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Short communication

Dual-channel flame photometric detector for sensitive spectrum acquisition and variable-wavelength operation

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Abstract

A dual-channel flame photometric detector has been constructed with the first channel offering high light-throughput to a variable-interference-filter wheel. The wheel can be used stationary or spinning. The former selects a wavelength for conventional FPD operation, the latter provides 100-point spectra at less than 20 nm optical bandpass. The second FPD channel is of the conventional type. The detection limit ($S/N_{p-p}=2$) for phosphorus is 0.2 pg/s for either the stationary wheel or the conventional channel, and 0.1 ng of phosphorus produces a clearly recognizable HPO spectrum. An illustrative experiment shows the change-over from CH to CC luminescence in a methane-doped flame.

Keywords: Flame photometric detection, dual channel; Detection, GC; Luminescence spectra; Tris(pentafluorophenyl)phosphine

1. Introduction

A recently described spectrum collection device [1] obtained 100-point luminescence spectra from peaks passing through a dual-channel flame photometric detector (FPD). The device used a rotating variable-interference filter and was supported by laboratory-developed hardware and software for acquiring, correcting and documenting typical FPD spectra.

While wheel and electronics served the intended purpose well, a problem arose from the relationship between light throughput and optical resolution. Very efficient light throughput was obtained from an image conduit–ball lens combination. Yet the wide angular range of light impinging on the filter caused considerable broadening of the optical bandpass. The

innate spectral resolution of the filter could be restored by restricting the beam to lower divergence. That, however, reduced the light throughput to about a fifth of the former value [1].

Our primary aim was therefore to devise an optical arrangement that would transmit a beam of greater intensity but smaller angle-of-incidence spread. Our secondary aim was to invert the earlier configuration [1] such that light for the wheel channel would be collected by a mirror, and light for the conventional channel by an image conduit. This arrangement seemed better able to meet certain analytical demands – e.g., those of correlational chromatography [2–4] – in which the light throughput of the two channels should preferably be similar.

An added benefit of the new configuration, for correlational chromatography as well as several types of trace analysis, is that one channel can be tuned to a particular purpose (wavelength). That is, the vari-

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able-interference filter can be turned by hand to the desired wavelength and kept stationary there for analysis. (This, in essence, mimics replacing the conventional FPD fixed-wavelength filter by a “filter monochromator” [5].)

2. Experimental

The optical layout of the dual-channel FPD is shown in Fig. 1. The detector body is a commercial Shimadzu unit, but with narrower jet and quartz chimney. The fixed-wavelength channel is shown on the left side. Light from the flame is transmitted by a 6×1/4 inch diameter (1 inch=2.54 cm) image conduit (item 38307, Edmund Scientific, Barrington, NJ, USA) to the photomultiplier tube (PMT), which may be used with or without a conventional 1-inch diameter interference filter. The end of the inserted block, which holds the image conduit, is coaxially turned and buffed to produce a spherical mirror of 27 mm diameter and 10.5 mm focal length. The mirror reflects the light (that bypasses the image conduit) toward a focal region on the rotatable filter (F), as shown on the right side of Fig. 1.

The flame is partly surrounded by the step-cut top of an aluminum tube enclosing the quartz chimney (see insert for its approximate shape). The inner surface is highly polished, reflecting light toward image conduit and spherical mirror. At the same time, this semicylindrical aluminum part prevents the

right-hand side PMT from viewing the flame directly. Thus only light reflected from the peripheral regions of the mirror reaches the filter, with angles-of-incidence between ca. 4 and 12°. The resulting change in calibration (0.33 and 3.3 nm at 550 nm, respectively, for an average wavelength scale displacement of 1–2 nm) is minor compared to the specified optical bandpass (17 nm maximum) but, at the discretion of the analyst, could be corrected by a simple software adjustment [1].

