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Second-channel designs for a single-channel flame photometric detector[☆]

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Abstract

An existing, one-channel flame photometric detector was modified so that it would operate with higher sensitivity on two channels. To do this, the available primary channel was first changed to holophotal mode by installing a parabolic mirror. Optical access to the flame was then secured for a secondary channel by drilling a coaxial hole through the parabola. Two alternative designs were used for the secondary channel: a light guide and a lens–mirror combination. They were tested with compounds of osmium, lead, sulfur and phosphorus. Both the new primary and either one of the two secondary channels yielded higher light throughput and lower detection limits than the initial, conventional channel.

1. Introduction[1]

Dual-channel flame photometric detectors (FPDs) [1,2] can reveal elemental compositions and remove interfering peaks [1–8]. A holophotal, *single*-channel version of the FPD has been described earlier [9]. It will be complemented in this study by a second channel using a lens/mirror combination or a light guide. For use in graduate research, a total second channel should cost less than US$ 1000. Also, it should be at least as sensitive as a good commercial channel. Since different elements need different conditions for signal/noise (S/N) optimization and since they produce different flame shapes, four test compounds (of S, P, Pb and Os) will be used by two different operators on two different instruments. This will ensure reproducibility and comparability with the literature [e.g. 10–14].

2. Experimental

This study used two different Shimadzu GC-8APFp gas chromatographs as described earlier [9]. The parabolic mirror of the holophotal

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☆ Part of graduate theses of J.A.G. and N.B.L.

[1] By request of the referees, the introduction and the experimental sections of this manuscript were severely shortened. Readers interested in the full text are invited to contact the corresponding author.

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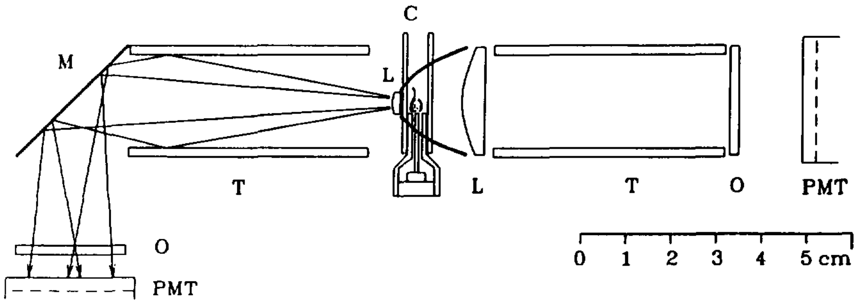

Fig. 1. "Lens/mirror" arrangement of second channel. PMT = photocathode of head-on photomultiplier tube; O = optical filter; M = aluminum mirror, T = light-reflecting aluminum tunnel; L = planoconvex lens; C = borosilicate or quartz chimney.

arrangement was coaxially drilled to provide a 1/4-in. (1 in. = 2.54 cm) opening.

2.1. The lens/mirror channel (on J.A.G.'s instrument)

A planoconvex lens of 6 mm diameter and focal length was cemented with high-temperature epoxy into the entrance of the parabolic mirror and a highly polished light tunnel. The mirror was cut at a 45° angle into an aluminum rod 1 in. in diameter. The resulting arrangement is shown schematically in Fig. 1.

2.2. The light-guide channel (on N.B.L.'s instrument)

A 1/4-in. diameter image conduit (Edmund Scientific) was bent 90° in the middle and connected to the parabolic mirror on one, to the photomultiplier tube on the other side. Fig. 2 shows the schematic.

