

Analyte noise in the flame photometric detector

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Abstract

As the concentration of analyte increases in the flame photometric detector (FPD), its observed noise changes from a predominantly fundamental to a predominantly multiplicative variety. This change-over occurs typically in the 10^{-9} to 10^{-8} g/s region, with the precise position apparently dependent on the nature of the analyte. In the multiplicative region, slow fluctuations can be seen appearing simultaneously on both channels of a dual-channel FPD. This suggests the possibility of suppressing such correlated noise episodes.

Keywords: Detectors, GC; Flame photometric detector; Noise; Analyte noise

1. Introduction

Noise, together with signal intensity, determines the detection limit. Often but not always, the signal-to-noise ratio (S/N) can be improved by increasing the time, or the intensity, or the number of measurements. If noise is “fundamental” in character, i.e., if it is caused by the quantum nature of light and matter, the S/N will increase as the square root of the signal intensity. If noise is “multiplicative” in character, e.g., if it is caused by “analyte flicker”, that advantage is lost [1].

The baseline noise of three chromatographic detectors [flame ionization (FID), flame photometric (FPD) and electron capture (ECD)] has been examined and found to be of the fundamental variety [2]. In conventional chromatographic systems, the type of noise important for detection limits and quantitation is the noise of the baseline, not the noise of the signal.

Why baseline, not signal? Imagine a series of

repeated injections: first of very small, then of fairly large sized peaks. For the small peaks, the noise on the signal is essentially identical to the noise of the baseline. But for the larger peaks, the variation of the signal correlates primarily with chromatographic factors: it is more likely to depend on the reproducibility of syringe injection than on the fluctuation of flame emission.

Given that baseline noise is fundamental in character, there would seem to remain little incentive for any detailed investigation of chromatographic noise – of the baseline or the signal variety. As its name implies, fundamental noise cannot be further reduced (for a given time constant and a given analytical system). And why investigate the nature of noise as it occurs on, say, the top of a large peak, when that noise does not affect quantitation? (The noise that occurs on the signal in, say, atomic absorption spectrometry (AAS) is quite a different matter.)

Yet there do exist cases in chromatography where, similar to AAS, the analyte is introduced not as a peak but as a constant flow into the detector. These

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cases, while limited in occurrence, are nevertheless important in their own right.

Two general categories come to mind. In the first, a continuous stream of doping compound is introduced into the detector in order to change (e.g. to increase or linearize) the response of analyte peaks emerging from the chromatographic column. A case in point is the doping of the FPD with analyte elements. It can both increase and linearize the response of quadratic sulfur [3,4] or (indirectly determined) halides [5].

To be relevant in the present context, the doping compound need not be of the same kind as the analyte, as long as it produces response by itself. An example may be the doping of the hydrogen-atmosphere flame ionization detector (HAFID) with silane [6]. In fact, most of the so-called “sensitized flames” could be seen (and could be investigated) from this point of view. So could flames plagued by a bleeding column or poisoned by a contaminated detector housing.

In the second category, and the one that holds our current interest, the analyte is continuously introduced into the FPD flame simply in order to obtain its spectrum [7]. Here, the error band of the spectrum is determined by signal, not baseline, noise. Introducing higher concentrations of analyte will improve the *S/N* of the acquired spectrum only if the noise is of a fundamental, not of a multiplicative nature.

We noted recently that the electrical noise character of an FID flame changes from fundamental to multiplicative when exposed to increasing levels of carbon compounds (e.g. column bleed). This change-over, from slope one-half to slope one in a log noise vs. log signal plot, occurred at a bleed or doping level of, very roughly, 2×10^{-8} gram carbon per second (g C/s).

It is, of course, well known, though not well understood, that chemiionization and chemiluminescence often show similar behavior in flames [8,9]. It would therefore not be surprising if, like the FID, the FPD would also go through a shift in predominant noise character from fundamental to multiplicative with increasing analyte concentration.

The following experiment is designed to investigate this possibility. It should elucidate the noise characteristics of large analyte peaks, and yield information on how much analyte is needed to obtain

adequate spectral scans [7] from the FPD flame. In addition, it may provide clues on the character of noise, and hence the *S/N* behavior, of doped flames.