3. Results and discussion

The design shown in Fig. 1 worked well. The intensity of the transmitted light was similar for the two channels, as can be seen from the same $S/N_{p-p}=2$ detection limits of 0.2 pg P/s or 15 pg tris(pentafluorophenyl)phosphine. The detection limits were determined by using in the left (“chromatographic”) channel a conventional 526-nm interference filter, in the right (“spectral”) channel the stationary wheel set at the same wavelength.

The optical resolution of the wheel is now almost as good as can be obtained with a parallel beam entering the filter through a narrow slit [1]. To demonstrate this, a tiny glass bead was salted and placed in contact with the flame. The resulting spectrum, as seen by the rotating wheel, is shown in Fig. 2. Its optical bandpass for the Na resonance

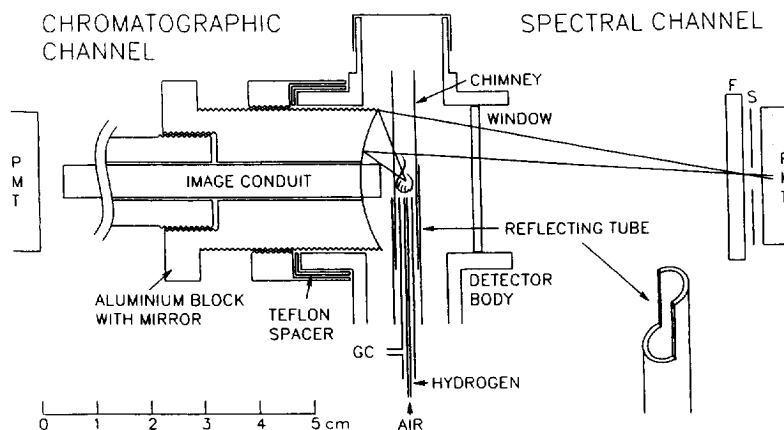


Fig. 1. Schematic of the dual-channel FPD. GC=gas chromatographic effluent; F=variable interference filter; S=slit (aperture); PMT=photomultiplier tube. Perspective drawing of reflecting tube not to scale.

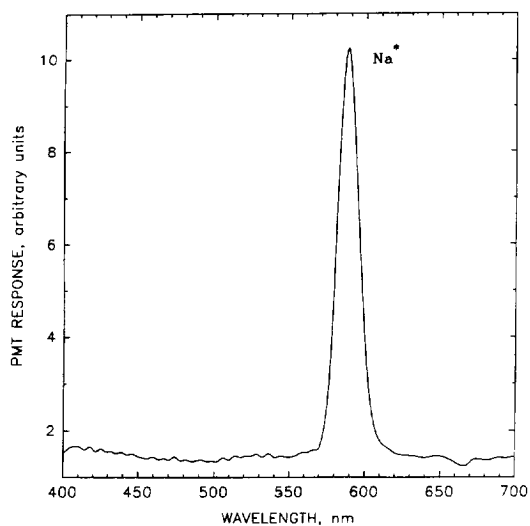


Fig. 2. Emission from a NaCl-doped flame. Rotating variable filter, no spectral correction, no data smoothing.

doublet is 17 nm (i.e., the same as the maximum bandpass specification of the filter).

An attempt was made to determine the lowest amount of analyte that would produce a discernable spectrum (as compared to a recognizable peak). Fig. 3 shows two HPO spectra derived from 1 and 10 ng of tris(pentafluorophenyl)phosphine, or 58 and 580 pg phosphorus, respectively. These amounts may seem high in comparison with the detection limit quoted earlier.

Suppose, however, that the 100 data points of the spectrum had been determined by 100 injections (while the – otherwise stationary – filter wheel had been manually turned). In order to produce a reasonable spectrum, the most intense HPO band would need to have an S/N_{p-p} ratio of at least, say, 10:1 (i.e., five times the detection limit). Since the minimum detectable amount of phosphorus is ca. 1 pg, that would require a total injected amount of $100 \times 5 \times 1 \text{ pg} = 0.5 \text{ ng P}$ (and more than a day's work). The wheel can make do with about ten times less.