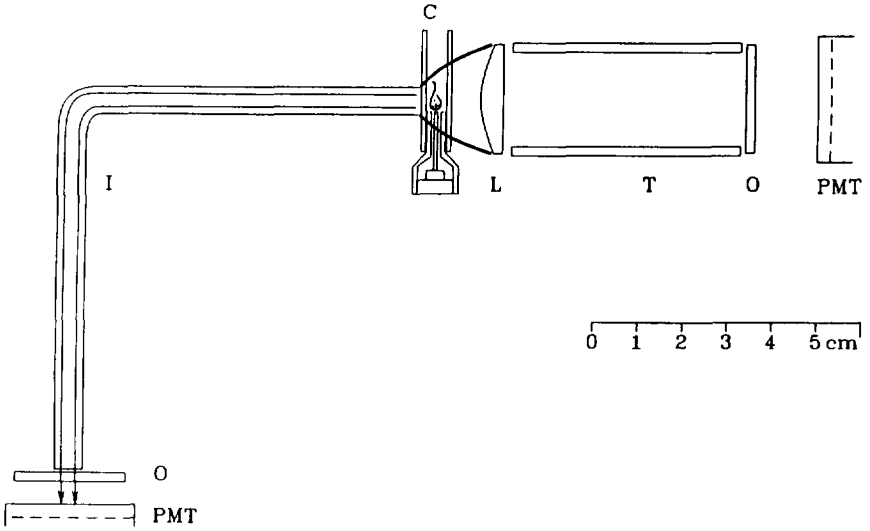

Fig. 2. "Light-guide" arrangement of second channel. PMT = photocathode of head-on photomultiplier tube; O = optical filter; I = image conduit (or a more gently bent quartz rod); C = borosilicate or quartz chimney; L = planoconvex lens; T = light-reflecting aluminum tunnel.

2.3. Measurements

The model compounds representing the four elements Os, Pb, S and P were tested in (at least) three types of channels. "Channel 1" is the "holophotal" channel; it is located on the right side of Figs. 1 and 2. "Channel 2" is the title channel of this manuscript; it is either of the "lens/mirror" or the "light guide" type and is located on the left side of Figs. 1 and 2. The "conventional channel" is the commercial, single-channel detector as purchased.

The lab-made readout device for two channels, nicknamed "dicorder", contains dual amplifier circuits that —after signal conversion from analog to digital and with the help of a dedicated microprocessor— feed moving-average noise filters and forward their output to a conventional 8-point matrix printer in real time. The dicorder costs about US$ 300 per channel, as compared to about US$ 3000 for the usual electrometer —analog filter— stripchart recorder combination. (The latter combination is, however, better suited to making noise measurements, for which it was used even in this study.) Together with the lab-made power supply, photomultiplier housing and detector parts, and the purchase price of the photomultiplier tube, a total second channel thus costs below US$ 1000.

All signals were roughly optimized for maximum S/N. This includes the gas flows, the photomultiplier voltage, the optical filter (if any), etc. The noise N was measured as the peak-to-peak fluctuation of the baseline, with drifts and spikes excluded, at an analog filter (RC) time constant of 1 s. The minimum detectable flows were determined separately, with analyte amounts in the detection-limit range. They are given as −log (mol X/s), where X = Os, Pb, S or P. The values are calculated for the two most popular definitions, $S/N_{p,p} = 2$ and $S/RMS = 3$ [15].

3. Results and discussion

Table 1 lists most of the obtained data, arranged according to element. It illustrates several interesting points. For one, in (almost) every case is the conventional channel the one with the lowest light throughput and the worst detection limit. While this was expected —and indeed already known— for the comparison with the holophotal channel as used on Os and Pb [9], it was highly questionable whether the same would also be the case for comparison with the second channels as used on Os, Pb, S and P.

After all, the second channels have access to the flame luminescence only through a tunnel of, at its narrowest, 6 mm diameter. In comparison, the narrowest part of the conventional (or, for that matter, the holophotal) channel is about 20 mm in diameter. Yet, because of the different distances from the flame, the light cone sampled (if the flame is —erroneously, of course— considered a point source) turns out to be larger for a second than for the conventional channel.

This points to an important difference between the configurations of the conventional and of the second channels used here. The conventional configuration views "the flame" and lots of space above and around it. The second-channel configurations, with their much narrower aperture situated in the immediate vicinity of the chimney, view the flame and little else.

