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Short communication

Converting a single-channel flame photometric detector to triple-channel operation☆

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Abstract

A commercial single-channel flame photometric detector was converted to triple-channel operation by inserting a vertical, mirror-finished aluminum wedge into an earlier installed, auxiliary second channel. The resulting split of the second-channel light beam caused only a minor (less than a quarter) decrease in signal-to-noise ratio, as was theoretically expected for a system dominated by photon shot noise. Light throughputs and detection limits were measured for the three channels and two (sulfur- and phosphorus-containing) model analytes.

Keywords: Detectors; Flame photometric detection

1. Introduction

Recently we converted a single-channel flame photometric detector (FPD) to "holophotal" operation [1], then gave it dual-channel capability [2]. The two channels–though either of them proved more sensitive than the original, high-quality commercial version–did nevertheless differ significantly in design, dimensions, optics and, consequently, analytical performance [2].

Still, for a number of projects we really needed *three* channels: All three to be highly sensitive, two to be highly similar. (The former reflects our interest in trace analysis, the latter our involvement with subtraction [3] and correlation chromatography (e.g. [4]).) Fortunately, one of the dual-channel FPD versions [2] proved amenable to such trifurcation.

2. Experimental

The current experimental approach built on the relevant "mirror" version of our dual-channel, holophotal FPD [2]. Also, the instrument (a Shimadzu GC-8APFp), the column (100 × 0.3 cm I.D., 5% OV-101 on Chromosorb W AW), and the test protocol and analytes were similar. The two model elements chosen for this study were those most frequently determined by the FPD: sulfur (as 5 ng thianaphthene) and phosphorus [as 1 ng tris(pentafluorophenyl) phosphine].

Peak-height currents and signal-to-noise ratios (S/N) were determined with the above amounts.

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In contrast, smaller analyte amounts–generating peaks much closer to the noise level–were injected to determine the detection limit (which used the $S/\sigma = 3$ criterion), thereby providing a more realistic assessment of actual detectability. This recommended practice also exposed potential difficulties caused by the partially quadratic calibration curve of sulfur, the probable tailing of solvents, and the possible drifting of baselines–difficulties that would have remained unnoticed in extrapolating from larger amounts.

One channel of the earlier two-channel version used a lab-made mirror to deflect the diffuse light beam by 90° onto the photocathode of a head-on photomultiplier (PMT). The mirror was cut at a 45° angle from a 1-in. aluminum rod, and was positioned between two 40-mm ports. One port held the photomultiplier, the other–shielded by the mirror from the light beam but not from the chamber atmosphere–held a package of silica gel.

It was easy to discard the silica gel and insert a second PMT into the now empty 40-mm port. All that had to be done to supply the new PMT with light was to cut a second, 45°-inclined mirror into the aluminum rod, such that it formed a central 90° edge with the first mirror. This wedge edge was positioned upright in the center of the light beam; it hence faced and paralleled the flame's vertical axis of symmetry, and it thus split the luminescence neatly in half.

Since the rod was designed to slide into its 1-in. port through O-rings, its wedge-shaped mirror–a physical beam splitter, so to speak–was easily moved and rotated to the desired position of equal and maximal light reaching the two PMTs. The rod was also drilled–from the side and through the rest of its length–to accept a 1/16-in. gas line, through which the arrangement could be purged with dry nitrogen.

The first ("holophotal") channel [2] was kept intact. An optical schematic of the three-channel arrangement is shown in Fig. 1. All costs for the modification, including the photomultiplier housing, power supply, and dicorder [2], were kept in-house. The only outside cost–not for this sequential study but for future simultaneous triple-channel experiments–would be that of a third filter/PMT set.