Given that one half of the revolving filter is opaque, and given other effects such as disparate time constants, the 0.06 ng of phosphorus necessary to produce a recognizable HPO spectrum thus seem entirely reasonable. Mutatis mutandis, the spectral sensitivities of other emitters – in relationship to

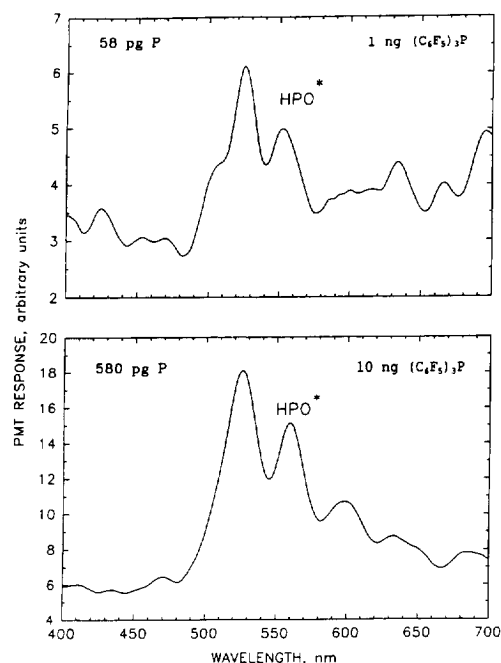


Fig. 3. Spectra from 58 pg (above) and 580 pg phosphorus (below), injected as 1 ng and 10 ng tris(pentafluorophenyl)phosphine, respectively. Both spectra smoothed by three passes of a three-point (9 nm) moving-window filter. Ordinates not comparable (different PMT voltages).

their chromatographic sensitivities – are similar. As a rule of thumb, analyte amounts that produce a clearly interpretable spectrum through the wheel are about two orders of magnitude higher than those that yield a just detectable peak on the chromatogram.

It is, of course, possible to obtain mere spectral confirmation of elemental identity at a far lower investment of sample and effort. For instance, a suspected organophosphate analyte could be injected a couple of times – while, say, the conventional channel was operated without filter, and the spectral channel was used with the (otherwise stationary) wheel turned successively to different wavelengths for which the response ratio of the two channels had been established earlier with the help of an authentic standard, and at which the agreement or disagreement of experimental and theoretical two-channel response ratios would confirm or deny, respectively, the presence of HPO emission.

The chromatographic/spectral dual-channel arrangement shown in Fig. 1 should prove particularly

helpful to the analyst who is interested in: (a) typical chemiluminescence spectra (including FPD baseline and memory spectra); (b) multi-element analyses of hetero-organic trace components present in complex environmental or physiological mixtures; (c) low-level confirmation reactions of biocidal residues; and/or (d) dual-channel correlation chromatography. Even for a single channel, however, it is convenient to have available an interference filter whose wavelength can be adjusted from the outside by the flick of a wrist.

Applications for such analyses would not be hard to find, but would demonstrate no more than the easily predictable. We have chosen instead to show an application that features not a typical analyte but a common interferent.

In considerations of analyte selectivity against carbon, the spectral response of the latter sometimes plays a role in the choice of the optical filter. The FPD literature does contain spectra from hydrocarbon peaks or flows, but not all of them are identical or even similar. This may, of course, be due to different flame conditions and carbonaceous structures. Such aside, however, it was interesting for us to explore whether the spectrum would change with no more than a change in concentration of the carbon compound.

For this purpose, a variable stream of methane (up to 75 ml/min) was introduced into the flame via the hydrogen supply line. The resulting spectra are shown in Fig. 4. They very clearly indicate that the predominant emitter is CH (and a non-identified continuum) at lower, but CC at higher concentrations. This appears to make sense, since the formation of CC from CH_4 should be a second-order reaction. (However, the conventional calibration curve of methane is linear, not quadratic.)