If, therefore, all of the luminescence occurs in or very close to "the flame", then the second channels will be the more sensitive. If, however, part or most of the luminescence should occur above the flame (as, depending on analyte amount, is often the case with the second-order emitter S_2), then the secondary channel may be at a disadvantage vis-a-vis the conventional one. Indeed, the Shimadzu FPD —whose flame is located at the bottom of the viewing area— is renowned for its excellent performance with sulfur-containing analytes. And it was indeed one case of sulfur —singular though it remained— where the performance of the conventional channel proved superior to that of the second channel.

A large viewing area —which the holophotal mode also offers to some degree— is, however, not unconditionally desirable. Depending on a variety of circumstances, the space above the flame, and in particular the inner surface of the

Table 1
Currents, signal-to-noise ratios, and detection limits

PMT, voltage, filter	Channel	Baseline current (A)	Peak current (A)	S/N[a]	MDL[b] at $S/N_{p-p}=2$
Osmium (5 ng osmocene)[c]					
R-1104,	1. Holophotal	$2.7\cdot10^{-7}$	$3.2\cdot10^{-7}$	910	14.7
−540 V,	2. Image conduit	$3.2\cdot10^{-8}$	$8.6\cdot10^{-8}$	490	14.4
475 nmLP	Conventional[d]	$1.3\cdot10^{-8}$	$8.2\cdot10^{-9}$	100	13.8
Lead (10 ng tetraethyl lead)					
R-1104,	1. Holophotal	$1.3\cdot10^{-7}$	$2.6\cdot10^{-8}$	35	13.5
−650 V,	2. Lens/mirror	$1.8\cdot10^{-8}$	$3.5\cdot10^{-9}$	14	13.0
665 nmLP	Conventional	$5.3\cdot10^{-9}$	$7.6\cdot10^{-10}$	5	12.7
Sulfur-1[e] (5 ng thianaphthene)[f]					
R-1104,	1. Holophotal	$1.7\cdot10^{-8}$	$9.3\cdot10^{-8}$	1800	13.7
−400 V,	2. Image conduit	$2.5\cdot10^{-9}$	$1.3\cdot10^{-8}$	1200	13.5
open	Quartz rod	$1.9\cdot10^{-9}$	$2.1\cdot10^{-8}$	380	13.0
	Conventional	$1.1\cdot10^{-9}$	$5.3\cdot10^{-9}$	550	13.4
Sulfur-2 (5 ng thianaphthene)					
R-268,	1. Holophotal	$7.6\cdot10^{-8}$	$1.1\cdot10^{-7}$	870	13.4
−500 V,	2. Lens/mirror	$3.7\cdot10^{-9}$	$2.0\cdot10^{-9}$	160	12.8
open	Conventional	$4.1\cdot10^{-10}$	$3.5\cdot10^{-9}$	440	13.1
Phosphorus-1 [1 ng tris(pentafluorophenyl) phosphine]					
R-1104,	1. Holophotal	$1.6\cdot10^{-7}$	$8.3\cdot10^{-8}$	200	15.1
−600 V,	2. Image conduit	$3.5\cdot10^{-8}$	$2.2\cdot10^{-8}$	90	14.7
550 nm WB	Conventional	$1.6\cdot10^{-9}$	$2.2\cdot10^{-9}$	42	14.4
Phosphorus-2 [1 ng tris(pentafluorophenyl) phosphine]					
R-1104,	1. Holophotal	$2.4\cdot10^{-8}$	$6.1\cdot10^{-9}$	150	14.9
−550 V,	2. Lens/mirror	$2.0\cdot10^{-9}$	$7.1\cdot10^{-10}$	75	14.6
550 nm WB	Conventional	$2.5\cdot10^{-10}$	$2.9\cdot10^{-10}$	46	14.5

[a] Peak height/peak-to-peak noise, no electronic filter.
[b] Minimum detectable limits of element X (X = Os, Pb, S or P), expressed as −log(molX/s), for amounts of X close to detection limits, at an RC = 1 second time constant.
[c] Amount injected for peak current and S/N measurement (but not for MDL measurement)
[d] Without chimney [16,17]
[e] Thoroughly "clean" conditions (after vacation)
[f] Note: sulfur response is mostly quadratic!

quartz chimney, can also luminesce. While the latter provides an outstandingly sensitive response mode for tin compounds, its contribution to the baseline can obviously derogate the S/N ratio.

