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Accurate spectral scans of single chromatographic peaks

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Abstract

A detector equipped with two channels can fetch accurate luminescence spectra either from migrating chromatographic peaks or from other inputs of sharply varying concentration. To achieve this, one (the scanning) channel is continually referenced to another (the constant-wavelength) channel: the ratio of the two hence portrays correctly the intensity distribution of the spectrum. As a model system tor testing this ratio approach on single gas chromatographic peaks, a flame photometric detector was connected to a 1/8-m scanning spectrophotometer. No significant differences were found in relative spectral amplitudes between scanning the ascent versus the descent of a peak. Similar spectral constancy was obtained when scanning non-chromatographic variable inputs. With a view to practical use, three experiments were carried out that demonstrated the sensitivity and/or the spectral resolution obtainable from reference scans of *single* peaks. To wit, 5 pg of phosphorus produced a clearly recognizable HPO spectrum: the vibrational levels of S_2 resolved well; and the presence/absence of atomic iron lines confirmed an earlier postulated energy limit for the chemiluminescent excitation reaction.

Keywords: Spectral scans; Detection, GC; Ferrocene; Tris(pentafluorophenyl)phosphine; Butyldisulfide

1. Introduction

A variety of gas chromatographic detectors monitor the emission or absorption of electromagnetic radiation: they do so by reporting the *concentration* profile of peaks. Often, however, the *spectral* profile of peaks is important as well. It can confirm the identity of a suspected analyte; it can also indicate structural characteristics of an unknown compound. Spectral information is of special value when environmental extracts containing hundreds of peaks are to be analyzed. And it becomes particularly important when, for reasons of spectral similarity or lack of sensitivity, common hyphenated techniques (GC–MS, GC–IR, etc.) fail to provide the desired answers.

Occasionally, the analytical task requires that the relative intensity of spectral features be precisely known. This poses a problem if chromatographic peaks or, more general, variable inputs are to be examined. The emission or absorption of light that constitutes a peak waxes and wanes quickly. The intensity distribution of a singly scanned spectrum must thus ineluctably follow the peak's rise and fall. (At least it must do so in *conventional* scanning; Fourier transform, diode array, high-speed monitoring, multiple injection, or stop-flow techniques are exempted from the statement.)

If the recorded amplitudes of spectral features are to agree with the true intensity distribution of the spectrum, they have to be measured relative to the

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latter's general light level. This means that an accurate spectrum can only be obtained from the ratio of two observation channels. Typically, one channel would be dispersive and wavelength-scanning, the other non-dispersive and of constant wavelength. Then, in a manner of speaking, the peak that furnishes the spectrum also acts as its own reference.

Referencing to an internal standard, a second light beam, or a second emission channel is common fare in spectroscopic analysis (e.g., Refs. [1–4]). Depending on how it is done, it can reduce noise, drift, background and/or interference, and it can improve precision and accuracy. Chromatographic inputs do, however, introduce their own set of problems. Take, as an example, the dual-channel flame photometric detector (FPD) [5–7]. Spectra can be obtained from its peaks in many ways. So far, all had their limitations. For instance, ten-point spectral envelopes could be reconstituted by computer from the ten simultaneous chromatograms provided by a rotating variable interference filter [8]. That procedure was sensitive but of very low spectral resolution. The same rotating filter was used to yield hundred-point time-integrated spectra [9,10]. These provided better resolution but were still limited by the filter's inherent bandpass (17 nm maximum) and spectral range (400 to 700 nm).

To our knowledge, a similar circular filter that would scan a wider spectrum —from the flame-photometrically important near-UV region to the very-near-IR region— is not commercially available. Even if it were, its bandpass would likely be broader. And that raises the obvious question whether one couldn't employ a conventional grating monochromator to provide a narrower bandpass and a wider wavelength range.

Experience argues against it. The FPD derives its amazing sensitivity [7,11,12] not from the strength of its signal but from the weakness of its noise. Since its noise is fundamental in character [13], the signal/noise ratio depends in well-known square-root fashion on light throughput. In this context, an interference filter offers a much higher light throughput than a grating monochromator. This is why —after many frustrated couplings of simple monochromators to FPDs— designers have always returned to the original interference filter–photomultiplier combination [14]. Analysis with interference filters (and even more so without them [15]) was simply orders of magnitude more sensitive.

It seemed therefore both challenging and worthwhile to connect a conventional scanning monochromator to an FPD — provided that, by suitable light collection and transfer, its sensitivity could be significantly improved. Still, typical monochromator scans are slow compared to the speed of a gas chromatographic peak. This mandates, as mentioned earlier, the referencing of spectral features to the varying input concentration.

