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# Chemiluminescent photon yields measured in the flame photometric detector on chromatographic peaks containing sulfur, phosphorous, manganese, ruthenium, iron or selenium

Walter A. Aue\*, Hameraj Singh<sup>1</sup>

*Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3*

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## Abstract

Photon yields — the number of photons generated per analyte atom — are of obvious analytical and mechanistic importance in flame chemiluminescence. However, such numbers are unavailable for spectral detectors in gas chromatography (as well as for most conventional spectroscopic systems). In this study, photon yields have been determined for the chemiluminescence of several elements in the flame photometric detector (FPD). The number of photons generated per atom of FPD-active element was  $2 \times 10^{-3}$  for sulfur (emitter  $S_2^*$ , test compound thianaphthene),  $3 \times 10^{-3}$  for phosphorus [ $HPO^*$ , tris(pentafluorophenyl)phosphine],  $8 \times 10^{-3}$  for manganese ( $Mn^*$ , methylcyclopentadienyl manganese tricarbonyl),  $3 \times 10^{-3}$  for ruthenium (emitter unknown, ruthenocene),  $4 \times 10^{-5}$  for iron ( $Fe^*$ , ferrocene) and  $2 \times 10^{-4}$  for selenium ( $Se_2^*$ , dimethylbenzselazole). Total flows, maximum thermocouple temperatures, and visible flame volumes have also been estimated for each element under signal/noise-optimized conditions in order to provide a database for kinetic calculations. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Spectral photon yields; Flame chemiluminescence; Flame photometric detector

## 1. Introduction

The flame photometric detector (FPD) is widely used as a selective and highly sensitive sensor for

gas chromatographic effluents [1]. Being a luminescence-based device, it holds spectroscopic interest as well.

From an analytical point of view, the FPD is a reliable and relatively inexpensive detector; in fact, it has become an indispensable tool for residue analysis. Its historic purpose and still major application involve compounds of sulfur and phosphorus [2], but occasionally it is also used to determine molecules containing B, Cr, Mn, Se, Sn

\* Corresponding author. Tel.: +1-902-494-7076; fax: +1-902-494-1310.

E-mail address: waue@is.dal.ca (W.A. Aue).

<sup>1</sup>Current address: Sepracor Canada Ltd., 24 Ivey Lane, Windsor, NS Canada B0N 2T0.

and Ge. In all, approximately 20 elements respond in the FPD with analytically interesting sensitivities. For those that respond best, detection limits are similar to, and sometimes better than, those of the well-known GC-MIP-AED-computer combination [3].

The typical flame of the FPD is small, hydrogen-rich, and of low temperature (300–600°C). These characteristics, together with the FPD's highly sensitive and selective behavior, suggest that most if not all of its responses are due to chemiluminescent (as opposed to thermal) excitation. There has been much speculation about the 'mechanism' of the FPD, particularly about the quadratic nature of its response to sulfur.

In this context, a prominent review laments that 'no estimates have been made of the relationship between number of detected S<sub>2</sub>-derived photons and the corresponding number of sample-containing [*sic*] sulfur atoms that actually entered the FPD' [1]. The sole numerical estimate of such S<sub>2</sub> photon yields that we are aware of — an estimate in the context of atomic sulfur collision rates — can be found in a doctoral thesis [4].

Even outside the chromatographic context, i.e. in the much older and wider realm of spectroscopy in general — absolute photon yield from flames, or from flames with additives, are still exceedingly rare. One of those rarities is the measurement of C<sub>2</sub> photons from air/hydrocarbon flames [5]. There, the largest photon yield — from among several series of experiments encompassing a wide variety of fuel gases, conditions and pressures — was obtained from a non-stoichiometric air-acetylene flame at 14 torr, which yielded  $1.12 \times 10^{-3}$  photons per molecule of O<sub>2</sub> consumed. Maximum light yields for five other gases varied from  $1 \times 10^{-5}$  to  $3 \times 10^{-4}$  hν/O<sub>2</sub>. Another example is the measurement of CH<sub>2</sub>O photons in an air-acetaldehyde 'cool' flame, which produced approximately  $10^{-6}$  photons per molecule of acetaldehyde [6].