Worse, such background luminescences can vary in intensity and spectral distribution with time and use. For instance, the level of illumination can change from heavy in the evening to light in the morning (if the detector had been kept hot during the night). Or it can show severe quenching effects, i.e. a protracted upside-down solvent tail. Clearly, then, a configuration that excludes most of the areas extraneous to the flame may, though less efficient in terms of light throughput, prove disproportionately more stable and less noisy in terms of its baseline.

In fact, this has been our experience with the primary holophotal channel vis-a-vis the secondary light-guide and lens/mirror channels. While the former is more sensitive, the latter are steadier. The second channels are, indeed, easier to use and maintain —to the point where we prefer them to the holophotal channel if highest sensitivity is not at issue. (Note: the conventional channel uses a chimney of larger diameter, whose surface is less subject to the effects of extraneous luminescence and contamination.)

The data given in Table 1 for the comparison of the holophotal with the conventional mode for osmium and lead are, in essence, repetitions of an earlier experiment. The only difference between then and now is that the parabola intacta of the earlier study [9] was drilled for the current one: the resulting difference, in figures-of-merit, is negligible.

Table 1 also contains a set of data for the light-guide arrangement tested with sulfur under extremely clean detector conditions. (Under ordinary conditions, the S/N ratios are lower —decreasing by one half for the holophotal channel but staying almost the same for the conventional channel.) Sulfur —as well as phosphorus— belongs to a group of elements that can easily contaminate a chromatographic system. Hence a relatively "clean" system can differ significantly from a relatively "dirty" one —not to mention that the emission of S_2 and HPO is often strengthened by a cooler surface, i.e. a "Salet effect" (for a review of this effect see ref. [2]); and that a background of sulfur, because of the quadratic nature of its emission, increases analyte response (and baseline noise).

Table 1 also includes a case where a 6 × 1/4 in. diameter plain quartz rod replaces the image conduit. It transmits less of the sulfur emission overall, but still does quite well —despite its length and bend. For emissions located farther in the UV, a quartz guide may, of course, be a necessity.

Our earlier study [9] demonstrated that the signal-to-noise ratio correlated roughly with the square root of light throughput, and suggested that the noise was mostly of a fundamental nature (photon shot noise). It was therefore interesting for us to appraise the new, "second" channels by the same measure.

Table 2 lists the relative light throughputs (measured as peak height currents). It also lists their average for the four elements. (The baseline currents could have been used for that purpose as well; however, they would have been less reliable.) From these throughputs, the average theoretical S/N is calculated by assuming quantum noise, i.e. a square-root relationship. The final column in Table 2 lists the average of the measured S/N values for comparison. (To save space we have used averages instead of treating each case separately. The interested reader will, however, find individual calculations easy to perform on the data of Table 1.)

The average signal-to-noise ratios suggest an overall "ranking" of the channels. The holophotal channel is clearly the most sensitive, in agreement with its highest light throughput. Of the second channels, the image conduit performs somewhat better than the lens/mirror combination. Very roughly, the averaged signal-to-noise ratios are one-half of holophotal for the image conduit and one-third of holophotal for the lens/

Table 2
Relative light throughputs (peak heights, percent of holophotal)

Channel	Os		Pb		S		P		Avg.	S/N	
										Calc.[a]	Meas.
1. Holophotal	100			100	100[b]	100	100	100	100	100	100
2a. Image conduit	27		ND[c]		14		27		23	48	55
2b. Lens/mirror		ND		13		2		12	9	30	36
Conventional	3			3	6	3	3	5	4	20	26

[a] Assuming fundamental noise; i.e., square-root dependence of the S/N ratio on light througput.
[b] Particularly clean detector.
[c] ND = not determined.

mirror arrangement. The corresponding value for the conventional channel is one-fourth to one-fifth of holophotal.