The intensity problem caused by a varying input in general, or by a chromatographic peak in particular, is common to spectral analysis. We therefore decided to investigate it together with the optical problems of maintaining reasonable sensitivity while achieving better resolution and accessing a longer wavelength range. Our goal was to obtain accurate and either highly sensitive or highly resolved spectra — in the near UV, visible and, if needed, very near IR — of the luminescence emitted by a single peak passing through our preferred model system, the dual-channel FPD.

2. Experimental

The gas chromatograph with FPD —a Shimadzu GC-4BMPF unit— had been in continuous use for a couple of decades, most recently for two studies of time-integrated spectra [9,10]. The chromatographic conditions set to obtain these spectra, as well as the analytical conditions of relevant earlier reports, were essentially maintained.

For the present study, the spherical aluminum mirror of 27 mm diameter and 10.5 mm focal length, with access for a second-channel light guide, was again used. The mirror focused (roughly) the flame luminescence onto the slit of an Oriel model 77250 eighth-meter monochromator with a No. 77298 grating, 0.02 to 3.2 mm variable slits, and a No. 77325 stepping motor [16]. The photomultiplier tubes (PMTs) were Hamamatsu [17] models R-1104 for the dispersive and R-374 and R-268 for the non-dispersive channel. Dry nitrogen gas could be piped into the monochromator and/or the PMT housing.

Detector housing and monochromator were con-

nected by a blackened tunnel, with a quartz window installed at the detector end to prevent water vapor from reaching the monochromator. The tunnel was also equipped with water-flushed cooling coils. The distances from the mirror and the monochromator to the flame could be adjusted via two connecting ports with threaded openings. The adjustments were done for the purpose of focusing the beam on, and almost filling the acceptance cone of, the monochromator aperture — while at the same time maintaining optimal light throughput. (Note that the difference in shape and size of different luminescent phenomena in the flame photometric detector makes focusing from the outside desirable. In this manner, optical distances could be easily adjusted for the test elements of this study until maximum peak height had been achieved at a given set of chromatographic and optical conditions.)

For the monochromator's stepping motor, a simple drive was built by the Department's Electronics shop. Speeds from 0.25 to 315 nm/min could be selected in stepwise fashion. The starting wavelength was chosen manually, with the motor set to run a predetermined time, i.e., to cover a fixed wavelength interval. (Full computer control, while easy to install, was considered superfluous for such simple spectral scanning.)

The chromatogram from the non-dispersive, and the spectrum from the dispersive channel were simultaneously monitored by an in-house dual-channel program called CHROM 8. The necessary interface and various associated algorithms and subroutines have been described [18]. The stored file was exported in ASCII format to a commercial spreadsheet (Sigmaplot [19]).

(Note: The laboratory-developed CHROM 8 program contains, inter alia, d.c.-offset, baseline-correction, smoothing, scaling, subtraction and plotting routines. By changing subtraction to division. i.e., by dividing the data from the spectral by those from the chromatographic channel, the whole procedure could have been carried out faster and more conveniently. This would have paralleled those commercial programs that include an "A/B" function for chromatographic data processing. Yet, with the existing CHROM 8 program being almost "full", we decided to establish first the viability of our basic approach and do so by using a general, commercially available spreadsheet. But, if the practice of single-peak scanning should take off in the future, it would be entirely reasonable (a) to add a division routine to the dedicated CHROM 8 program and (b) to increase the maximum scanning speed. Both improvements should be easy to accomplish.)

The conditions used to process the selected test compounds of phosphorus, sulfur and iron were close to settings typical of flame photometric detector routines. Where opportune, the analyte peaks were slowed down by selecting a lower temperature and/or a lower carrier gas speed. In separate experiments, test compounds were also introduced on a continuous basis by doping the carrier gas stream with volatile liquids coated onto 80–100 mesh glass beads and packed into an otherwise empty column. A sudden rise or fall in the latter's temperature and/or a change in carrier gas flow then produced the desired steep change in analyte concentration.

3. Results and discussion

Introduction of the analyte as a variable stream or as a chromatographic peak always produced the anticipated result: that the relative amplitudes of referenced spectral features remained independent of the rise or fall in analyte concentration. Examples of these types of experiments are given in Figs. 1 and 2.

Fig. 1 shows a near-UV scan of some iron lines as obtained from a variable input of ferrocene. Scans A and B were taken when the concentration of ferrocene in the feed stream was strongly changing; for purpose of illustration they are scaled to lend the lowest-wavelength feature (which consists mostly of the 344.061 nm resonance line) a similar amplitude in all readouts. The intensity distribution changes noticeably in the dispersive-channel-only spectra; in contrast, the dual-channel-ratio spectra of the self-same events are nigh congruous.