2. Experimental

A variety of compounds were doped at constant flows into a nitrogen stream, either from the head-space of a liquid (contained in a vapor-saturated reservoir replacing the chromatographic column), or from a gas cylinder. The instrument was an ancient and in many previous experiments ([10]) repeatedly modified unit (Shimadzu GC-4BMPF), through which the detector supply gases, air and hydrogen, flowed at 50 and 200 ml/min, respectively. The R-1104 (Hamamatsu) photomultiplier tube (PMT) was run at -400 V; behind an 1/4-inch diameter image conduit (Edmund), and a variable interference filter (Oriel) selected to probe the maximum response from carbon (CH^* , 432 nm) or phosphorus (HPO^* , 526 nm).

Noise was measured peak-to-peak, with drifts and spikes excluded, on a 1-mV stripchart recorder (Fisher) connected to an electrometer (Shimadzu) with a time constant of $\text{RC}=0.22$ s.

3. Results and discussion

Fig. 1 presents typical results from two runs involving a hydrocarbon and an organophosphate. On the left side, the precise square-root dependence (slope=1/2) is drawn as a line starting from the dark-current value of the PMT. As has been shown earlier, this line represents the minimum noise. It can be estimated from the counting statistics of the lowest rate of quantum events (here: the generation of photoelectrons) [2].

The first datapoint is that of the “clean” (undoped) flame. As the dopant adds its luminescence to that of the flame, the noise maintains its square-root relationship for low, but shifts to a linear (drawn precisely at slope=1) relationship for high dopant concentrations.

Since hydrocarbons luminesce far less intensely than phosphorus-containing compounds, the square-root range of the former is shorter. In this particular

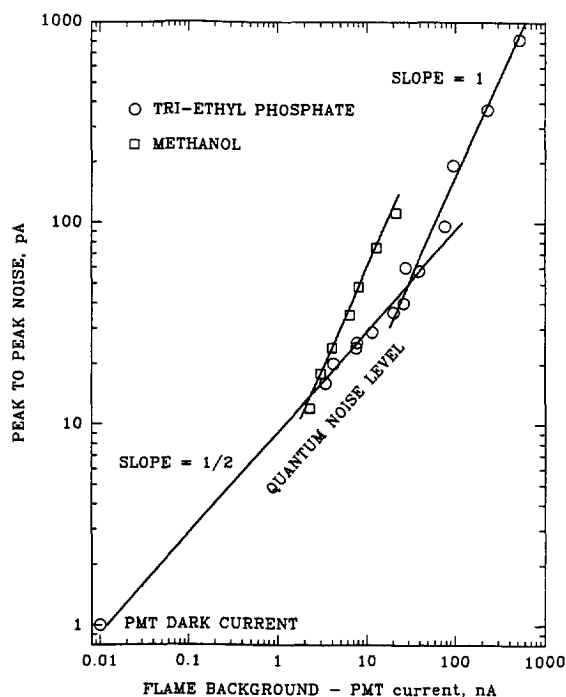


Fig. 1. Noise vs. light from an FPD doped with methanol or triethyl phosphate vapor.

case, the change-overs from square-root to linear noise behavior occur at carbon flows of ca. $3 \cdot 10^{-8}$ and $3 \cdot 10^{-9}$ g C/s for methanol and triethyl phosphate, respectively. (Note that, in an FID, the analogous transition of noise was measured at a similar $2 \cdot 10^{-8}$ g C/s for a flow of methane or for bleed from Carbowax-20M [2]. This, however, involved the *ionization* of/in an *air-rich* flame.)

Other compounds (methane, tri-*n*-octyl phosphine, hexane, diphenylsulfone) were also run: All showed the change-over from slope 1/2 to slope 1. The points at which this occurred did, however, differ. Many more compounds would obviously have to be tested to correlate, quantitatively and reliably, the position of these change-over points to dopant structures.

Such correlations, while interesting, are nevertheless beyond our present objectives. Still there is no doubt about the prime finding of this study: that the nature of observed signal noise changes with analyte concentration. This appears similar to the optical

behavior of typical spectroscopic flames [11] or, for that matter, the electrical behavior of a typical FID flame.

Interesting as this finding is, it has, in our estimate, no practical bearing on the conventional quantitation of gas chromatographic peaks. It does, however, suggest that for spectral scans of the FPD flame, and perhaps for the response of similarly behaving "sensitized" flames, the improvement obtainable by higher analyte or higher sensitizer concentrations is limited to conditions below the change-over region from fundamental (slope 1/2) to multiplicative (slope 1) noise.

Above that region, efforts to improve the spectral *S/N* by a higher light throughput are bound to fail, since noise then increases proportional to signal. (The onset of multiplicative noise in the baseline should also, for instance, influence the *S/N* when the FPD is provided with a sulfurous background in order to obtain a lower detection limit for organosulfur analytes [13–15].)