It must be realized, however, that such numbers are highly condition- and element-dependent. To illustrate by the example of minimum detectable limits, the advantage of the holophotal over the conventional channel is (in this study) very roughly eightfold for both osmium and lead, but twofold for sulfur and fourfold for phosphorus. Flame shapes and positions, jet dimensions, detector contaminations, chimney effects, and a host of other parameters strongly modify the ideal scenario of light throughput from a constant point source (which would have yielded the same improvement ratio for each of the four elements).

The minimum detectable limits given in Table 1 (from which these ratios were derived) are calculated according to the (by chromatographers) most often applied condition $S/N_{p-p} = 2$. For convenience (and perhaps also for comparison with data obtained by spectroscopists), Table 3 lists detection limits similarly determined but differently defined. Here the (less strict) condition is $S/RMS = 3$.

To return to the "ranking" of channel types, it should be noted that the minimum detectable limit is only one, and often not even the most important one, of analytical criteria. By that measure, the image conduit has an edge over the lens/mirror combination. The reason for that, namely the higher (visible) light throughput, is indeed expected (compare Figs. 1 and 2). Construction-wise, also, the image-conduit arrangement seems simpler than the lens/mirror combination. On the other hand, with the help of a quartz lens, the lens/mirror setup should do a good job on emission in the ultraviolet and, for that purpose, may be preferable to a quartz rod. There may also be other advantages, as yet unrealized, to lab-made aluminum mirrors.

The "first" channel of this study represents an (only marginally degraded) "holophotal" arrangement. Its reason for being here is obvious: it connects the current data to those of an earlier study, and it provides an estimate of the maximum reasonable light throughput. Yet, because the holophotal configuration monitors most of the combustion chamber and chimney, its baseline is far less steady than those of the "second" channels that monitor little but the flame region. Although, say, an image-conduit channel is less sensitive than a holophotal channel, it is still more sensitive than a conventional one. For many purposes, then, it may be preferable to have two image conduits view the flame from opposite sides (i.e., in a geometry reminiscent of the first dual-channel construction [1]).

In fact, since a 0.25-in. image conduit of the type we used here can easily exit through, say, a common 0.25-in. Swagelock, one can imagine four of these conduits squarely positioned around a 0.25-in. O.D. chimney held in, perhaps, a detector housing of 1-in. quadratic cross-section. Such an arrangement would be easy to construct even with primitive machining support, and the glass conduits could be bent in a flame to accommodate any surrounding instrumental geometry. In terms of the crucial light path, this

Table 3
Minimum detectable flows [calculated as $-\log(\text{mol X/s})$ at $S/\sigma = 3$]

Channel	Os	Pb	S	P
1. Holophotal	15.3	14.1	14.2[a] 13.9	15.6 15.5
2a. Image conduit	15.0	ND[b]	14.1	15.3
2b. Lens/mirror	ND	13.6	13.3	15.2
Conventional	14.6	13.2	13.9 13.6	14.9 15.0

[a] Particularly clean detector.
[b] ND = not determined.

arrangement would exactly reproduce, four times over, the geometry and hence the performance of the single channel shown in Fig. 1 —simply, cheaply, and effectively. And each of the four conduits would, as in Fig. 1, be just 3–4 mm away from the center of the flame.

While it can be argued that four equivalent and simultaneous high-performance channels are, for practical purposes, one or two too many, the thought experiment demonstrates the validity, flexibility, and applicability of this approach. (And one of the image conduits could always be used just for watching colorful peaks come through the flame.)

Acknowledgements

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