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CONSTRUCTION AND CHARACTERISTICS OF A "COLD FLAME" PHOTOMETRIC DETECTOR

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SUMMARY

The construction of photometric detector prototypes for gas chromatography is described. These prototypes were designed to monitor "cold" chemiluminescence phenomena such as the reactions of O₂ analyte with P₄ vapor or the reaction of organic compounds with O₃. They have also been used, via the quenching of chemiluminescence, to detect the passage of organic compounds through steady "cold flames", generated by such systems as P₄/O₂ or SiH₄/O₂. An example of their selectivities as compared to standard flame-ionization detection response is given and some further developments are suggested.

INTRODUCTION

Chemiluminescent reactions¹⁻⁴ are often of considerable analytical utility. In conjunction with gas chromatography (GC), the best-known examples of their use are the Brody-Chaney type flame photometric detector⁵ and the (non-flame) Bruening-Concha detector⁶ based on the ozone reaction.

We have recently used "cold flames" of various origins for the detection of GC effluents via quenching of light emission (negative peaks)⁷, and have monitored oxygen by its gas-phase reaction with P₄ vapor (positive peaks)⁸.

Three detector constructions have been utilized. They differ in the manner effluent and reagents are mixed, in the relative position of the chemiluminescent zone and light-gathering channel, and, last but not least, in the ease with which the detector can be opened and cleaned. All three detectors incorporated the optical channel of a Bendix "SPED" photometric detector, which uses a glass-fiber light guide. This arrangement happened to be available to us and proved very convenient in day-to-day detector operation; however, a construction along the lines of other, "direct"-light-transmission type flame photometric detectors would have been equally feasible.

The first detector prototype has been schematically described⁸, the next two, which were of a more permanent nature and much easier to clean, are described below.

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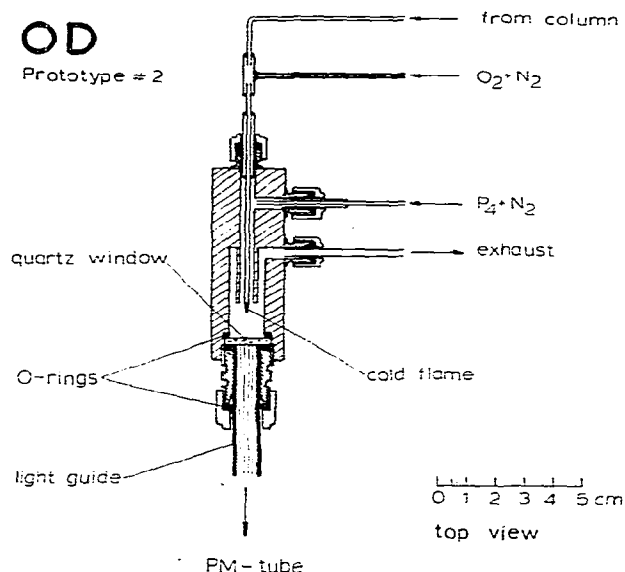


Fig. 1. Cold flame photometric detector prototype No. 2.

EXPERIMENTAL

Detector constructions

Fig. 1 shows prototype No. 2 in cross-section as seen from the top. The cold flame, "burning" in horizontal position and pointing away from the gas chromatograph, was viewed head-on by the light guide through a quartz window. (Quartz was a convenient material to use; it was not chosen for its UV-transmitting capabilities which would have been to little avail in view of the restricted spectral range of the light guide.)

The detector body was made of brass, which acquired a black coating when used with phosphorus vapor. The gas streams indicated in Fig. 1 are those of the P_4/O_2 system. The entrance line marked " $P_4 + N_2$ " in Fig. 1 was used in the SiH_4/O_2 and O_3 systems for " $SiH_4 + N_2$ " and " $O_3 + O_2$ " reagents. Entrance lines were all $1/16$ in. O.D. stainless-steel tubing; the one accommodating $O_2 + N_2$ was a capillary to dampen out any short-term flow fluctuations. The exhaust line was $1/8$ in. O.D. copper tubing, soon expanding to $1/4$ in. O.D. and finally entering the high-flow exhaust duct of a laboratory hood. The system was occasionally checked for leaktightness by closing a valve in the exhaust line and watching the rotameter of both the N_2 supply to the GC column and the phosphorus-doping line, drop to zero.

The flow lines entered and exited through standard connections (sawed-through Swagelock unions), silver-soldered to the detector body. The body was heated by a brass piece of similar size which contained a 250-W heating cartridge and was screwed tightly to the underside of the detector (not shown). The heated area was surrounded by Marinite insulation. A few coils of $1/8$ in. copper tubing were wrapped around the entrance section of the light guide, and tap water was circulated through the coils to cool this area when unusually high detector temperatures were needed.