This dearth of hard data is not surprising: absolute (as opposed to relative) measurements of light yield are beset by problems [7,8]. Furthermore, chemiluminescent processes — for which photon yields are of particular mechanistic importance — have sometimes been considered a nuisance

rather than an advantage in conventional flame systems. Thus, Alkemade et al. point out that 'soft [meaning < 5.5 eV] chemiluminescence may cause a relative overpopulation as high as 10<sup>2</sup> in low-temperature flames of 1500–1800 K. This effect is of no practical use in analytical chemistry, since an emission enhancement of the same order can be obtained by choosing a flame with a temperature of 2500 K or higher' [9].

Such flames differ greatly, of course, from the small, hydrogen-rich, and comparatively cool flame of the FPD, which represents a spectroscopic system *sui generis*. In this system it would be of obvious mechanistic interest to determine the photon yields of several important elements, under conditions characteristic of conventional FPD analysis. To preserve general relevance, e.g. to permit kinetic calculations — these photon yields have to be accompanied by some information on gas flows, flame volumes and flame temperatures.

This study is therefore designed to obtain photon yields, plus supporting data, for a variety of typical analytes. The experimental approach employs a photomultiplier tube (PMT) whose gain and quantum efficiency are precisely known. It is used to measure the number of photons constituting a particular spectrum and to correlate that number with the number of photoelectrons generated, as well as to monitor peaks in the conventional manner. A complementary experiment employs a phosphorescent light source shaped like a typical FPD flame and kept in the usual position (i.e. sitting on the jet tip inside the quartz chimney). This source permits a measurement of the fraction of (total emitted) light reaching the PMT. Together, the two types of measurement allow the calculation of the initial photon generation rate, and hence of the photon yield, for a particular analyte element.

## 2. Experimental

### 2.1. Instruments

This study was carried out on a Shimadzu model GC-4BMPF gas chromatograph with dual-chan-

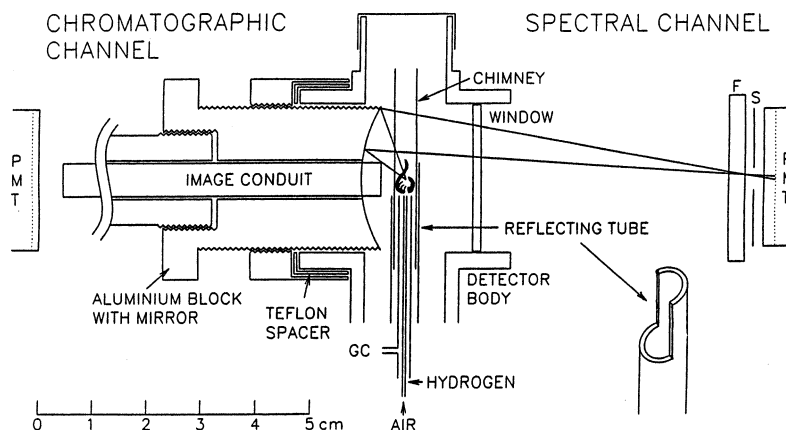


Fig. 1. Schematic of the dual-channel FPD [14]: GC, gas chromatographic effluent; F, filter or quartz window; S, slit or aperture; PMT, photomultiplier tube. The 'reflecting tube' can be removed, and the right-hand PMT can be replaced by a monochromator (see text).

nel flame photometric detector (FPD). For more than two decades this particular instrument had been used for similar projects — meaning that its behavior was well known — and lately it was modified to allow spectral scans of single peaks passing through the detector [10].

Briefly, the primary optical ('spectral') channel used the central flame (contained in a 4-mm i.d. quartz chimney) with an aluminum mirror positioned behind it. This channel functioned in two interchangeable modes. In the 'scanning' mode, it was coupled to an Oriel 1/8-m monochromator (a model no.77250 instrument with a no.77298 ruled grating of 1200 grooves/mm and 350 nm blaze; Oriel, 250 Long Beach Blvd., Stratford, CT

06497, USA). In the 'conventional' mode, the channel was simply fitted with the PMT (this is the configuration Fig. 1 shows). For the purpose at hand, the same, special Hamamatsu R-1104 tube (Hamamatsu, 360 Foothill Rd., Bridgewater, NJ 08807, USA) was used for both modes, i.e. detector, monochromator and PMT were connected and disconnected as needed. The special R-1104 tube had been calibrated by the factory in regard to gain and quantum yield.

The secondary ('chromatographic') channel used a light-guide and served only for ratioing single-peak signals, i.e. it was employed only to obtain concentration-corrected spectral scans by monitoring the rise and fall of passing peaks [10].