The onset of multiplicative noise should, however, be limiting only for *single-channel* systems. If multiplicative noise contains (true) low-frequency components originating from the FPD flame (such as flame and/or analyte flicker), subtracting one suitable channel of a dual-channel FPD from the other may be able to cancel them.

That low-frequency components are indeed present is demonstrated by Fig. 2. It shows heavy constant-analyte noise being simultaneously recorded by two operationally independent but physically similar FPD channels. Several slow noise episodes evidently correlate between channel A and channel B.

To confirm the correlation, a record of their subtraction ($A-B$) is included. Clearly, the multiplicative (though, of course, not the fundamental) noise contribution *decreases* substantially. This is emphasized by the result of the opposite operation, i.e. the addition ($A+B$). The addition, as is obvious and therefore not demonstrated here, *increases* the noise level dramatically, viz. the intensity of the correlated slow-noise episodes doubles and the combined drifts make the trace go off scale. In contrast, as is well understood [2,12] and therefore not illustrated here either, the pure flame background shows the expected $2^{1/2} = 1.4$ fold increase from the

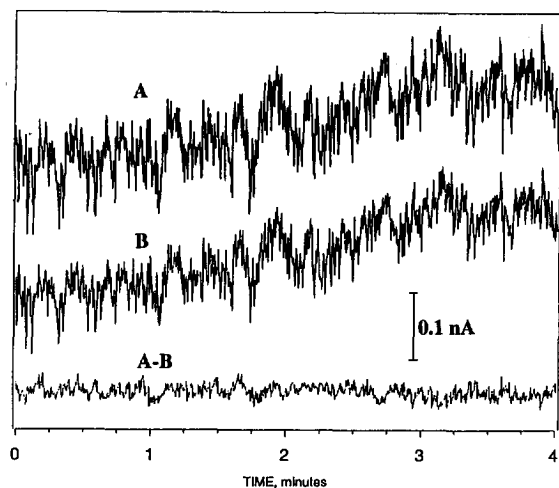


Fig. 2. Noise traces of single-channel and dual-channel subtraction monitoring of a triethyl phosphate-doped FPD flame burning in multiplicative-noise mode, as observed by two physically similar, synchronous FPD channels.

(equivalent) A or B channel to the (equivalent) (A-B) or (A+B) channel.

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References

- [1] J.D. Ingle, Jr. and S.R. Crouch, *Spectrochemical Analysis*, Prentice Hall, Englewood Cliffs, NJ, 1988, mainly Ch. 5.
- [2] W.A. Aue, H. Singh and X.-Y. Sun, *J. Chromatogr. A*, 687 (1994) 283.
- [3] S.O. Farwell and C.J. Barinaga, *J. Chromatogr. Sci.*, 24 (1986) 483.
- [4] W.A. Aue and C.G. Flinn, *J. Chromatogr.*, 158 (1978) 161.
- [5] Y.-Z. Tang and W.A. Aue, *J. Chromatogr.*, 408 (1987) 69.
- [6] H.H. Hill and D.G. McMinn (Editors), *Detectors for Capillary Chromatography*, Wiley, New York, 1992, pp. 16–20.
- [7] H. Singh, B. Millier and W.A. Aue, *J. Chromatogr. A*, 724 (1996) 255.
- [8] C.T.J. Alkemade, T. Hollander, W. Snelleman and P.J.T. Zeegers, *Metal Vapours in Flames*, Pergamon Press, Oxford, 1982.
- [9] P. Bocek and J. Janak, *Chromatogr. Rev.*, 15 (1971) 111.
- [10] B. Millier, X.-Y. Sun and W.A. Aue, *J. Chromatogr. A*, 675 (1994) 155.
- [11] C.T.J. Alkemade, W. Snelleman, G.D. Boutilier and J.D. Winefordner, *Spectrochim. Acta*, 35B (1980) 261.
- [12] X.-Y. Sun, H. Singh, B. Millier, C.H. Warren and W.A. Aue, *J. Chromatogr. A*, 687 (1994) 259.
- [13] R.S. Hutte and J.D. Ray, in H.H. Hill and D.G. McMinn (Editors), *Detectors for Capillary Chromatography*, Wiley, New York, 1992, pp. 199–200.
- [14] H.P. Tuam, H.-G. Janssen, C.A. Cramers, A.L.C. Smit and E.M. van Loo, *J. High Resolut. Chromatogr.*, 17 (1994) 373.
- [15] A.R.L. Moss, *Scan* (Pye Unicam, Cambridge), 4 (1974) 5.