The O-rings were of regular or fluorinated silicone rubber; gaskets made from polytetrafluoroethylene were also used. For cleaning the detector (mainly: the quartz window which acquired a central circular spot of reaction products), the light guide assembly could be easily screwed out.

Prototype No. 3 is shown in Fig. 2 in cross-section as if seen from the side of the instrument. It incorporated, *mutatis mutandis*, most of the features of prototype No. 2, but differed in the following aspects. The cold flame "burned", upside down, on a concentric tube assembly, which could be easily removed from the top of the detector if modification was desirable for accommodating different reactions. The normal cleaning of the detector was achieved by removing the bottom (standard Swagelock) part, which allowed the quartz tube to fall out. In the case of P_4/O_2 operation, the tube was immersed in water to remove phosphorus oxides, and re-inserted. This procedure was usually accomplished without cooling the detector; it took less than 5 min to complete.

The detector body and all Swagelock terminals were of stainless steel; a 200-W heating cartridge was used. No significant deposits were noted on the quartz window.

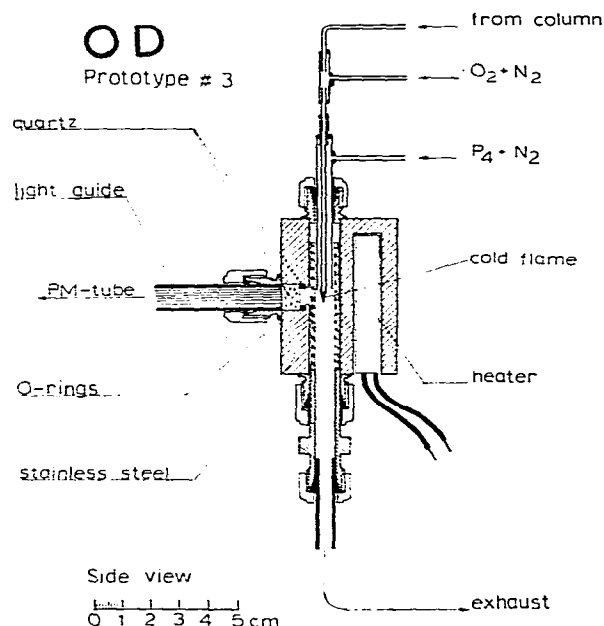


Fig. 2. Cold flame photometric detector prototype No. 3.

Reagents

For the P_4/O_2 system, nitrogen carrier gas (ca. 25 ml/min for the GC column and ca. 20 ml/min for the P_4 doping line) was freed of most oxygen by passage through a heated gas-purifier cartridge (Supelco). Part of it was passed over the surface of white phosphorus (a very efficient method to scavenge oxygen) and then, in a second glass tube heated to ca. 50°, over the surface of liquid phosphorus (to dope the N_2 stream with P_4).

For O₂ determination, no other gas was needed. For quenching of the P₄/O₂ cold flame by GC solutes, O₂ was added as "high purity" grade nitrogen in very small amounts, regulated by a differential flow controller and a damping capillary. This nitrogen contained *ca.* 14 ppm O₂ and was adjusted to give full-scale background current on a 1-mV recorder for 50 K attenuation of the Bendix SPED electrometer (*ca.* $5 \cdot 10^{-6}$ A PM-tube current). This setting corresponds approximately to the maximum in the signal to noise profile for quenching GC solutes. The detector was routinely cleaned after 12 h operating time.

For the SiH₄/O₂ system, non-optimized flows were *ca.* 100 ml/min of 0.5% SiH₄ in N₂ (Matheson); and dry air so as to give full-scale response for the background current on the 2-K attenuation range (*ca.* $2 \cdot 10^{-7}$ A PM-tube current). The detector was routinely cleaned after 4 h operating time.

For the monitoring of chemiluminescence derived from the reaction of various compounds with ozone, a stream of oxygen, *ca.* 70 ml/min, was passed through a quartz tube (as used in an earlier photolysis study⁹) surrounding a low-pressure Hg discharge (quartz pencil lamp, Black Light Eastern), and on to the detector.

Operating conditions

The GC conditions were routine. A 150 × 0.2 cm glass column was packed with 3% OV-101 on Carbowax 20M deactivated¹⁰ Chromosorb W, 100–120 mesh. The standard program (as used for the chromatograms shown in Fig. 3) was 1 min at 30° isothermal, then 4°/min up to 120°. The instrument was equipped with a conventional flame-ionization detector (FID) kept at 220°; the luminescence detectors were generally operated at 150°.

RESULTS AND DISCUSSION

Most of our experience with the detector prototypes was based on the two methods utilizing phosphorus vapor^{7,8}. Silane could be used, in analogy to phosphorus, for the detection of oxygen (positive peaks) or the detection of various GC effluents via their quenching action on the SiH₄/O₂ chemiluminescence (negative peaks); and there are most likely other systems which could serve in a similar manner. Obviously, the analytical objective could be reversed if P₄ or SiH₄ were to be determined in gas streams or in gas chromatographic effluents.

