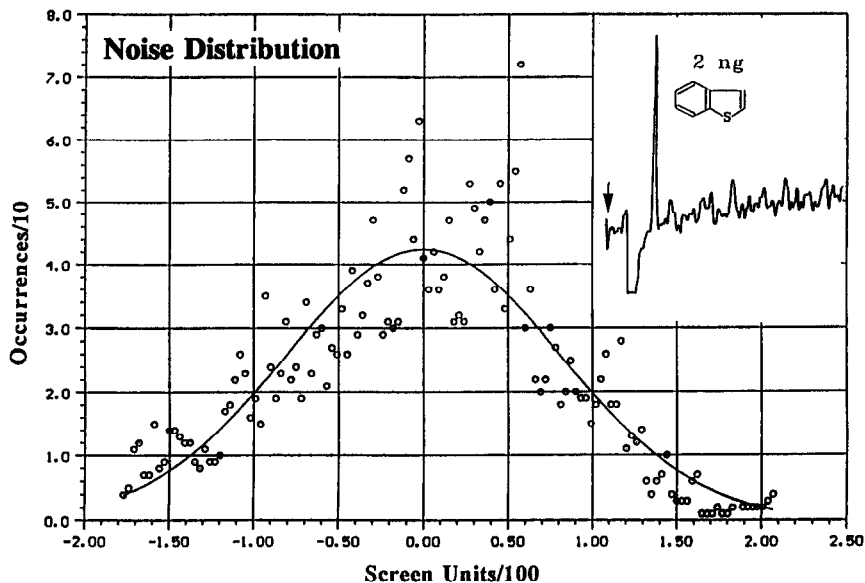


Fig. 7. Typical peak of 2 ng thianaphthene in the linear mode near the detection limit, and least-squares Gaussian fit of the baseline fluctuation.

REFERENCES

- 1 B. Millier, X.-Y. Sun and W. A. Aue, presented at the 75th Canadian Institute of Chemistry Conference, Edmonton, June 1992.
- 2 X.-Y. Sun, B. Millier and W. A. Aue, *Can. J. Chem.*, 70 (1992) 1129.
- 3 W. A. Aue, X.-Y. Sun and B. Millier, *J. Chromatogr.*, 606 (1992) 73.
- 4 S. O. Farwell and C. J. Barinaga, *J. Chromatogr. Sci.*, 24 (1986) 483.
- 5 P. T. Gilbert, in R. Mavrodineanu (Editor), *Analytical Flame Spectroscopy*, Philips Technical Library/Macmillan, London, 1969, pp. 181-376.
- 6 R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra*, Chapman & Hall, London, 4th ed., 1976.
- 7 S. Kapila, D. O. Duebelbeis, S. E. Manahan, in R. M. Harrison and S. Rapsomanikis (Editors), *Environmental Analysis Using Chromatography Interfaced with Atomic Spectroscopy*, Ellis Horwood, Chichester, 1989.
- 8 M. Dressler, *Selective Gas Chromatographic Detectors (Journal of Chromatography Library, Vol. 36)*, Elsevier, Amsterdam, 1986, pp. 133-160.
- 9 W. A. Aue and C. R. Hastings, *J. Chromatogr.*, 87 (1973) 232.
- 10 W. A. Aue, B. Millier and X.-Y. Sun, *Can. J. Chem.*, 70 (1992) 1143.
- 11 W. A. Aue and C. G. Flinn, *J. Chromatogr.*, 158 (1978) 161.
- 12 N. B. Lowery, unpublished Ph.D. work, 1992.
- 13 Y.-Z. Tang, *Ph.D. Thesis*, Dalhousie University, Halifax, 1987.
- 14 S. E. Eckert-Tilotta, S. B. Hawthorne and D. J. Miller, *J. Chromatogr.*, 591 (1992) 313.
- 15 S. V. Olesik, L. A. Pekay and E. A. Paliwoda, *Anal. Chem.*, 61 (1989) 58.
- 16 M. Maruyama and M. Kakemoto, *J. Chromatogr. Sci.*, 16 (1978) 1.
- 17 C. G. Flinn and W. A. Aue, *J. Chromatogr.*, 153 (1978) 49.
- 18 C. G. Flinn and W. A. Aue, *Can. J. Spectrosc.*, 25 (1980) 141.
- 19 C. G. Flinn and W. A. Aue, *J. Chromatogr.*, 186 (1979) 299.
- 20 X.-Y. Sun and W. A. Aue, *Mikrochim. Acta*, I (1990) 1.
- 21 J. A. Gebhardt, unpublished Ph.D. work, 1992.
- 22 X.-Y. Sun and W. A. Aue, *J. Chromatogr.*, 467 (1989) 75.
- 23 W. A. Aue, B. Millier and X.-Y. Sun, *Anal. Chem.*, 62 (1990) 2453.
- 24 X.-Y. Sun and W. A. Aue, *Can. J. Chem.*, 67 (1989) 897.
- 25 B. Gutsche and R. Herrmann, *Dtsch. Lebensm.-Rundsch.*, 67 (1971) 243.