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## PHOTOMETRIC AND ELECTRON-CAPTURE MODES IN A DUAL-CHANNEL SENSOR\*

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### SUMMARY

A simple, radioactive sensor was developed for potential use with gas chromatographic effluents and/or process streams. The sensor relies on earlier developed response modes of photometric detectors, particularly to (a) nitrogen in high-purity argon and (b) aroyl compounds in nitrogen. Its sole energy source is the weak  $\beta$  radiation from a  $^{63}\text{Ni}$  foil. The radiation creates not only luminescence but also ion pairs, and some of the latter can provide a second response channel for electron-capturing substances.

Typical minimum detectable concentrations/amounts are 2 ppm of nitrogen in argon and 1 pg/s of benzaldehyde in nitrogen by photometry, as well as 0.1 pg/s of hexachloroethane in nitrogen by electron capture; with linear ranges of about two orders of magnitude in each case. Some analytes, *e.g.* fluorinated aroyl compounds in nitrogen, respond simultaneously on both channels. The sensor can also be run as a general detector (minimum detectable amount *ca.* 50 pg/s) by monitoring the quenching of background luminescence (the latter having been established by, for instance, a constant level of benzaldehyde in nitrogen).

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### INTRODUCTION

The flame photometric detector is widely used for the selective detection of gas chromatographic (GC) analytes containing sulfur, phosphorus or other hetero-elements<sup>1</sup>. The energy for producing the monitored luminescence is provided by a hydrogen-rich flame. Recently, such a flame was replaced in its role as the provider of energy by a steady stream of atoms or molecules in excited, metastable states. These energy carriers were produced in a strong electrical field, with a constant input of electrons being generated by the  $\beta$  radiation from a small  $^{63}\text{Ni}$  foil. Metastable energy transfer then leads to a variety of response modes different from those of the typical

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flame photometric detector. For instance, molecular nitrogen was detected in high-purity argon<sup>2</sup>; and a variety of simple aroyl compounds (benzaldehyde<sup>3</sup>, benzophenone, anthraquinone<sup>4</sup> and the like) were determined with high sensitivity and selectivity in nitrogen.

Although the strong electrical field was necessary for producing a large number of metastable energy carriers and hence a strong detector response, it turned out that, in the absence of the strong electrical field, the radiation alone could provide enough energy for a luminescence level commensurate with the detection of GC analytes<sup>5</sup>. This effect seemed interesting and potentially useful in a variety of analytical contexts; however, its sensitivity needed improvement. One of the simplest and most obvious avenues for improving the performance of such a  $\beta$ -driven device would be to increase the light level reaching the photomultiplier tube.

The original study of a GC detector driven solely by  $\beta$  radiation<sup>5</sup> made use of a (slightly modified and obviously flameless) Shimadzu flame photometric detection (FPD) unit. The noise in a real detector originates usually in the flame (flicker noise); hence there had obviously been no advantage in maximizing light throughput from the flame to the photomultiplier tube of the Shimadzu detector *vis-a-vis* other design considerations, and a considerable distance had been put between light generation and light measurement by a connecting cylinder equipped with cooling coils, an interference filter, etc. When the detector is run without a flame, however, and the light level itself turns out to be the sensitivity-limiting parameter, the photosensitive cathode needs to be brought as close to the luminescence region as possible.

When, with this in mind, we drew up a blueprint that had a capillary carry the analyte close to a window adjoining the photomultiplier tube, it became immediately apparent that a sensor of this type could provide an additional response mode: the capillary could easily double as an electrode, and the weak  $\beta$  emitter was already in place. In short, the layout resembled that of an electron-capture detector. All that needed to be done was to add a source of polarization and a second electrometer, as well as to pay some attention to geometry and to which parts of the detector ought to be conducting, which insulating. Thus the constructing and testing of an exploratory dual-channel sensor became the objective of this study.

## EXPERIMENTAL

The very simple prototype sensor consists of a photomultiplier tube (Hamamatsu R 374) and its housing (from the Shimadzu flame photometric detector), into which is fitted the luminescence-cum-ionization chamber with its various gas lines and electrical connections. The principal aim in designing this prototype was not to come up with the best and most conveniently operated device—that may be safely left to a second or third generation effort should the need for its exist or arise—but to demonstrate feasibility of concept in the most easily accomplished manner.

Fig. 1 shows the basic construction of the dual-channel sensor. The analyte flows from a gas chromatograph or other sample source via a heatable 1/16 in. stainless-steel tube, which connects to a similar introduction tube, 2, through an electrically insulating connector (a drilled-out 1/8 in. Swagelock union around a PTFE tube holding the two 1/16 in. tubes via suitable ferrules; not shown). The sample streams to the ionized and luminescent zone of gas surrounded by the cylindrical <sup>63</sup>Ni/Au foil, 4.