The ozone mode was added to show the applicability of the detector prototypes Nos. 1 and 3 to other types of chemiluminescent reactions. Chemiluminescence due to ozonization has been much studied (*e.g.*, ref. 11), and forms the basis of several air-pollution monitors^{12,13}. In agreement with Bruening and Concha's pioneering efforts in the GC area^{6,14}, detector temperature exerted a major influence on what types of compounds were detected.

Of various tested analytes, only olefins and sulfur compounds responded at 100°, while these plus a variety of amines, aldehydes and ketones gave signals at 200°. The best responding substances were CS₂¹⁵ and a number of α -diketones like diacetyl. Beyond the choice of temperature, it would be reasonable to expect further selectivity increases from the use of optical filters for the various emission systems known to arise from ozonization.

The photolytic production of O₃ was convenient and inexpensive, utilizing

parts available from an earlier study of a GC photochemical reactor⁹. However, this type of source provides at best a few ppm of ozone (*cf.*, ref. 16) and does not measure up to the output of a typical ozone generator which produces O₃ concentrations about 10,000 times higher. This and the sophistication of the Bruening-Concha light-gathering system make it understandable that their minimum detectable amounts were in the nanogram range whereas ours barely reached submicrogram levels. We thought it important, though, to include the ozone option for this type of detector construction*.

In analogy to the P₄/O₂ and SiH₄/O₂ systems, it should be possible to produce steady "cold flames" from ozone and a variety of compounds like ethylene, trimethylethylene, methanethiol¹⁷, carbon disulfide or diacetyl. The first three compounds, for instance, differ widely in the magnitude and spectral distribution of their light output¹⁷. Thus, a quenching of luminescence by GC solutes, augmented by selection of the appropriate spectral region (*e.g.*, *ca.* 510–530 nm for trimethylethylene), may produce selective responses for different solute structures.

It should also be possible to mix excess ozone with column effluent prior to its entrance into the detector, where then a reaction with, say, one of the above-mentioned compounds would have signaled effluents that had reacted with O₃ on the way to the detector (as negative peaks). Or, catalytically or thermally controlled selective degradation could have been carried out. However, none of these possibilities have been further investigated.

It may be added that, after some obvious modifications like the addition of an ignitor coil, prototype No. 3, downside up, could also have been used for conventional, "hot flame" photometric detection of gas chromatographic effluents. Some aspects of its construction are similar to those used in the commercial flame photometric detectors of Bendix and Shimadzu. This possibility was not further investigated, however, since "cold flames" were the primary objectives of this study.

Here, most work was done on the quenching of P₄/O₂ luminescence. Minimum detectable amounts of various compounds varied from 2 ng (benzaldehyde) to 0.3 mg (dichloromethane), in apparent relation to their ease of oxidation, with linear-response ranges from 1 to 2 orders of magnitude, and temperature dependences of response generally small and dependent on compound structure⁷.

Prototype detectors Nos. 2 and 3 both performed well, and more or less with similar results. We prefer No. 3 because of its easier cleaning (a necessity in a type of detector where non-volatile reaction products are constantly being generated).

The system uses an excess of P₄ vapor, and oxygen (which determines baseline and response) must therefore be delivered to the detector in a smooth, constant stream to avoid excessive noise. This has apparently been achieved since experiments showed that baseline noise (but not baseline drift) was nearly exclusively generated by the photomultiplier tube, thereby raising the possibility of future improvements in sensitivity.

* When this study was completed, we managed to borrow an ozonizer of the type commonly used for organic synthesis. A short check confirmed that higher ozone levels did indeed improve sensitivity; *e.g.*, 10 ng thiophene could now be easily detected¹⁹.