Fig. 2 shows a scan of the HPO bands [20] obtained from a single peak of tris(pentafluorophenyl)phosphine. One scan was taken during the ascent, the other during the descent of the peak. Clearly, the dual-channel ratio approach can compensate adequately for the analyte's waxing and waning concentration.

While the system thus works as expected, a

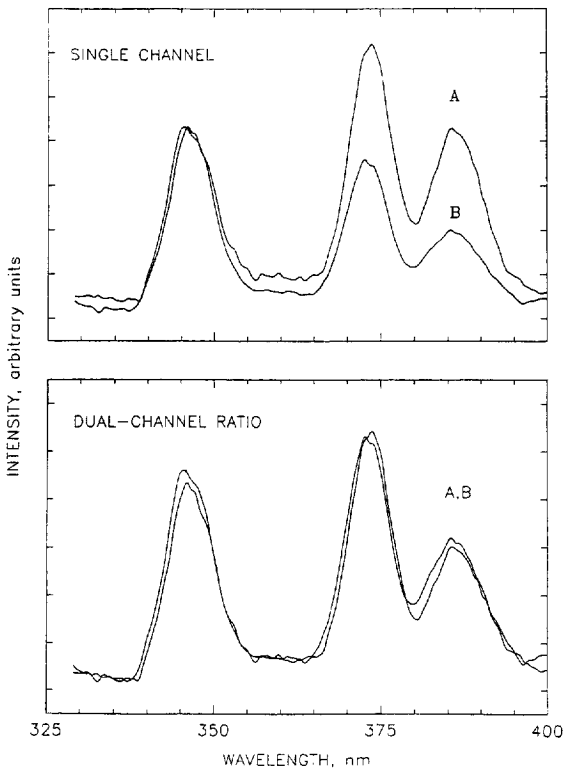

Fig. 1. Ultraviolet emission from ferrocene doped into the hydrogen supply of a flame photometric detector. Spectrum A: ferrocene level rising, Spectrum B: ferrocene level falling. Hamamatsu R-374 PMTs, 3 passes of a 25-point (0.6 nm) moving-average filter.

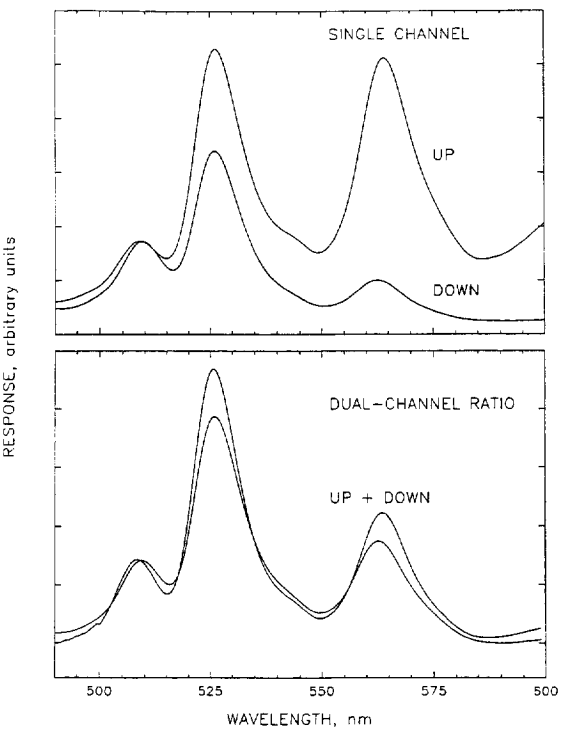

Fig. 2. HPO emission from a single peak containing 2 μg of tris(pentafluorophenyl)phosphine, from scans up and down the flanks of the peak. R-374 PMTs; no smoothing.

number of potential pitfalls need to be avoided. First, the measurements must be of the spectrum only, not of spectrum and background combined. This means for the non-dispersive channel that the chromatographic signal must be measured from the baseline up. And it means for the dispersive channel that the spectral background, if strong, must be deducted. Both corrections are easy to implement, either by dedicated algorithm or by spreadsheet.

Second, measurements carried out on that basis will be in error if the analyte affects the baseline, i.e., if the background emission is decreased (or, less commonly, increased) by the presence of analyte. Examples for this type of behavior, while not overly common, can nevertheless be found in practically any spectroscopic technique. The problem becomes particularly worrisome if the changes of background under a peak —which cannot be seen in a conventional chromatogram— should happen to be strongly wavelength-dependent.