Table 1  
Test compounds and conditions

Analyte	Test compound	Gas flows ml/min <sup>a</sup>			Flame conditions		
		N <sub>2</sub>	H <sub>2</sub>	Air	t <sub>max</sub> °C	V <sup>b</sup> mm <sup>3</sup>	Shape <sup>b</sup>
S	Thianaphthene	22	100	45	310	31	Prolate spheroid
P	Tris(pentafluorophenyl)phosphine	22	120	35	290	43	Ovoid
Mn	Methylcyclopentadienylmanganese Tricarbonyl	22	120	26	277	42	Prolate spheroid
Ru	Bis(cyclopentadienyl)ruthenium	22	50	47	627	14	Spheroid
Fe	Bis(cyclopentadienyl)iron	22	80	36	346	14	Spheroid
Se	Dimethylbenzelenazole	22	93	25	337	34	Spheroid

<sup>a</sup>As measured at ambient temperature and pressure.

<sup>b</sup>Of the analyte luminescence.

The basic dual-channel FPD set-up has been described earlier but, in accordance with a referee's request, is shown again in schematic form for readers' convenience (Fig. 1).

Chromatographic conditions and detector flows were similar to typical earlier-used settings, which reflected maximum signal/noise ratios in a directly attached PMT. This ensured analytical relevance; however, higher photon yield could have been obtained in some cases by neglecting the noise and optimizing only the signal. Test compounds, flow conditions, maximum flame temperatures and the visible volume and shape of analyte luminescences are summarized in Table 1.

Measurements for compounds containing linearly responding elements were done with amounts corresponding to the upper part of their linear calibration range. Measurements for compounds containing S and Se — which show predominantly quadratic response — were done with amounts slightly beyond the upper end of their quadratic range, where a tangent of unity slope touches the log/log calibration curve (i.e. at the point of maximum photon yield).

Spectral scans were stored in computer memory by using a lab-developed interface and software program called CHROM.<sup>2</sup>

The spectra were exported in ASCII format to a commercial spreadsheet (Sigmaplot, Jandel Scientific, San Rafael, CA, USA): first for corrections in regard to chromatographic peak shape, spectrophotometer light transmission and PMT quantum yield; then for spectral integration. This was necessary in order to derive, for each particular spectrum, the number of photoelectrons generated per number of photons arriving at the PMT's photocathode.

## 2.2. Calibration

Collimated light from a tungsten filament (flashlight bulb) or a deuterium lamp was used in conjunction with a Jarrell-Ash 1/4-m monochro-

mator to determine (approximately) the light transmission of the Oriel 1/8-m scanning spectrophotometer. ('Approximately' refers to the likely different polarization for calibration light source and FPD luminescence in the 1/8-m instrument, as well as to other parameters that can affect such measurements.) The result turned out to be close to the available average of typical horizontally and vertically polarized grating efficiency curves [11], and was stored in the spreadsheet as '%T'.

Further included in the spreadsheet was the quantum efficiency curve of the factory-calibrated R-1104 PMT. Also, its current amplification curve was extended by gain ratio measurements, so that gain values became available all the way from 300 to 1500 V.

## 2.3. Determination of the average photon / photoelectron ratio of a particular spectrum

Spectra were measured by scanning single peaks as described earlier [10]. The ratioed (i.e. concentration-adjusted) spectrum was then multiplied by  $100/\%T$  to account for the light transmission of the spectrophotometer. Note that this partially corrected 'working spectrum' was expressed in relative, not absolute intensity units. It was transformed in two different ways:

First, the initial working spectrum was changed from current to photoelectrons/s

$$e^-/s = A/1.6 \times 10^{-19} \times (g)$$

where  $A$  is the (relative) photomultiplier current in amperes,  $g$  is the gain (which need not be included for the later ratio calculation), and  $1.6 \times 10^{-19} \text{ C}/e^-$  is the charge of the electron. The curve was then integrated over the available wavelength range, yielding the average number of PMT photoelectrons/second for the whole working spectrum.

Second, the initial working spectrum was also changed from current to photons/s

$$h\nu/s = A/QE \times 1.6 \times 10^{-19} \times (g),$$

where  $QE$  is the appropriate value on the quantum efficiency curve of the calibrated PMT. Inte-

<sup>2</sup> Researchers interested in this or other programs for non-commercial purposes are invited to contact Mr Brian Millier of our Department for an executable copy.

grating the spectrum then produced the numbers of photons per second for the whole working spectrum.

