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Journal of Chromatography A, 688 (1994) 153–159

JOURNAL OF CHROMATOGRAPHY A

Holophotal flame photometric detection☆

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Received 1 June 1994

Abstract

A commercial flame photometric detector was modified such that a larger fraction of its luminescence would reach the photomultiplier tube. As tested with compounds of lead and osmium, these modifications resulted in up to fifty times enhanced light transmissions and —in rough accordance with the square-root dependence of quantum noise— typically sevenfold improvements in signal-to-noise ratio.

1. Introduction

A recent study by our group demonstrated that the noise of a flame photometric detector (FPD) was largely, if not exclusively, random in character and high in frequency [1]. Under these circumstances the signal-to-noise ratio (S/N) is proportional to the square root of light reaching the photomultiplier tube (PMT).

Improving the light throughput of the FPD should hence improve the S/N; provided the square-root relationship remains intact. The obvious question is how much improvement could be expected in theory, and how much of that could be realized in practice.

The conventional FPD used for this study has an acceptance cone of about 16°; i.e. approximately 0.5% of the light emitted by the flame reaches the photocathode of the PMT. (This percentage is obviously a rough estimate: it considers the flame an isotropically emitting point source and neglects such effects as light reflection off existing walls. It also disregards the significant absorption by the interference filter.) Yet, despite the coarseness of the estimate, there is no doubt that only a small fraction of the generated light reaches the PMT.

If all of it would, an S/N dominated by photon shot noise should improve by a factor of $2d/r$, where d is the distance between the flame and the photocathode and r the radius of the latter. [In our case, that turns out to be 14 times. This number can also be obtained from the given percentages, i.e. $(100/0.5)^{1/2} = 14$.]

Physical limitations make such a perfectly holophotal performance impossible to achieve. There will always be mechanical obstructions and optical imperfections; there will always be absorption, transmission and reflection losses.

Furthermore, shapes of luminescence differ for different elements and different flame conditions. It is also possible that the square-root law should be only partially applicable, or perhaps applicable only to certain flames. So, how much of that theoretical improvement can be translated into practice by a simple optical modi-

☆ Part of theses of J.A.G. and N.B.L.

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0021-9673/94/$07.00
SSDI 0021-9673(94)00901-5

fication (not a complete rebuilding) of the detector?

To provide an acceptable (i.e., a reasonable, reliable and relevant) answer to that question, two essentially identical instruments were tested by two different operators with two different types of test compound. Each worked under individually optimized conditions.

2. Experimental

This study used two Shimadzu gas chromatographs, both Models GC-8APFp with single-channel FPD. Modifications that had earlier been made to one or both units included the substitution of a variable PMT power supply, the provision of a larger bucking current, the removal of in-line flow restrictors, the installation of wider-range flow controllers and rotameters, the replacement of the detector cap by a differently shaped one, and the insertion of a PTFE gasket into the detector base (to keep gas exchange with the atmosphere to a minimum in that region of the detector).

Yet these earlier modifications are mentioned here *for the record only*. The two Shimadzu units performed to our full satisfaction as received. They were modified solely to accommodate a variety of research projects that demanded unconventional conditions, and we did not want to "unmodify" them for the present study. These earlier changes thus do not change the basic performance of the instruments. Nor —which is of crucial importance here— do they change the character of their noise.

Modifying the FPD for higher light throughput started by raising the flame, on a thinner jet, to the center of the light path (the optical axis). A parabolic mirror was installed with the flame at its focal point. It had been lathed into a 1-in. (1 in. = 2.54 cm) aluminum rod, which was then inserted through the (normally covered) second opening of the detector. The parabolic mirror was drilled —perpendicular to its optical axis and centered at its focal point— to accept the detector jet and its quartz chimney (both more slender than in the original FPD).

Since the two flames were of different size and shape, their centers (their visually observable locations of highest analyte emission intensity) were made to coincide with the focal point of the parabola. The Pb luminescence was relatively tall and lanceolate in shape; it therefore had to reside on a slightly (ca. 2 mm) shorter jet than the smaller and roughly spherical Os luminescence.