The above limitations may sometimes be remedied by limiting the wavelength range of the non-dispersive reference channel to exclude a strong background emission (e.g., the OH bands at ca. 306 nm) whose amplitude may be susceptible to interference by the analyte; or to include only the spectral region of interest; or to observe just, say, the strongest band of the analyte. Which of these avenues is entered depends on the type and variability of the sample, the chemical nature of the analyte, the conditions of the detector, and the motivation and responsibilities of the analyst. In general terms, the most accurate intensity correction should be obtained by monitoring a major band of the analyte itself as reference. Clearly, however, this requires prior knowledge of the analyte's spectrum.

Third, measurements of spectra that consist of several emission systems should be carried out *within* linear range of *all* individual calibration

curves. (In practice that means staying safely within the linear part of the calibration curve as obtained from a spectrally inclusive reference channel.) As long as all emission systems are linear, their spectra will represent constant fractions of the total amplitude. If one system already exceeds its linear range while another doesn't yet, constancy will be compromised.

Fourth, measurements of an emission whose location varies with concentration —a variation caused perhaps by the flame itself changing shape in response to a large dose of analyte, or by the emission being of other than the first order (as in the case of S_2)— may lead to spectral discrepancies if the two channels monitor radically different areas of the flame. (Note that spatially discrepant sampling obtains, for instance, in this study.) If necessary, that can be circumvented by using a beamsplitter or a bifurcated light guide — but only at a significant cost in sensitivity.

Fifth, the need to deduct baselines before calculating the ratioed spectrum may lead to some difficulties. Since the net signal from the dispersive channel is divided by the net signal from the non-dispersive one, a low signal level from the latter would cause the ratio to be high and excessively noisy. During the passage of most of the peak, this will of course not occur: the non-dispersive channel, even with an interference filter added, will always maintain a much stronger signal than the dispersive one.

Though the net raw spectrum —the output of the dispersive-channel scan minus the background— may get close to or even touch zero, its absolute noise and hence the noise of the ratio readout, will not markedly decrease. (Its relative noise will, of course, strongly increase). This because the d.c. offset (the background correction) does not diminish the noise level: the latter is still characteristic of the spectral signal plus optical background plus photomultiplier dark current. In other words, the valleys of a referenced spectrum are unlikely to be much smoother than its peaks (compare Fig. 1). For spectral information content that matters little. It does, however, offer some hints for discussing whether noise —hence the spectral detection limit— can be further decreased by dual-channel methodology.

There is no doubt that large concentrations of analyte, continuously introduced, will lead to the observation of flicker (pink) noise in the response of the flame photometric detector [21]. (At lower analyte levels, or at baseline level, the observed noise is white and fundamental in character [13].) Yet the apparent relative contributions of pink and white noise do depend on the absolute signal levels (which include the photomultiplier dark currents). This is important here because the photomultiplier of the non-dispersive channel receives a much higher light input than that of the dispersive channel: its flicker noise (as fraction of the total noise) is hence also higher.

Fourier transforms (i.e., noise power spectra) show this to be essentially correct: on these $V^2/\Delta f$ vs. f graphs (V=noise in volts, f=frequency), the contribution of pink noise can be estimated by deducting the apparent (horizontal) white-noise level. (The white-noise level of a constantly doped-in analyte on a single channel, as measured on Fourier transforms at higher frequency —i.e., safely away from the $1/f$ noise region— is close to the fundamental (quantum) noise level as estimated from the square root of the photoelectron emission rate [13].)

Perhaps the easiest way to demonstrate that ratioing of channels does indeed remove some of the flicker noise is to smooth a dual-channel file with a simple moving-average filter of variable window width. The result is shown in Fig. 3. The basic data file holds the chromatographic record of 26.6 min of luminescence, as generated by a strong, constant doping stream of organophosphate. It represents, so to speak, a time-extended look at what happens at the apex of a strong organophosphate peak at the wavelength of maximum emission.