The division of the two integrals (really: the sums of the 0.2 nm data points)

$$\Sigma(h\nu/s)_\lambda / \Sigma(e^-/s)_\lambda = h\nu/e^-$$

thus resulted in the desired ratio of photons to PMT photoelectrons, i.e. the inverse of the average quantum efficiency — for the total spectrum under investigation, as seen by the particular, calibrated photomultiplier tube.

#### 2.4. Measurement of the FPD light-collection efficiency

A cone-shaped model of the FPD flame was covered with luminescent paint (Small Parts Inc., Miami Lakes, FL 33014-0650, USA). The first-order decay of its phosphorescence was determined after saturation illumination inside a reflective box equipped with several strong lights. This decay curve satisfactorily defined the emission intensity of the flame model for several hours after the initial illumination, and thus allowed ample time for experimental setup (carried out in semi-darkness when necessary) and measurement.

Two related types of measurement were carried out. In the first, the luminescent flame model was held inside a first-surface parabolic mirror, as close as possible to the photocathode of the head-on PMT. Alternatively, the mirror was replaced by black tape in order to monitor (just about) half of the total emission. The largest emission encountered in these and similar experiments was taken to be the ‘total’ emission of the flame model.

In the second measurement, the same PMT was used in the conventional FPD position, with the phosphorescing flame model occupying the place of the FPD flame on top of the detector jet. The ratio of the two types of measurement — which were made several times to ascertain reproducibility — thus defined the fraction of emitted FPD light measured by the PMT.

#### 2.5. Determination of emitted light and photon yield

Analyte peaks were measured with the conventional FPD arrangement, i.e. with the PMT directly viewing the flame. The peak area expressed by the number of photoelectrons was therefore

$$\#e^- = A \times 2\sigma / 1.6 \times 10^{-19} \times g$$

where  $A$  is the peak height in amperes,  $g$  is the overall gain, and  $\sigma$  is the standard deviation of a Gaussian peak (measured here as width of the peak in seconds at 60.7% of its height).

This translated to the total number of photons emitted by the flame,

$$\text{photons emitted} = \#e^- \times CE^{-1} \times (h\nu/e^-),$$

where  $CE$  is the fractional light collection efficiency as measured with the luminescent flame model, and  $(h\nu/e^-)$  is the ratio of photons to photoelectrons as determined earlier from the ‘working spectrum’. The photon yield is then easily calculated according to the definition used in this study:

$$\text{photon yield} = \frac{\text{photons emitted}}{\text{analyte atoms injected.}}$$

(Note that, in the cases of sulfur and selenium, this definition means atoms of S and Se, not molecules of the emitters  $S_2$  and  $Se_2$ .)

#### 2.6. Ancillary measurements

If the determined photon yields are to be used for kinetic purposes, some however approximate information on temperature, flow, and flame volume need to be included. Thermocouple (TC) temperatures of the hottest parts of the flame were determined by using a thin-wire iron-constantan TC. (Note: The ‘excitation temperatures’ are, of course, much higher. No difference was found in this context between phosphoric acid-coated and uncoated TCs.) Quoted gas flows were measured at ambient conditions of temperature and pressure. The listed flame volume is the visually estimated volume of analyte emission

(which is usually somewhat larger and often differently shaped than the visual volume of the only weakly emitting pure hydrogen–air flame).

### 3. Results and discussion

#### 3.1. Methodology assessment

The methodology applied to measuring photon yields in the FPD relies on two key features: the representation of the FPD flame by a similarly shaped and sized luminescent model; and the use of the *same* photomultiplier tube — whose gain and quantum efficiency are known — both in the conventional FPD position and behind a spectrophotometer.

It is obvious that the flame model can only approximate the behavior of a real FPD flame: the latter is translucent and changes its shape according to the flow conditions and to the nature (and sometimes the amount) of the analyte. A considerably less accurate value for the light transmission efficiency could be obtained by presuming that the flame (*sans* back mirror and other reflections) is a point source that emits light evenly in all directions. The fractional light transmission then equals the ratio of the PMT photocathode area to the surface area of a sphere whose radius is the distance between flame and photocathode. When this type of calculation was compared with the measurements of this study, the measured light transmission was approximately twice as large as the theoretically calculated one. This is quite reasonable, given the presence of reflective surfaces in the connecting metal cylinder and the variety of other physical parameters (flame shape, inhomogeneous photocathode, etc.) that affect the actual transmission efficiency.