Instead of the conventional window, an inexpensive planoconvex lens of 50 mm focal length (Edmund Scientific, 101 East Gloucester Pike, Barrington, NJ 08007-1380, USA) was inserted and backed up by an aluminum tube. The tube was thin-walled to minimimize heat conduction, and had been internally polished to a mirror surface. Fig. 1 shows to-scale schematics of the optical components. It also indicates some light-paths used in the "conventional", "holophotal" and "comparative" FPD measurements. (Several "intermediate" configurations were tested as well, but these are easily described by reference to the displayed three archetypes.)

The "conventional" measurements were done with the detectors as received from the manufacturer —except for leaving in place the earlier listed but, in this context, inconsequential modifications, and except for removing the commercial quartz chimney. The removal of the chimney results, for reasons unknown, in a larger analyte signal.

The "holophotal" measurements were carried out on the detectors supplied with the most effective combination available of parabolic mirror, centered slender jet and chimney, reflecting tube, etc.

The "comparative" measurements were performed with the detectors using the light path of the conventional mode, but the jet and chimney of the holophotal mode. This hybrid version merely allowed reliable determination of the light throughput ratio.

All versions were tested under conditions optimized for the individual detector, analyte and analyst. For analytic relevance and academic expedience, the authors made use of ongoing thesis topics dealing with the FPD characteristics of organometallic compounds: J.A.G. tested her

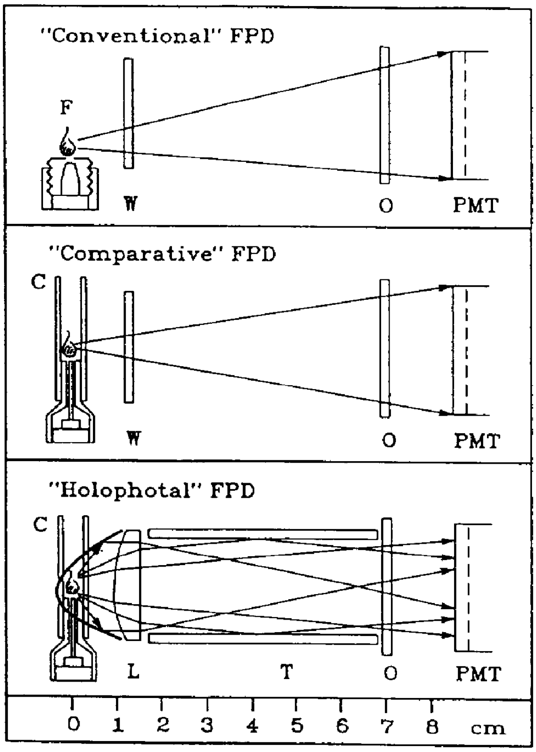

Fig. 1. Optical layout of "conventional", "comparative" and "holophotal" FPD configurations. C = Glass or quartz chimney; F = flame; L = planoconvex lens, focal length 5 cm; O = optical filter; PMT = photocathode; T = internally polished aluminum tube; W = quartz window. Not labelled but shown in bold line: aluminum parabolic mirror, focal length ca. 2.5 mm. In the holophotal configuration, the top of the jet is slightly lower than shown for Pb, and slightly higher than shown for Os (see text for explanation of the ca. 2 mm difference).

FPD versions with the σ-bonded tetraethyllead, N.B.L. hers with the π-bonded osmocene (dicyclopentadienyl osmium).

The tetraethyllead determination was carried out on a 100 × 0.3 cm I.D. borosilicate column packed with 5% OV-101 on Chromosorb W AW, 100–120 mesh (ca. 150–125 μm diameter particles) at 130°C. Flows were nitrogen 30, hydrogen 73 and air 13 ml/min (i.e., strongly hydrogen-rich). A Hamamatsu R-1104 PMT at −650 V was used behind a 665 nm longpass colored-glass filter (Oriel, 250 Long Beach Boulevard, Stratford, CT 06497, USA; item 51 330). The injected amounts of tetraethyllead were 10 ng for the "holophotal", 10 and 20 ng for various "intermediate", 50 ng for the "comparative" and 100 ng for the "conventional" configuration (all data are, however, reported "per 100 ng").