When a single channel of this file is smoothed by averaging the contents of a moving window —see filled circles in Fig. 3— the peak-to-peak noise $N_{p\text{-}p}$ and particularly the RMS noise hardly change over three orders of window width (corresponding to 0.1–100 s acquisition time). This indicates the dominating presence of a pink noise too slow for smoothing. Not surprisingly, then, if one channel is appropriately scaled and deducted from the other, the slow flicker noise components do not enter the subtraction record. That leaves mostly shot noise for the filter to deal with. The "A–B" curves —the empty triangles in the upper part of Fig. 3— hence reveal a signifi-

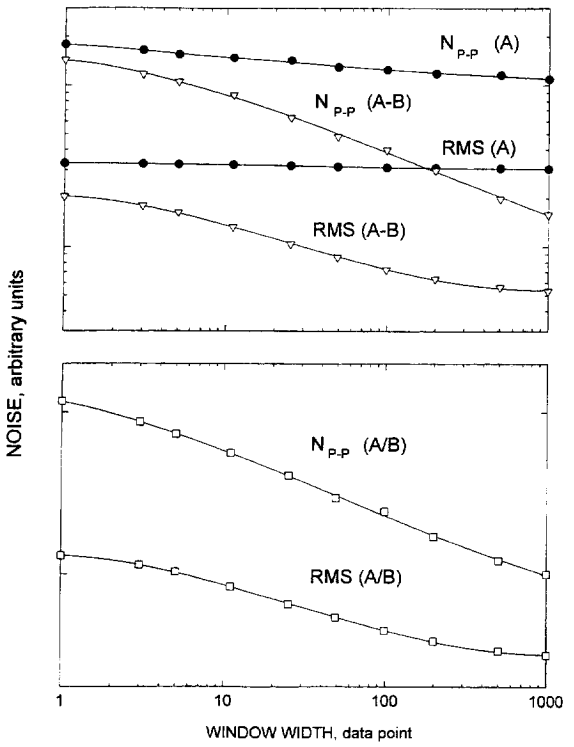

Fig. 3. Noise collected during 26.6 min of HPO emission from a constant stream of tris(pentafluorophenyl)phosphine, and its dependence on window width of a moving-average smoother, as expressed by peak-to-peak and root-mean-square measurements for single-channel A (full circles), difference of channels A and B (empty triangles), and ratio of channels A and B (empty squares). R-374 PMTs.

cant impact of the filter algorithm. Note that the theoretical slope for RMS shot noise is 1/2, i.e., close to the measured one. This simply confirms an earlier study of analyte noise [21].

When the ratio (rather than the difference) of the two channels is calculated and smoothed, a very similar picture emerges (see bottom of Fig. 3). Like subtraction, division removes some flicker noise, leaving mostly shot noise for the filter to suppress. This suggests (for upper parts of tall peaks and for wavelengths of strong emission) that both types of two-channel correlation reduce noise and that the effect increases with the time constant of the measurement and/or the digital filter. (It also shows that, in general agreement with the behavior of shot noise in a single channel [22], the $N_{p\text{-}p}$/RMS ratio of subtracted or divided double channels also decreases substantially with the filter's time constant.)

While the noise reduction is thus real, it should not be taken to imply that dual-channel ratioed spectra carry of necessity less noise than single-channel spectra. One reason for this relates to the contribution of shot noise. While flicker noise can be subtracted or ratioed out, shot noise obviously can not. If A be the signal of channel A and $\pm a$ the standard deviation of its shot noise, then dividing it by channel $B \pm b$ results, as is well known, in a square-root type increase in the relative standard deviation band of the ratioed spectrum:

$$\text{ratio} = \frac{A}{B} \pm \sqrt{\left(\frac{a}{A}\right)^2 + \left(\frac{b}{B}\right)^2}\ \text{RSD}$$

The other reason why a ratioed spectrum may fail to show lower noise than its numerator component has already been alluded to. Even if all of the spectral scan is taken close to the apex of the chromatographic peak, and even if that apex carries strong flicker noise, the regions of low emission in the scan —the valleys of the spectrum— will benefit less. In comparison to the regions of high emission, their fraction of flicker noise in the signal will be smaller, of shot noise larger. In other words, the total noise of the dispersive channel is less strongly correlated to the total noise of the non-dispersive channel at wavelengths of low than at wavelengths of high emission. (Consider in this context an interesting question that bears on the extent of noise correlation, hence possible noise reduction: During peak elution, is flicker noise present only on the spectral analyte signal or does it also occur on the spectral background signal? Causatively expressed: Is the flame induced to fluctuate by the high load of analyte, or is it just the flow of analyte itself that varies?)

Noise reduction in ratioed spectra is thus seen to depend on the presence or absence of certain basic perturbation mechanism in the flame, on the condition of the detector, on the concentration of analyte, on the extent of flicker noise the latter induces, and on the intensity of the spectral features. During this study, a slight noise reduction could often be observed on top of some spectral bands, while noise in the valleys was usually similar to or

worse than that of single-channel outputs. Thus, at least in a typical flame photometric detector, it would make little sense to carry out ratioing solely for the purpose of spectral noise reduction. (However, noise reduction in other spectral systems, including some coupled to chromatographic-type outputs, can be an entirely different matter [2].) In this study, ratioing was performed not for reducing noise but for accurately measuring spectral features of variable analyte inputs, most notably of single chromatographic peaks. (Note: these concentration-wise "accurate" spectra are not yet "corrected" for photomultiplier quantum yield, grating efficiency and other instrumental variables.)