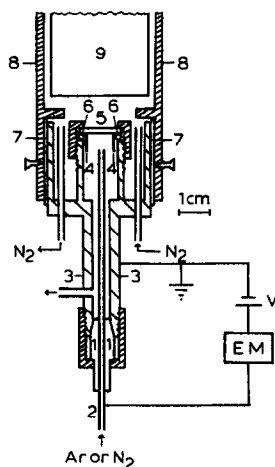


Fig. 1. Schematic of multifunctional sensor. 1 = PTFE ferrule; 2 = sample inlet tube; 3 = sensor base, fits into photomultiplier tube housing; 4 = cylindrical  $^{63}\text{Ni}$  foil; 5 = quartz window; 6 = silicone O-ring; 7 = PTFE insulator sleeve; 8 = photomultiplier tube housing; 9 = photomultiplier tube; V = low-voltage supply; EM = electrometer.

The analyte input line and the lower part of the detector can be heated by externally applied resistance tape (the upper part of the photomultiplier tube housing could be kept at lower temperature, *e.g.* by cooling coils wrapped around it, but this was not done here). To avoid possible condensation and provide additional cooling, a flow of nitrogen passes between the quartz window, 5, of the luminescence chamber, and the quartz window of the photomultiplier tube, 9. Most of the experiments were carried out with the luminescence region at *ca.* 80°C. In its present configuration, the analyte path can not be heated much above 100°C.

The lower part of the sensor, which inserts into the photomultiplier tube housing, is separated from it by an insulating PTFE sleeve, 7, which serves as heat, light and electrical insulation (the latter to protect the electron-capture measurement from photomultiplier tube stray currents). The low-voltage power supply, V, polarizes only the sample inlet tube as the anode (as well as the floating electrometer, EM). Simple RC damping ( $R = 10 \text{ k}\Omega$ ,  $C = 200 \mu\text{F}$ ) is used for high-frequency noise reduction.

The main sample input is provided by a Shimadzu GC-4BMPF gas chromatograph, housing a  $50 \times 0.25 \text{ cm}$  I.D. borosilicate column packed with 15% Carbowax 20M on Chromosorb W-AW, 45–60 mesh. Other inputs rely on an exponential dilution flask, or simply on mixing two gas streams (nitrogen analyte and various quenchers). The GC carrier gases, nitrogen of “high purity” and argon of “prepurified” grade, are further cleaned (or so one hopes) by sequential passage through molecular sieve 5A and a heated oxygen-scavenger cartridge (Supelco).

## RESULTS AND DISCUSSION

In its photometric mode of operation, the sensor should be capable of two basic types of responses: to nitrogen in argon; and to aryl compounds in nitrogen.

The first of these modes was thought to hold some potential interest for the

determination of nitrogen in high-purity argon streams. However, first there existed the need to establish that the system would respond at all. In the high-field photometric detector<sup>2</sup>, the luminescence of molecular nitrogen comes from its second positive system ( $C^3\Pi_u \rightarrow B^3\Pi_g$ ), which is excited by energy transfer from argon metastables,  $^3P_2$  and  $^3P_0$ . In the high field (*ca.* 5000 V) set-up<sup>2</sup>, the current can rise up to almost 100 nA. It has been estimated for a comparable system that the population of argon metastables is many times that of its ions<sup>6</sup>. Thus there should be available a large population of metastables.

In contrast, the maximum possible current under weak-field conditions simply represents the ion pairs created by  $\beta$  radiation, *i.e.* less than 2 nA for the particular foil used in the sensor. It is obvious that there exists the chance of metastables being created—from direct  $\beta$  impact, for instance, or from the excess energy of secondary electrons (the average energy expended by the  $\beta$  ray per ionization event is considerably larger than the ionization potential of argon—but their number must be orders of magnitude less than under strong-field conditions. It should be mentioned in this context that the reaction of nitrogen molecules with argon metastables is obviously not the only conceivable reaction channel for producing luminescence; for instance, direct  $\beta$  impact and/or ion pair recombination (*cf.* ref. 7) may directly transfer the necessary energy to molecular nitrogen. Furthermore, luminescence other than that from the second positive system of nitrogen can not be ruled out. Under high-field conditions, the latter band system was the only one found. However, under low- or no-field conditions, spectra were not determined because of the very low light levels involved. Hence it was unclear how much nitrogen response to expect, and an experiment was definitely called for.