If a first-order formation of CH competes with a second-order formation of CC, the simplest kinetic scenario suggests that the CC/CH ratio should become a linear function of the carbon concentration. Fig. 5 shows this indeed to be the case, at least until the amounts of methane introduced into the flame become very heavy and, in all likelihood, change its character (that is, its capacity for, and perhaps even type of, chemiluminescent excitation).

A careful analysis of this particular problem would be difficult and is definitely beyond the scope of this manuscript. (Besides, even much of the literature on

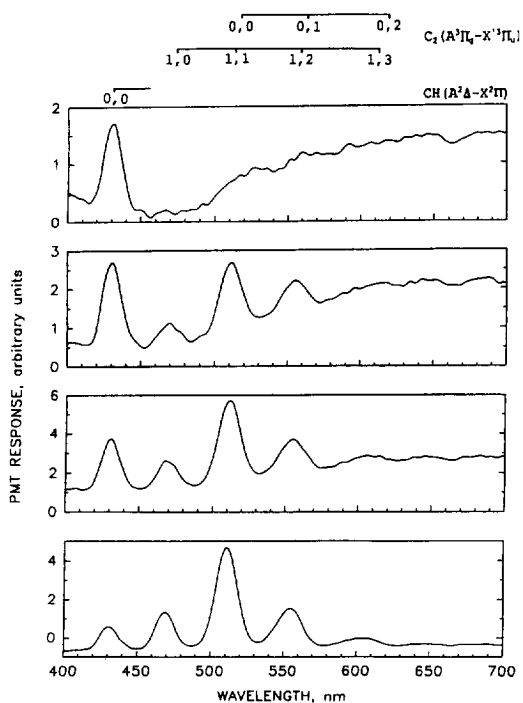


Fig. 4. Spectra from different levels of methane in a hydrogen/air flame. Flows in ml/min: H_2 200, Air 50, N_2 20. CH_4 flows doped into hydrogen stream in ml/min ($\mu\text{g C/s}$), from top to bottom: 1.8 (15), 9.2 (75), 13.3 (108), 60 (489). PMT: R-1104 at -300 V. Pure flame background subtracted. No smoothing, no spectral correction. Sampling time 2 min. The wavelengths for the vibrational levels of several strong bands of CC and CH are indicated on top of the figure.

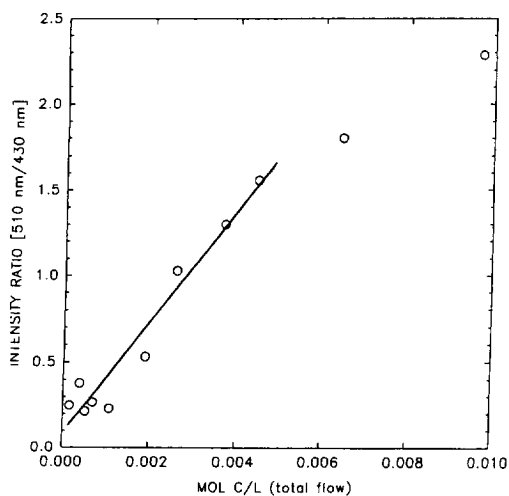


Fig. 5. Intensity ratio of 510 nm (CC) vs. 430 nm (CH) with increasing levels of methane doped into a hydrogen/air flame. Other conditions as in Fig. 4.

this subject is not without controversy.) What Fig. 4 and Fig. 5 demonstrate, however, is the ease with which relevant spectral and kinetic data can be obtained with the help of the described device. The spectra also illustrate that the photometric selectivity of an analyte vis-a-vis a carbon compound can drastically change with a mere change in concentration.

Not that this is an isolated incident: there exist several cases (e.g., those of S [6] and Sn [7]), where the spectra of analytes change with their concentration. For these and related types of analytical problems, the availability of a spectral channel can help to better understand and hence more reliably use this interesting chemiluminescent system.

Acknowledgments

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