If spectra are to be obtained from a single peak, the immediate question arises at how low an analyte level this can be achieved. If sensitivity is poor, spectra may be accurate in theory but unattainable in practice. Typical scanning spectrophotometers have so far needed chromatographic inputs corresponding to the top of the linear range of strongly emitting analytes, at least if they were expected to provide an adequately resolved spectrum from a typical FPD flame. The spectra of weakly emitting analytes could only be obtained from a "filter monochromator" with its far higher light throughput [11]. This raises the immediate question whether the current set-up is sensitive enough to deal with typical FPD spectra. Since sensitivity can be traded for resolution and vice versa (but in a manner quantitatively dependent on the nature of spectral features, e.g., lines vs. bands), this study attempts to characterize the performance of the system by three illustrative runs representing typical case studies of flame photometric response.

The first is a case of high sensitivity but low resolution. A ratioed spectrum is obtained from a peak of 80 pg tris(pentafluorophenyl)phosphine, i.e., from less than 5 pg of phosphorus. For noise-related reasons, only the main part of the peak (approximately from halfheight to halfheight) is subjected to a single, fast scan; the rest is disregarded. The top part of Fig. 4 shows the result; it is accompanied, for purpose of comparison, by a similar scan of a much larger peak on the bottom. This demonstrates clearly that a diagnostic "spectrum" of two HPO bands can be acquired from a peak containing only $5 \cdot 10^{-12}$ g P: a rather satisfying performance for a simple

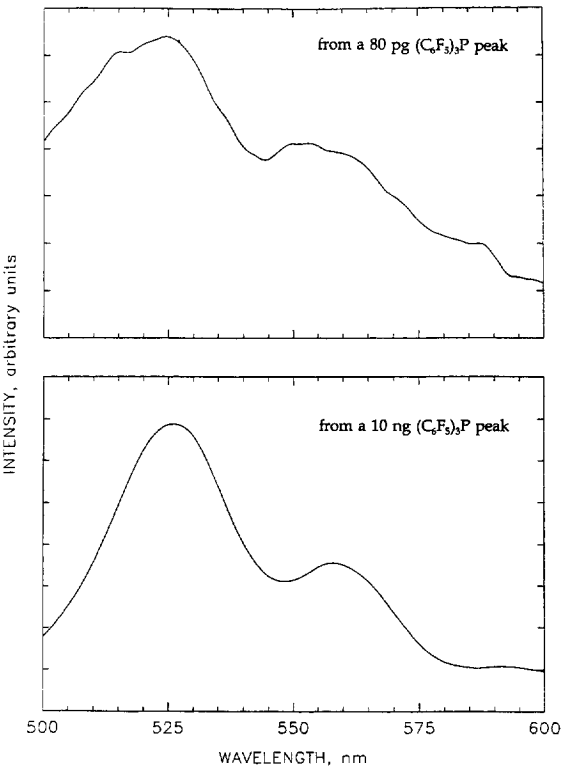

Fig. 4. High-sensitivity, low-resolution, referenced (ratioed) scan of HPO bands, as obtained from parts of a single peak containing 80 pg tris(pentafluorophenyl)phosphine (upper spectrum). Slits 3.16 mm (nominal bandpass 20 nm); single pass of a 19.5 nm moving average; R-1104 (monochromator) and R-268 (reference) PMTs. Lower spectrum: similar but 10 ng peak.

grating spectrophotometer. To achieve it, a 20 nm bandpass and a moving-average filter of 19 nm window width were used for the spectrum of this prominent FPD element.

The other prominent FPD element, sulfur, is shown at somewhat higher resolution (2 nm theoretical bandpass, 1.8 nm digital filter) in Fig. 5. The series of S_2 bands originating from the upper vibrational state of $v'=0$ is clearly visible. Even the $v'=1$ series is quite noticeable, at least where not dwarfed by the $v'=0$ bands. The objective here was clearly to secure a good spectrum from a single peak, rather than to demonstrate the highest sensitivity.

The third case is one of still lower sensitivity and higher resolution. It involves an element of weaker response in the flame photometric detector, i.e., iron.