Fig. 2 shows the calibration curve for nitrogen in a stream of prepurified-grade argon, obtained by exponential dilution flask (which had earlier been calibrated in its upper concentration ranges by direct injections of nitrogen into the argon supply line). The minimum detectable concentration ( $S/N = 2$ ) is about 2 ppm; the linear range about two orders of magnitude.

This is quite remarkable considering the very small energy input, but it is admittedly worse than the minimum detectable concentration in the high-field photometric detector ( $0.3 \text{ ppm}$ )<sup>2</sup>. Although the sensor's lower limit is significantly

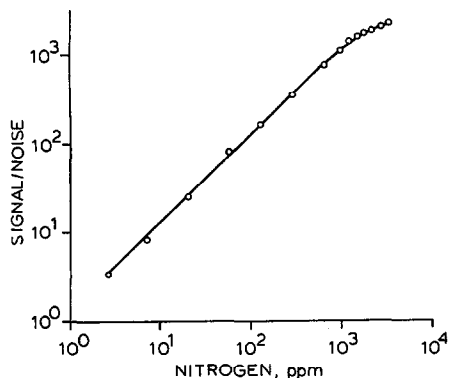


Fig. 2. Calibration curve of nitrogen in a stream of argon.

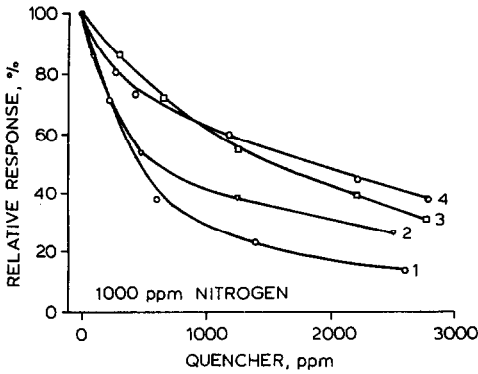


Fig. 3. Relative response of 1000 ppm (v/v) nitrogen in argon, as influenced by various background levels of (1) *n*-butane; (2) oxygen; (3) hydrogen; (4) nitrogen.

better than that of the no-field (*i.e.* solely  $\beta$ -driven) FPD-type detector (25 ppm)<sup>5</sup>, it remains, at best, of marginal value for most practical applications. The only real interest it holds is (a) that it works at all and (b) that, if such is needed for a specialized purpose, detection limits could undoubtedly be improved.

For mechanistic as well as practical reasons, and in view of the very low level of energy available, the quenching of nitrogen luminescence by other gases needed to be looked at. Fig. 3 shows the correlation of a (directly injected) nitrogen peak of *ca.* 1000 ppm (v/v) peak concentration on a background of various additives established by exponential dilution flask. The efficiency of quenchers varies (on a volume, *i.e.* molar basis) in the order *n*-butane > oxygen > hydrogen. That is the sequence one would expect on general considerations of quenching cross-sections.

Nitrogen, as the injected analyte, is of course also quenched by a competing, (pseudo) constant level of nitrogen in the carrier. This does not really prevent analytical use, as long as the concentration of background nitrogen does not become exorbitant. The calibration curve for nitrogen analyte simply shifts slightly to the right. In fact, the very calibration curve shown in Fig. 2 represents such a case. It is extremely difficult to remove the last traces of nitrogen from argon streams, and it is not easy to keep traces of the atmosphere from diffusing into analytical instrumentation: hence, injected (analyte) nitrogen had really been determined not in a pure but in a nitrogen-contaminated stream of argon to start with.

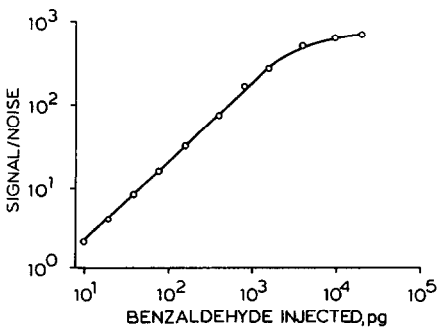


Fig. 4. Calibration curve of benzaldehyde in nitrogen.

The second of the photometric response modes, *i.e.* to aroyl compounds in nitrogen, was explored with the simplest structured analyte capable of producing strong luminescence, namely benzaldehyde (benzaldehyde also happens to be a product of the oxidative pyrolysis of various materials, and is therefore, among other possible applications, of potential interest as an indicator of low-level combustion processes).