The osmocene determination was carried out on a 100 × 0.3 cm I.D. borosilicate column packed with 5% OV-101 on Chromosorb W AW, 100–120 mesh, at 180°C. Approximate flows were nitrogen 25, hydrogen 16 and air 40 ml/min (i.e., stoichiometric or close to it). A Hamamatsu R-2228 PMT was used at −900 V, behind a 630 nm longpass colored-glass filter (Oriel, item 51 320). The amount of osmocene injected was 5 ng for all configurations.

We shall distinguish these two independent sets of experiments by the symbols of the FPD-active elements involved, i.e. "Pb" and "Os".

3. Results and discussion

It is important to note that tetraethyllead and osmocene serve here only as two disparately behaved analytes, chosen to conduct two independent test series with similar optical objects but different analytical subjects. Some information on the FPD's response to the main-group element lead and the transition metal osmium can be found in earlier work from our group [2,3]; more will be reported in the forthcoming theses of two of the present authors (J.A.G. and N.B.L.).

The particulars of commercial detector construction, FPD response characteristics, and optical requirements for high light-throughput demanded —for reasons more of formal logic than of analytical practice— that a two-pronged experimental approach be employed in answering the central question of this study: Can light throughput and S/N be significantly improved?

If light throughput is to be the crucial parameter, then it should be measured —in both the conventional and the holophotal mode— with the *same* light source operating under *identical* conditions. In this study, close to holophotal conditions are obtained with a parabolic mirror. If that mirror is to intercept as much light as possible, its focal length must be very short.

Accordingly, it needs to approach the flame within a few millimeters. But if it does, the flame will become disturbed and develop flicker noise. Such disturbance can be avoided by a glass or quartz chimney separating mirror and flame.

The presence of a chimney would not seem to pose a problem: the commercial detector uses a quartz chimney as well. Yet several elements respond better in the FPD when that chimney is removed (e.g. [4]). Given that the parabolic mirror (the holophotal mode) cannot be rationally tested without a chimney, the question arises how then to test the conventional mode. *Without* a chimney the conventional response becomes stronger but the intended comparison with the holophotal mode becomes weaker; *with* a chimney the opposite occurs.

A similarly formal argument can be made about the circumference of the chimney (in the commercial detector it is wider) and about the fact that, for efficient light gathering, the flame needs to be in the center of the light tunnel (in the commercial detector configuration it is positioned near the bottom). Thus, the objectives of this study require that not just one but two questions be asked.

First the analytical question: Can a significant improvement in S/N be obtained when the best commercial configuration is changed to the best holophotal configuration, with each operating at individually optimized conditions?

Second the mechanistic question: If the light source —i.e. the flame and its conditions— do remain the same, will the increased light throughput achieved by the newly introduced optical elements lead to the square-root improvement in S/N that one expects for quantum-type noise?

Since both questions are important in their own right, this study will answer both. To do so, at least *three* detector configurations need to be tested. (We actually tested many more.)

To wit, the "conventional" measurements will represent the best the commercial detector can do, the "holophotal" measurements the best the fully modified detector can do. Additionally, the "comparative" measurements will represent a hybrid configuration in which the "flame jet and chimney" unit, as developed for the "holophotal" arrangement, is used in a detector environment otherwise resembling the "conventional" mode: this allows, first, direct measurement of the light throughput and, second, comparison of the theoretical with the experimental S/N improvement.

Table 1 shows the relative light intensity as measured from the baseline (baseline current minus dark current) and from a peak (peak apex current minus baseline current). Table 1 also shows the resulting S/N for both sets of five experimental configurations.