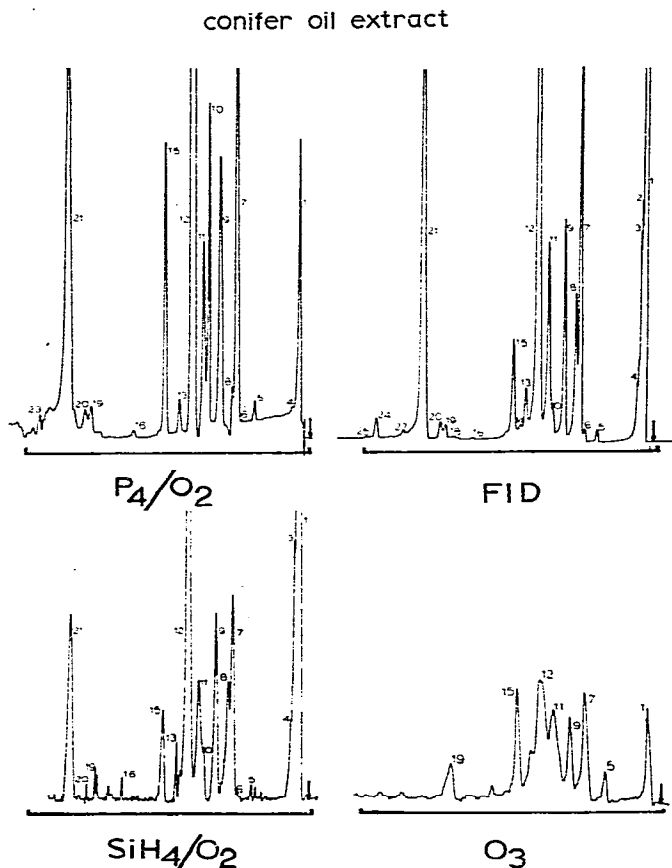


Fig. 3. Response of four detection modes to a conifer-oil extract. 5 ml "Kneipp Fichtennadel Latschenkiefer Ölbad" (Kneipp, Würzburg, G.F.R.) extracted with 1 ml hexane, extract diluted 1:10 with dichloromethane; injected: 1 μ l for FID, P_4/O_2 , and SiH_4/O_2 ; 4 μ l for O_3 . Attenuations 50 K for P_4/O_2 , 1 K for SiH_4/O_2 , and 100 for O_3 .

Fig. 3 shows the chromatography of a terpenoid mixture from a commercial bath-oil using the P_4/O_2 , SiH_4/O_2 , and O_3 systems together with conventional FID response (the first two produce negative, the latter two positive peaks; but all four are shown in the same direction). Differences are evident even in this mixture of closely related compounds. The clearest, overall, are seen between O_3 and the other three detectors, the former presumably responding to unsaturation in this case. Major differences exist, for instance, in the responses of compounds 8, 9 and 10 among the four detection modes. The SiH_4/O_2 system showed, in other experiments, good sensitivity for a number of organometallics, *e.g.*, tetraethyllead. The question whether this fact is related to the Pb/SiH_4 interaction in a recently developed ionization detector¹⁸ has not been further pursued.

The mechanisms of response in these and other, similar detection modes are largely unknown at the moment. It appears, however, that the described detector provides one convenient way of studying them, besides offering analytical advantages for selective determination of certain compound types.

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REFERENCES

- 1 E. N. Harvey, *A History of Luminescence*, The American Philosophical Society, Philadelphia, Pa., 1957.
- 2 V. Ya. Shlyapintokh, *Chemiluminescence Techniques in Chemical Reactions*, Consultants Bureau, New York, 1968.
- 3 A. Fontijn, D. Golomb and J. A. Hodgeson, in M. J. Cormier, D. M. Hercules and J. Lee (Editors), *Chemiluminescence and Bioluminescence*, Plenum, New York, 1973, p. 393.
- 4 J. H. Glover, *Analyst (London)*, 100 (1975) 449.
- 5 S. S. Brody and J. E. Chaney, *J. Gas Chromatogr.*, 4 (1966) 42.
- 6 W. Bruening and F. J. M. Concha, *J. Chromatogr.*, 112 (1975) 253.
- 7 W. A. Aue and Z. M. Mielniczuk, *ACS 31st Annual Summer Symposium on Analytical Chemistry, Boulder, Colo., June 1978*.
- 8 Z. M. Mielniczuk, C. G. Flinn and W. A. Aue, *Anal. Chem.*, 50 (1978) 684.
- 9 W. A. Aue and R. Aigner, *172nd ACS Meeting, San Francisco, Calif., August 1976*.
- 10 C. R. Hastings and W. A. Aue, *J. Chromatogr.*, 89 (1974) 369.
- 11 D. A. Hansen, R. Atkinson and J. N. Pitts, Jr., *J. Photochem.*, 7 (1977) 379.
- 12 W. R. Seitz and M. P. Neary, *Anal. Chem.*, 46 (1974) 188A.
- 13 U. Schurath, A. Wiese and K. H. Becker, *Staub*, 36 (1976) 379.
- 14 W. Bruening and J. F. M. Concha, *J. Chromatogr.*, 142 (1977) 191.
- 15 H. Ogino, S. Suzuki and S. Araki, *Bunseki Kagaku (Jap. Anal.)*, 25 (1976) 319; *Anal. Abstr.*, 31,5 (1976) 437.
- 16 *Bulletin 110A*, Ultra-Violet Products, San Gabriel, Calif., 1973.
- 17 W. A. Kummer, J. N. Pitts, Jr. and R. P. Steer, *Environ. Sci. Tech.*, 5 (1971) 1045.
- 18 H. H. Hill, Jr. and W. A. Aue, *J. Chromatogr.*, 122 (1976) 515.
- 19 M. Siu and W. A. Aue, unpublished results.