3. Results and discussion

Notwithstanding the minimal cost of the third channel, it met and in one case even exceeded our expectations. If a light beam is split into two equal halves, and its baseline noise is fundamental in nature (i.e. if it consists predominantly of

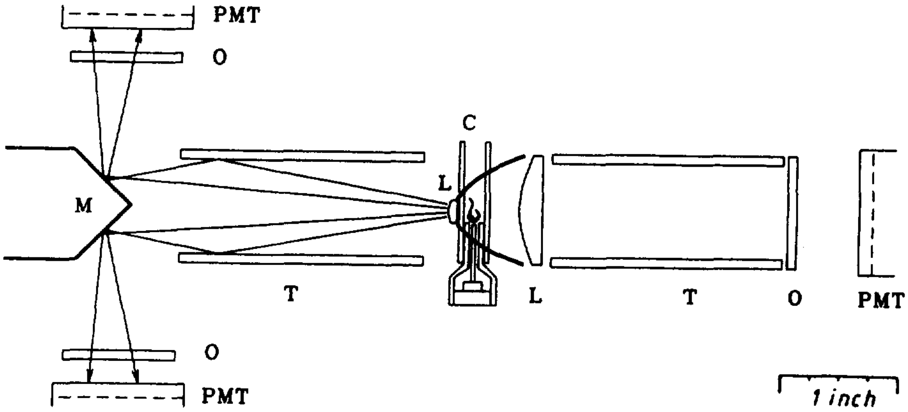

Fig. 1. Optical schematic of three-channel FPD. Right side: holophotal channel ("channel 1"); left side: two identical wedge-mirror channels ("channel 3"). M = wedge-terminated 1 in. diameter aluminum rod with mirror finish on 90° wedge surfaces; O = insertable optical filter of variable thickness; T = light tunnel with internal mirror finish; L = lens (as in Ref. [2]); C = quartz chimney. The left-hand section containing the wedge-shaped mirror and the two PMTs is rotated 90° for easier drawing, i.e. the real mirror's edge is plumb (and thus parallel to the vertical axis of the flame).

photon shot noise), the theoretical expectation is that the S/N for each half decreases by the square root of 2.

But the wedge mirror may throw toward the two PMTs somewhat more (or somewhat less) light than the earlier plain mirror deflected toward just one PMT. The spatial luminescence is diffuse and varies with flow conditions and target element, while the optical system–except for the easy lateral optimization of the wedge mirror–remains the same. The wedge mirror is positioned inside a light cone of sorts, and it is (on average) situated a bit closer to the flame than is the plain mirror. As Table 1 shows, the light throughput to each of the two wedge-mirror channels is 75% for sulfur and 46% for phosphorus peaks, as compared to the 50% expected from equally splitting the light of a single, plain-mirror channel.

For the photon shot noise conditions common in the FPD [5], the theoretical S/N for either of the two wedge-mirror channels would therefore be 87% (S) and 68% (P) of the value of the single, plain-mirror channel: a loss negligible under most circumstances. The experimental values (see column "$S/N_{\text{p-p}}$" in Table 1) are 75% and 71%, respectively. Thus, calculated and measured S/N values agree roughly within the relatively large error limit.

The raw data for baseline-corrected peak currents and dark-current corrected baseline currents, as well as for the $S/N_{\text{p-p}}$ signal-to-noise ratios and detectable molar flows, are given in Table 1. The table also provides comparative data for channel 1, i.e. the "holophotal" channel [1,2].

Sulfur and phosphorus are the two main analytes in the FPD; this is the reason they are used

Table 1
Comparison of three flame photometric detector channels

Channel	Baseline current [a] (A)	Peak-height current (A)	$S/N_{\text{p-p}}$	Detection limit [b]
Sulfur (as 5 ng thianaphthene) [c]				
Channel 1 [d] (holophotal)	$7.6 \cdot 10^{-8}$	$1.1 \cdot 10^{-7}$	870	13.9
Channel 2 [e] (plain mirror)	$3.7 \cdot 10^{-9}$	$2.0 \cdot 10^{-9}$	160	13.3
Channel 3 [f] (wedge mirror)	$2.8 \cdot 10^{-9}$	$1.5 \cdot 10^{-9}$	120	13.1
Phosphorus (as 1 ng tris(pentafluorophenyl) phosphine) [g]				
Channel 1 (holophotal)	$2.4 \cdot 10^{-8}$	$6.1 \cdot 10^{-9}$	150	15.5
Channel 2 (plain mirror)	$1.9 \cdot 10^{-9}$	$7.1 \cdot 10^{-10}$	75	15.2
Channel 3 (wedge mirror)	$7.6 \cdot 10^{-10}$	$3.3 \cdot 10^{-10}$	53	15.1