As shown in Fig. 4, benzaldehyde has a minimum detectable limit ( $S/N = 2$ ) of about 10 pg (*ca.* 1 pg/s). This is approximately ten times worse than with a high (*ca.* 5000 V) electrical field<sup>3</sup>, but five times better than without such a field in the typical FPD configuration<sup>5</sup>. The sensor construction thus did have the desired effect of significantly improving sensitivity for both types of response modes—benzaldehyde in nitrogen, and nitrogen in argon—and further improvements could no doubt be made with a stronger (larger) radioactive foil, a more sensitive light detection system, etc. The linear range is two orders of magnitude shorter than under high-field conditions but still adequate for analytical purposes and, indeed, quite remarkable if one considers that the only energy input comes from a *ca.* 5 mCi <sup>63</sup>Ni foil.

Following the same logic as used above for nitrogen in argon, the quenching of luminescence by contaminants or co-elutants needed to be looked at. This is shown in Fig. 5, with 1 ng of benzaldehyde being injected into the gas chromatograph, and quenchers being added to a separate gas input via the exponential dilution flask. It should be realized that 0% quencher means 0% deliberately added quencher. There is always *some* quenching going on: from impurities in the detector, from contaminants in the gas supply, from column or septum bleed, from atmospheric diffusion into the analytical system, etc.

The additives were chosen for a variety of reasons: oxygen, because its diradical structure makes it a very efficient quencher under a variety of circumstances, and also because it happens to be a major constituent of the atmosphere; *n*-butane, because it can represent hydrocarbon contamination in a continuous stream, or a co-eluting compound in a GC effluent; and hydrogen, because it is the lightest and simplest non-noble gas (and, as well, because it is generally more difficult to determine than various other gases and the hope existed that any quenching effect, if strong enough, could be developed into an analytical method).

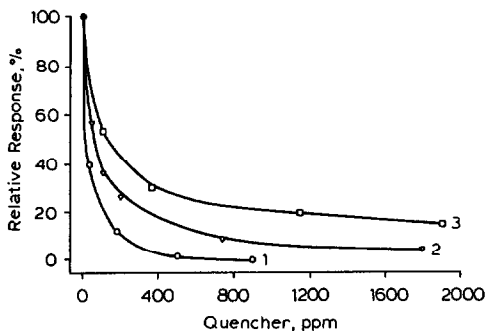


Fig. 5. Relative response of 1 ng benzaldehyde in nitrogen, as influenced by various background levels of (1) oxygen; (2) *n*-butane; (3) hydrogen.

The results of the quenching experiments show oxygen to be the strongest of the three quenchers on a molar basis, followed by butane and hydrogen (note, however, that—as earlier—hydrogen is a fairly strong quencher on a weight basis). This order is different from the one reported above for nitrogen–argon, but that is not surprising since the two systems differ in the carrier/reagent gas and the emitter (in other words, the quencher does not work on the same excited nitrogen species). The mechanism for benzaldehyde (or other aroyl) luminescence is not known at present; possibly, a metastable nitrogen intermediate is involved. It should be noted again that, although benzaldehyde luminescence is likely based on the same spectrum as had been obtained under high-field conditions<sup>3</sup>, the low- or no-field emissions were not scanned because of the extremely low level and the spatially diffuse nature of the luminescence.

The fact that oxygen is a strong quencher rules out the direct trace analysis of an atmospheric sample (as, perhaps, in a sensor expected to signal the heat-up of polystyrene insulation); although trace benzaldehyde could, of course, be determined in air by using a preseparating technique such as GC.

It does not seem impossible to develop a GC detector for hydrogen on the basis of its quenching effect, but such an approach would have to be able to compete with other established and simpler methods. At the moment, its analytical utility remains questionable.

The same could be said for using the quenching effect to determine other analytes; yet, such an experiment still holds a certain interest because it can provide some insight into the magnitude of the process. A luminescence background was therefore established by doping a nitrogen carrier stream with benzaldehyde, then a variety of analytes were piped in from the gas chromatograph. The minimum detectable amounts of these analytes (a series of alkanes and carbon disulfide) were about 0.05 ng/s. Fig. 6 shows a calibration curve for the latter compound (which, incidentally, does not respond to any significant extent in a flame ionization detector—but does respond, and with much higher sensitivity than here, in a regular flame photometric detector).