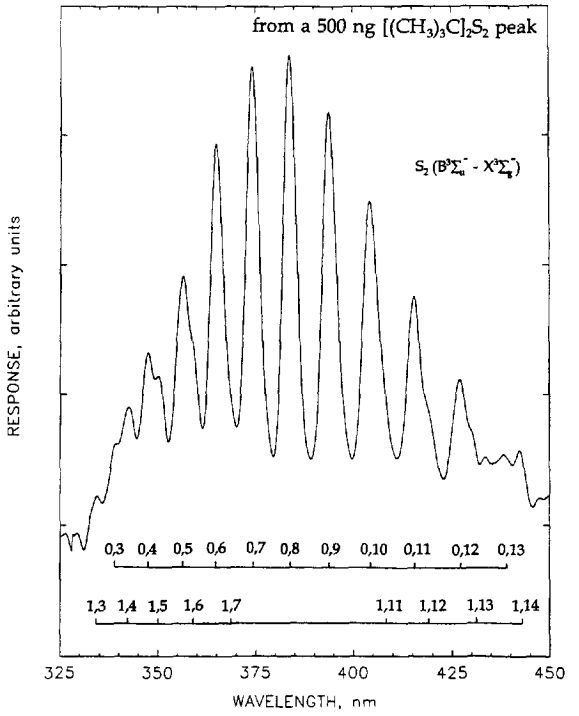

Fig. 5. Referenced 1/8-m monochromator scan of S_2 bands, as obtained from the central parts of a single peak containing 500 ng *tert.*-butyldisulfide. Slits 0.31 mm (nominal bandpass 2 nm); one pass of seven-point (1.75-nm) moving-average window; cooled R-1104 (monochromator) and R-374 (reference) PMTs. Vibrational levels as cited in [20].

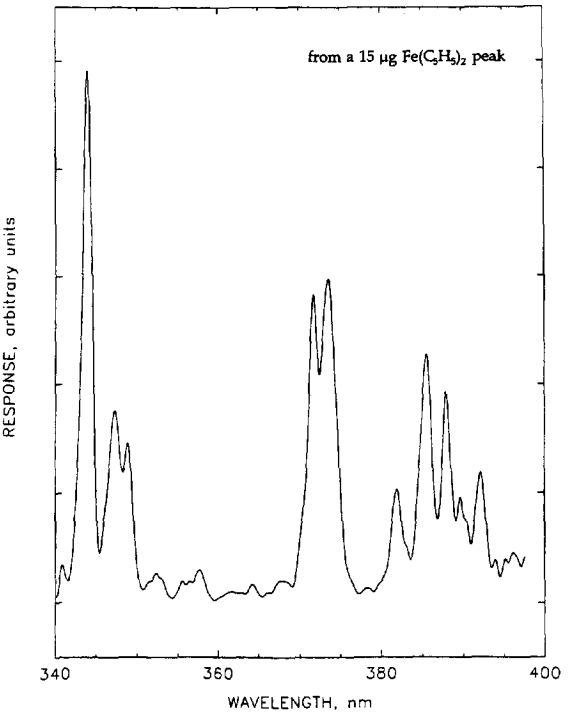

Fig. 6. Referenced 1/8-m monochromator scan of iron lines, as obtained from parts of a single peak containing 15 μg ferrocene. Slits 0.08 mm; one pass of 0.5 nm moving average; cooled R-1104 (monochromator) and R-374 (reference) PMTs.

The single peak —only part of which was scanned— contained 15 μg of ferrocene: an amount close to the upper end of iron's linear range. The objective here was to check whether the light throughput was large enough to approach the limit of resolution for the simple spectrophotometer. As Fig. 6 illustrates, it was. (The theoretical bandpass is about 0.5, the measured one about 1.5 nm.) The features shown are all atomic lines, some overlapping. The strongest emission is the resonance line at (precisely) 344.061 nm [23].

Beyond providing illustration, Fig. 6 serves yet another purpose. An earlier paper from our group concluded that the strong UV emission observed when ferrocenes pass through the FPD was due to the iron *atom* [24]. In view of the small size and low temperature of the FPD flame, that conclusion could be doubted — particularly since the resolution then obtained was not good enough to exclude molecular emitters. Even further out on the limb, the presence of some (assumed) lines and the absence of others was hypothetically linked to the upper energy limit of the chemiluminescent reaction. Judging from the (presumed) atomic emissions of several transition elements in the FPD, an approximate upper energy limit of 3.6 eV was postulated [11]. The earlier iron spectrum was, however, ambiguous: it could have contained some lines exceeding that hypothetical limit.