The increase in light throughput, from "conventional" to "holophotal" FPD configurations, is 31-fold (Pb) and 34-fold (Os) for the baseline, and 48-fold (Pb) and 37-fold (Os) for the analyte peak. If shot noise were the sole parameter to consider, S/N values should improve 5.6, 5.8, 6.9 and 6.1 times. The measured improvements are (Pb) 9.7 and (Os) 7.2 times.

The latter numbers provide a fair assessment of what can be achieved by a simple optical update: they document the success of the operation. Despite that success, a serious discrepancy appears to exist between calculated and measured S/N improvement factors. The main reason for this is the difference in light source —meaning different locations and conditions of the flame— in the two measurements.

That difference can, however, be removed. If the *same* jet-and-chimney is used for the comparison of the "comparative" with the "holophotal" configuration, the increase in light throughput for the *analyte peak* is (Pb) 51 and (Os) 33 times. That would predict S/N improvements of 7.2 and 5.7, respectively. The measured values, 7.1 and 6.2, are now in excellent agreement.

S/N values predicted on the *baseline* (8.2 and 4.8) show poorer agreement. That light throughput measured on a peak produces data of higher predictive ability than light throughput measured on the baseline should not come as a surprise.

It occurs most likely because the peak (= signal) enters directly, while the baseline enters only as the square root (= noise) into the S/N calculation. Also, the peak height determi-

Table 1
Comparison of different FPD configurations

FPD configuration	Baseline[a] current (A)	Peak current (A)	S/N
Tetraethyllead (100 ng)			
Holophotal[b,c,d]	$1.6 \cdot 10^{-7}$	$3.8 \cdot 10^{-7}$	340
Intermediate I[c,d]	$2.8 \cdot 10^{-8}$	$1.2 \cdot 10^{-7}$	210
Intermediate II[b,d]	$5.8 \cdot 10^{-8}$	$1.6 \cdot 10^{-8}$	114
Comparative[d]	$2.4 \cdot 10^{-9}$	$7.4 \cdot 10^{-9}$	48
Conventional[e]	$5.1 \cdot 10^{-9}$	$8.0 \cdot 10^{-9}$	35
Osmocene (5 ng)			
Holophotal[b,c,d]	$1.2 \cdot 10^{-7}$	$1.3 \cdot 10^{-7}$	230
Intermediate I[c,d]	$3.4 \cdot 10^{-8}$	$2.5 \cdot 10^{-8}$	87
Intermediate II[b,d]	$3.5 \cdot 10^{-8}$	$4.5 \cdot 10^{-8}$	160
Comparative[d]	$5.2 \cdot 10^{-9}$	$4.0 \cdot 10^{-9}$	37
Conventional[e]	$3.5 \cdot 10^{-9}$	$3.5 \cdot 10^{-9}$	32

[a] The typical dark current, $1.4 \cdot 10^{-9}$ A for Pb and $3 \cdot 10^{-10}$ A for Os, is not included.
[b] Parabola.
[c] Lens and light tube.
[d] Small, centered jet with chimney.
[e] Large, low jet without chimney.

nation is experimentally more robust, cancelling or minimizing contributions from the PMT dark-current, from room stray light, etc. It should also be noted that the eventual quantitative effect of all this may be influenced by the relative light levels of peak and baseline (which in practice means by the amounts of analyte injected).

From the agreement between calculated and measured S/N values we can safely assume —at least for our FPDs and their conditions— that the S/N increases with the square root of the light throughput from the flame. Detection limits and linear ranges should improve accordingly.

It is also obvious from Table 1 that Pb and Os —and the two instruments that process them— agree in the relative trends but differ in the absolute numbers. This is, again, not surprising. The working conditions for Pb and Os *are* very different —one reason we chose those particular analytes for testing. Besides, mirror surfaces lose reflecting power, chimneys get dirty, gas flows change with time, light leaks appear and vanish, etc.