The use of the same, calibrated PMT for both non-dispersive (direct) and dispersive (via the monochromator) measurements allowed us to obtain an average photon/photoelectron ratio for each particular spectrum from the latter, and to apply that ratio to data from the former. The accuracy of this application depends on the correctness of the PMT's absolute quantum effi-

ciency calibration. Also, but to a lesser degree, it depends on the correctness of the monochromator's relative light transmission calibration. (The *absolute* values have no bearing on the final result.) Since the polarization of light reaching the grating from the FPD flame and from the tungsten calibration source may be different — and since both polarizations are unknown — some error is possible. For instance, the relative intensities of different bands in a molecular spectrum that stretches over a long wavelength range may deviate somewhat from the true ones. In terms of the final photon/photoelectron ratio for each spectrum, however, this type of bias should be minimal.

We cannot assess the accuracy of the PMT's factory calibration, but consider any error in this regard to be negligible. Clearly, if the 'typical' specifications for a run-of-the-mill PMT had been used, the likely deviation would have been much larger. This is because any calibration error in the gain, as well as in the quantum efficiency, directly affects the calculated photon yield. A similarly direct effect obtains in case of the experimentally determined FPD light collection efficiency. Hence, it is these three factors that primarily determine the accuracy of the obtained photon yields.

In addition, photon yields determined from chromatographic peaks would be in error if the analyte were impure or would prematurely decompose in the gas chromatograph. The analytes of this study had all been used before, most of them together with sister compounds containing the *same* hetero-element and yielding essentially the *same* hetero-elemental response. We therefore consider the chromatographic and/or structural error to be negligible in the present context.

Table 1 listed the test compounds used for the six chosen elements. All these compounds contain carbon, of course; one contains fluorine and another one nitrogen. Nitrogen produces a small positive response in the FPD, fluorine has essentially no effect, and carbon yields a very small positive or negative signal. (The signal is positive in a 'clean' detector, with aromatics responding somewhat stronger than aliphatics; however, it is negative in a 'dirty' detector, when residues of sulfur or other strong emitters are present.) These

contributions would amount at most to a few percent of the major emission, i.e. they would not influence a photon yield of one significant digit.

### 3.2. Photon yields in the FPD

Table 2 presents the final results, i.e. the chemiluminescent photon yields for six popular elements as measured in the flame photometric detector. Since this is the first study of its kind, a working parameter — the QE values (the quantum efficiencies of the calibrated PMT for each particular spectrum) have been included.

The latter photoelectron/photon ratios (QE values) do serve a purpose, despite the fact that such numbers are valid only for one individual photomultiplier tube. The differences between the numbers are relatively small, particularly when compared to the vast differences in chemiluminescent response among different FPD-active elements. Besides, response is highly condition-dependent in the FPD — much more so than in some other spectroscopic techniques — and even though the present FPD was optimized separately for each element, an FPD from another manufacturer may have yielded somewhat different numbers. Given accurate curves for the PMT's gain and quantum efficiency, and an accurate number for the fractional light transmission from flame to phototube, the value of the average quantum efficiency — which had to be painstakingly measured in this study for each individual spectrum

— could perhaps be just estimated in future projects, without unduly increasing the overall uncertainty of the photon yield. With one set of elements now having been measured, even conventional interelemental response ratios (commonly known as 'selectivities') could give at least an order-of-magnitude estimate of the elemental photon yields involved.

In this context it should be stressed again that the photon yields of Table 2 are numbers typical of analytical settings, i.e. of flow rates optimized for the highest signal/noise ratio. This means that still higher photon yields may have been obtainable at signal-only optimized conditions.

For kinetic purposes, the determined photon yields can also serve at least as mechanistic limits. It may be noted in this context that none of the excitation reactions for FPD-active elements has yet been established beyond doubt-owing, in part, to the lack of even order-of-magnitude photon-yield values. For sulfur, several possible reactions have been proposed [1]. For some other elements, a specific mechanism has not even been suggested. Relatedly, the concentrations of potential flame and analyte reactants are mostly unknown. A similar statement applies to the extent of collisional quenching (if any) of the excited analyte state.