The current spectrum allows a more informed assessment. Almost all lines that can be clearly identified are transitions to the ground state (or to levels very close to the ground state such as 416 and 704 cm^{-1} [23]). The line from the highest upper level that can be reasonably assigned is the one at 347.545 nm (29469→704 cm^{-1}). Its upper state lies at 3.65 eV, not far from that of the dominant line at 3.60 eV, and still close enough to the threshold postulated for the excitation reaction. (Incidentally,

the nature of this reaction is still unclear.) There is no evidence for some of the otherwise (e.g., in an arc [23]) strongest iron transitions, for instance those at 358.12 and 382.043 nm, which occur from upper states of 4.92 and 4.10 e V, respectively.

Fig. 6 illustrates the extent to which a single peak traversing a very weak, very small flame can offer spectral data and in turn, provide basic information on an analytically and spectroscopically interesting process. (For the record, the background and solvent flames are approximately conical with a volume of ca. 0.002 cm^3; the luminescence of the ferrocene peak is roughly spherical with a volume of ca. 0.01 cm^3.)

In conclusion, single peaks from a dual-channel flame photometric detector can yield spectra that are amplitudinally accurate and of sufficient sensitivity/resolution to be of value for several types of qualitative analytical tasks. Due to the possibility of using a conventional grating spectrophotometer as the wavelength-selective channel, a wide range of optical conditions can be accessed. The methodology should be particularly applicable to cases where a compound —of known, suspected or unknown nature— can be obtained only as a gas chromatographic peak at trace level. The presence of a (mass-wise) overwhelming matrix with co-eluting components would enhance the appeal of the methodology, as would a dearth of available sample.

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References

[1] J.D. Ingle and S.R. Crouch. Spectrochemical Analysis, Prentice Hall, Englewood Cliffs, NJ, USA, 1988, p. 129.
[2] J.F. Karnicky, L.T. Zitelli and S. van der Wal, Anal. Chem., 59 (1987) 327.
[3] J.M. Bostik. J.W. Strojek. T. Metcalf and T. Kuwana, Appl. Spectr., 46 (1992) 1532.
[4] P.W. Farnsworth, M. Wu, M. Tacquard and M.L. Lee, Appl. Spectr., 48 (1994) 742.
[5] M.C. Bowman and M. Beroza, Anal. Chem., 40 (1968) 1449.
[6] V.A. Joonson and E.P. Loog, J. Chromatogr., 120 (1976) 285.
[7] M. Dressler, Selective Gas Chromatographic Detectors, (Journal of Chromatography Library, Vol. 36), Elsevier, Amsterdam, 1986.
[8] B. Millier, X.-Y. Sun and W.A. Aue, J. Chromatogr. A, 675 (1994) 155.
[9] H. Singh, B. Millier and W.A. Aue, J. Chromatogr. A, 724 (1996) 255.
[10] H. Singh, C.G. Eisener and W.A. Aue, J. Chromatogr. A, 734 (1996) 405.
[11] X.-Y. Sun, B. Millier and W.A. Aue, Can. J. Chem., 70 (1992) 1129.
[12] W.A. Aue, B. Millier and X.-Y. Sun, Anal. Chem., 63 (1991) 2951.
[13] W.A. Aue, H. Singh and X.-Y. Sun, J. Chromatogr. A, 687 (1994) 283.
[14] S.S. Brody and J.E. Chaney, J. Gas Chromatogr., 4 (1966) 42.
[15] C.R. Hastings, D.R. Younker and W.A. Aue, Trace Substances in Environmental Health. 8 (1974) 265.
[16] Catalogue, Oriel Instruments, 250 Long Beach Blvd., Stratford, CT, 06497, USA.
[17] Catalogue, Hamamatsu Corp., 250 Wood Ave., Middlesex, NJ, 08846, USA.
[18] W.A. Aue, B. Millier and X.-Y. Sun, Can. J. Chem., 70 (1992) 1143.
[19] Catalogue, Jandel Scientific, San Rafael, CA, USA.
[20] R.W.B. Pearse and A.G. Gaydon, The Identification of Molecular Spectra, Fourth Edition, Chapman and Hall, London, 1976.
[21] H. Singh and W.A. Aue, J. Chromatogr. A, 724 (1996) 251.
[22] X.-Y. Sun, H. Singh, B. Millier, C.H. Warren and W.A. Aue, J. Chromatogr. A, 687 (1994) 259.
[23] W.F. Meggers, C.H. Corliss and B.F. Scribner, Tables of Spectral Line Intensities, Part 1, National Bureau of Standards Monograph 145, U.S. Government Printing Office, Washington, DC, 1975.
[24] X.-Y. Sun and W.A. Aue J. Chromatogr., 467 (1989) 75.