Furthermore, a whole host of *non*-entropic circumstances —which, moreover, involve principle rather than practice, and are therefore much easier to describe and defend— can lead to apparent discrepancies in the observed S/N behavior. For instance:

(1) Baseline luminescence and peak luminescence often differ drastically in their intensity distributions in and around the flame —not to mention on the surface of the chimney.

(2) Because of their disparately shaped analyte —never mind baseline— luminescences, the Pb and Os flames differ in the beam divergence they cause, and in the slightly different jet heights used to center their maximum emission intensities. Differently sized jets, by virtue of being opaque, intercept different fractions of the light thrown forth by the parabola.

(3) The peak and baseline currents often show disparate dependencies on conditions, for instance the signal-to-background ratio often varies with flow-rates. Such effects may be moderated or exacerbated by the linear entry of the peak vs. the square-root entry of the baseline into the S/N calculation, and by the relative levels of peak and baseline.

(4) In that context, analyte peaks can depress

("eat into", "quench") the baseline on their run through the flame, just as the background can quench the analyte. (The latter phenomenon is readily apparent and has been widely researched [5,6]; the former remains obscure and has been nigh totally ignored.)

(5) The dark current of the PMT (which is normally considered part of the background, though not in this paper) remains essentially independent of (a moderate) light input. Configurations in which the dark current forms a sizeable fraction of the total PMT baseline current need therefore be treated with due caution.

(6) Although the FPD flame under our conditions produces mainly fundamental (i.e. photon shot) noise, the presence of minor contributions from "excess" (e.g. $1/f$) noise cannot be ruled out, particularly when narrow jets and chimneys are used, or when flames are run on the verge of extinction.

More types of S/N perturbations are possible and indeed probable. It is clear, however, that the anticipated S/N improvement could be successfully realized in this study. The largest credit for that goes to the parabolic mirror and to the aluminum tube with its internal mirror surface. As it turned out, the former was of greater relative benefit to the case of Os, the latter to the case of Pb. The parabolic mirror worked well even though it demanded the use of a chimney that depressed the response of both test compounds.

In other experiments, a commercial first-surface mirror of 10 mm focal length (Edmund Scientific, item 43 464) also worked well, with or without a chimney. So did two planoconvex lenses of 25 mm focal length (Edmund 45 098) that replaced the quartz window.

The choice of focal length (50 mm) for the planoconvex lens installed in the holophotal configuration represents a compromise. Its contribution to S/N improvement is small to start with, and it becomes almost negligible when the lens is used in conjunction with a parabolic or spherical mirror. On the other hand, why not use a lens instead of a window when the main task of either is merely to protect the PMT channel from the hot and humid atmosphere of the flame chamber?

Whether the achieved improvement in FPD performance is worth the trouble in FPD modification depends, inter alia, on laboratory priorities related to maximum analyte sensitivity vs. minimum instrument downtime. The hardware costs are negligible, but machining skill is definitely required for fashioning the parabolic mirror. In this context we should like to give special mention to one of the simplest, cheapest and yet most effective devices used in the FPD modification: the outside threaded, inside polished light propagation tube.

Beyond improving light propagation, such a tube serves other worthy causes as well: it shuts out room light, it allows the easy exchange of a window or lens, and it permits adjustment of the tension on the silicone rubber O-ring (thus helping to keep flame water from distilling into the PMT housing).

Because this tube is, furthermore, easily machined and installed on the commercial detector, we show its detailed blueprint in Fig. 2. Use of the internally reflecting tube (plus lens) alone —i.e. without the parabolic mirror— increased the S/N 4.4 and 2.4 times for Pb and Os, respectively. (The numbers seemed to differ too much among the two methods; however, a special cross-check in which lead was run on the Os instrument, and osmium on the Pb instrument, supported their validity.)

It may be noted in this context that optical improvements do not add up linearly: the tube, when added to an already installed parabola, is much less effective. So is, of course, the parabola when added to an already installed tube.