FPD spectra, befitting their chemiluminescent nature, are remarkably 'clean', i.e. they often appear to originate solely from one emitter. Still, the presence of small contributions from other emitters is difficult to exclude. For instance, there

Table 2  
Photon yields in the FPD

Analyte	Test compound	Predominant emitter	Quantum efficiency <sup>a</sup>	Photon yield <sup>b</sup>	%R.S.D. ( <i>N</i> ) <sup>c</sup>
S	Thianaphthene	S <sub>2</sub>	0.17	1.60 × 10 <sup>-3</sup>	7.07 (7)
P	Tris(pentafluorophenyl)phosphine	HPO	0.093	2.59 × 10 <sup>-3</sup>	4.49 (5)
Mn	Methylcyclopentadienylmanganese tricarbonyl	Mn	0.13	7.65 × 10 <sup>-3</sup>	2.13 (4)
Ru	Bis(cyclopentadienyl)ruthenium	?	0.10	2.71 × 10 <sup>-3</sup>	6.83 (6)
Fe	Bis(cyclopentadienyl)iron	Fe	0.16	4.52 × 10 <sup>-5</sup>	4.43 (6)
Se	Dimethylbenzelenazole	Se <sub>2</sub>	0.12	1.81 × 10 <sup>-4</sup>	2.41 (5)

<sup>a</sup>Number of photoelectrons per photon emitted, for the total observable spectrum.

<sup>b</sup>Number of photons emitted per analyte atom introduced.

<sup>c</sup>Percent relative standard deviation (from *N* numbers of samples injected).

may well have been some traces of respective oxide bands under the atomic spectrum of Fe [10,12] or the molecular spectrum of  $\text{Se}_2$ . Similarly, very small amounts of (red) HSO may have accompanied the predominant (blue) emission of  $\text{S}_2$  [13], and so forth. Also, the very weak contributions from other test-compound atoms — such as the ubiquitous carbon (CH, also CC) [14] or the occasional nitrogen — have already been mentioned. Yet, inspection of the low-resolution spectra did not reveal any obvious evidence of such minor luminescers. It therefore seems reasonable, and still within experimental error limits, to attribute the measured photon yield to the ‘predominant emitter’ (or emitters in case of the atomic iron lines) as given in Table 2. Certainly this should be correct for photon yields of only one significant digit.

While single-digit numbers are given in the Abstract, three-digit photon yields are now given in Table 2. In accordance with referees’ wishes, precision data have also been included. These cover the main experimental procedure as far as accessible, i.e. from initial injection to final photon yield. The percent relative standard deviation varies between 2 and 7% for the photon yields of various elements, a rather satisfactory result.

What of the absolute magnitudes? From an analytical, particularly a chromatographic point of view, conversion efficiencies of analyte molecules to response carriers in the  $10^{-2}$  to  $10^{-5}$  range are not unusual. For instance, the ubiquitous flame ionization detector needs close to  $10^6$  (reduced) carbon atoms in order to produce one electron for the signal current.

From a spectrochemical point of view, very few data exist from comparable large-flame systems. However, the two references cited [5,6], with  $1.12 \times 10^{-3}$  as the highest photon yield obtained from a wide range of experimental conditions, suggest that the FPD is doing well indeed.

Sulfur and phosphorus were the initial target elements of the FPD [2], and may be characterized as ‘strong’ among the 20 or so emitters that provide analytically noteworthy responses. Manganese and ruthenium belong to this group as well. Iron and selenium produce emitters of inter-

mediate strength. Iron was deliberately included here because it produces a rich spectrum of atomic lines (at a temperature of only 346 (!)°C — while at higher temperatures and more oxygen-rich conditions, oxide bands begin to dominate and the signal/noise ratio becomes much lower because of the fast increasing noise level [12]). Selenium was included as a sulfur analogue, i.e. as another ‘quadratic’ emitter. If organotins had been used in this test, under conditions that favor the blue surface luminescence [15], the quantum yield would likely have exceeded unity. However, since the blue tin (and germanium) luminescences take place on a quartz surface — and not in the gas phase as all the other processes — and since, in certain circumstances, the quartz surface may retain some tin and luminescence for an extended period of time after passage of the original organotin peak (as often evidenced by strong peak tailing), we felt that tin should not be included in this initial study of chemiluminescent photon yields.

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