[a] PMT dark current deducted for measurement of percent light transmission.

[b] Measured from peaks comparable to the noise level at an analog filter (RC) with time constant of 1.0 s, and calculated as − log (mol S/s) or − log (mol P/s) at $S/\sigma = 3$.

[c] Flow-rates: column N_2 30 ml/min, H_2 14 ml/min, air 18 ml/min; R-268 PMT at −500 V. Optical filter removed [9] to lower the detection limit. Same physical PMT installed for measurements at all three channels. Smaller analyte amount used for determining the detection limit.

[d] Holophotal channel as shown on right-hand side of Fig. 1 (cf. Ref. [2]).

[e] Plain-mirror channel as described in Ref. [2].

[f] Either second or third wedge-mirror channel, as shown on the left-hand side of Fig. 1.

[g] Flow-rates: column N_2 35 ml/min, H_2 60 ml/min, air 31 ml/min; R-1104 PMT at −600 V, 550 nm wideband filter (Oriel 57570). Same physical PMT-plus-filter combination installed in all three channels. Lower analyte amount used for detection limit.

here. However, they also differ considerably in optimal flame conditions, calibration curves, and shapes of luminescence. It is therefore not surprising that differences between the two emerge. Such differences have been discussed at great length in Ref. [2]. They should not detract from the main result of this study, namely that it is easy to make two channels out of one, and that that can be achieved at negligible cost, fiscal as well as analytical.

The in-house physical beam splitter–i.e. the wedge-cut aluminum rod–is simple, sturdy, easily (re)polished and easily (re)positioned. It reflects all the spectral regions of interest. There are available, of course, all kinds of commercial beam splitters (see, e.g., Ref. [6]) that could have been used for the task–though none would have been as cheap to acquire and as simple to adapt as the aluminum rod.

The rod could also have been used to split the "holophotal" light beam (i.e. be installed at the right side of Fig. 1). This would obviously have improved the absolute detection limits for the two resulting ("semiphotal") channels. Yet, as discussed earlier [2], the holophotal channel samples light from the whole chimney volume–not just from the flame region–and it suffers therefore more than channel 2 (or channels 2 and 3) from baseline instabilities. Also, one highly sensitive channel is usually enough: typical dual-channel correlation chromatographies (e.g. [7]) need the highest stability and constancy [8] much more than they need the lowest detection limit [2].

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References

[1] W.A. Aue, C.G. Eisener, J.A. Gebhardt and N.B. Lowery, J. Chromatogr. A, 688 (1994) 153.

[2] W.A. Aue, C.G. Eisener, J.A. Gebhardt and N.B. Lowery, J. Chromatogr. A, 699 (1995) 195.

[3] W.A. Aue, B. Millier and X.-Y. Sun, Can. J. Chem., 70 (1992) 1143.

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

[5] W.A. Aue, H. Singh and X.-Y. Sun, J. Chromatogr. A, 687 (1994) 283.

[6] Catalogue, Oriel, 250 Long Beach Blvd., Stratford, CT 06497, USA.

[7] B. Millier, X.-Y. Sun and W.A. Aue, Anal. Chem., 65 (1993) 104.

[8] X.-Y. Sun and W.A. Aue, J. Chromatogr. A, 667 (1994) 191.

[9] W.A. Aue and C.R. Hastings, J. Chromatogr., 87 (1973) 232.