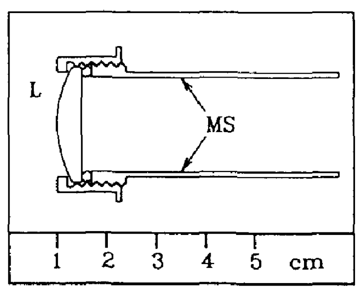

Fig. 2. Mechanical details of light-propagating tube and modified window holder. L = Lens; MS = mirror surface.

A simple, internally reflecting tube (or other type of light guide) may thus prove to be of minor cost but major benefit. It may also broaden the effective bandpass of the interference filter, owing to the wider angle of photon incidence. Fortunately the latter effect should be small and of little concern to most analytical methodologies.

The chosen "holophotal" modification is by no means the only or even the most effective one that can be envisioned. Moving a better-cooled PMT closer to the flame would, for instance, provide a —fairly obvious but in practice also fairly tricky— option. And a parabola is not necessarily the optically most efficient shape under the circumstances. One could, for instance, think of an ellipse, with the flame (enclosed by a gas-tight chimney) in one of its focal points, and with the plane of the PMT photocathode close to the other.

Such modifications would, however, have required more work on the detector body —work we considered unnecessary, both in terms of the argument being put forth by this paper and the performance already achieved by the two instruments.

Spherical mirrors and lenses have been used before in FPDs (e.g. [7–10]) —inspired, no doubt, by spectroscopic instrumentation (cf. [11]) in which their use is vital. Whether they yield the desired improvement in individual cases depends not only on the shape of the luminescence and the optical layout of the detector, but also on the nature of the baseline noise.

If the latter is dominated by flame flicker, the S/N will be independent of light throughput. If, on the other hand, it is dominated by PMT dark-current noise (i.e. if the background luminescence is at a negligible level), the S/N will be directly proportional to light throughput.

The two cases of this study, with their roughly square-root relationship between light throughput and S/N, are intermediate in their behaviour (and therefore in their potential for improvement). These cases —dominated as they are by photon shot noise— are, however, just the ones most typical of multi-element FPD methodology, and the ones most often encountered in routine chromatographic practice.

Acknowledgements

This study was supported by NSERC research grant A-9604. The most competent assistance of B. Millier in electronic design and J. Müller in quartz blowing are gratefully acknowledged.

References

[1] X.-Y. Sun, H. Singh, B. Millier, C.H. Warren and W.A. Aue, *J. Chromatogr. A*, 687 (1994) 259.

[2] W.A. Aue, X.-Y. Sun and B. Millier, *J. Chromatogr.*, 606 (1992) 73.

[3] X.-Y. Sun and W.A. Aue, *Mikrochim. Acta*, I (1990) 1.

[4] X.-Y. Sun, B. Millier and W.A. Aue, *Can. J. Chem.*, 70 (1992) 1129.

[5] S.O. Farwell and C.J. Barinaga, *J. Chromatogr. Sci.*, 24 (1986) 483.

[6] W.A. Aue and X.-Y. Sun, *J. Chromatogr.*, 641 (1993) 291.

[7] S.S. Brody and J.E. Chaney, *J. Gas Chromatogr.*, 4 (1966) 42.

[8] P.W. Grant, in D.H.Desty (Editor), *Gas Chromatography 1958 (Proc. Symp., Amsterdam, May 1958)*, Butterworth, London, 1958, pp. 153–163; as cited in D. Jentzsch and E. Otte, *Detektoren in der Gas-Chromatographie*, Akademische Verlagsgesellschaft, Frankfurt/Main, 1970, pp. 177–178.

[9] P.L. Patterson, R.L. Howe and A. Abu-Shumays, *Anal. Chem.*, 50 (1978) 339.

[10] B. Millier, X.-Y. Sun and W.A. Aue, *J. Chromatogr. A*, 675 (1994) 155.

[11] J.D. Ingle, Jr. and S.R. Crouch, *Spectrochemical Analysis*, Prentice Hall, Englewood Cliffs, NJ, 1988.