Clearly the most attractive feature of the sensor is its ability to detect and determine a variety of aroyl compounds, of which benzaldehyde is the simplest

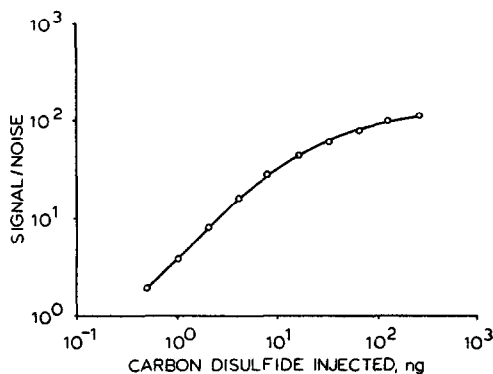


Fig. 6. Calibration curve for carbon disulfide, as determined by quenching a constant background of benzaldehyde luminescence in nitrogen.

example. In the high-field detector, some 18 compounds have so far shown luminescence at an intensity comparable to that of benzaldehyde (comparable meaning within one order of magnitude). These are simple aromatic aldehydes and ketones, including quinones. As a rule-of-thumb (cleanly obeyed up to now), substituents like Br, I, NO<sub>2</sub>, OH, and *ortho*-alkyl obliterate response (such peaks are, in fact, weakly negative, *i.e.* one observes a quenching of the background luminescence). Not all simple structures respond; for instance, *p*-benzoquinone or the naphthaldehydes do not<sup>8</sup>.

For this study, a number of the structures that had responded well in the high-field detector were tested in the sensor and yielded the expected results. These were mainly substituted benzaldehydes—some of the less volatile compounds, particularly the anthraquinones, were beyond the thermal limits of the sensor. However, there is no reason to believe that these would behave any different than their faster-eluting counterparts, as experiments with the thermally better equipped,  $\beta$ -driven FPD-type detector<sup>5</sup> have demonstrated.

If the sensor is to be used as a GC detector for substances of high elution temperature, the thermal barrier between the photomultiplier tube and the quartz window bordering the luminescence region ought to be improved. This could, for instance, be done by replacing the quartz window (see Fig. 1) by one end of a large-diameter light guide, whose other end would terminate at the face plate of a cool (or even cooled) high-quality photomultiplier tube. In essence, this construction would be analogous to replacing one end piece of a cylindrical electron-capture or argon ionization detector by a light conduit.

This suggests a discussion of the sensor's second channel, the electron-capture response mode. It is made possible by two features: First, the carrier gas nitrogen, indispensable for obtaining the aroyl luminescence, is also an excellent choice as an ECD carrier gas; second, the luminescence does not need a strong electrical field (which the electron-capture detector could not tolerate).

The cylindrical construction of the detector—forced here, really, by the need for concentrating radiation, hence luminescence, inside a relatively small volume—is conventional. The reversal of flow is not conventional, but should make little difference. This is borne out by the sensor's performance under one of the simplest ECD regimes possible, *i.e.* the d.c. mode of operation. Fig. 7 shows the response profile

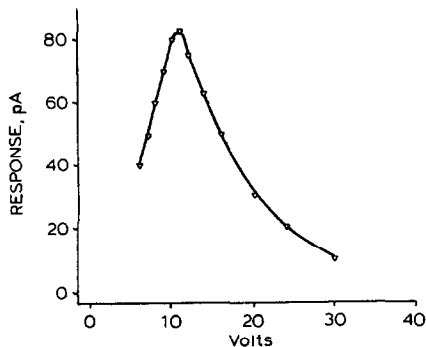


Fig. 7. Response vs. d.c. voltage for 15.5 pg hexachloroethane.



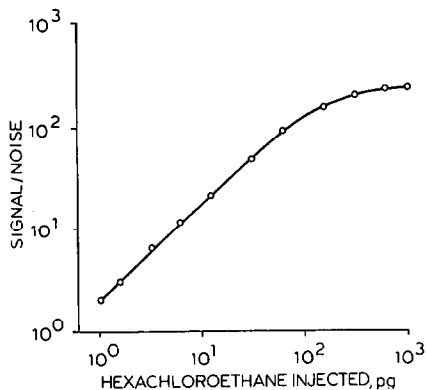


Fig. 8. Calibration curve for hexachloroethane in ECD mode at 11 V d.c. polarization.

over a range of voltages for a typical electron-capturing compound, hexachloroethane; which conforms to expectation.

Fig. 8 adds the calibration curve of hexachloroethane and, again, the minimum detectable limit of 1 pg (0.1 pg/s) is what one would expect. Thus, conventional ECD behaviour can be safely assumed for other compounds (and other polarization modes) as well.

It remains to be demonstrated that the two channels can operate simultaneously. This is done in Fig. 9 with a mixture of benzaldehydes, one of which carries a fluorine substituent (peak No. 1). Again, the responses are as hoped for in the two modes of detection. The luminescence is undisturbed by the simultaneous collection of electrons. (If, for instance, the luminescence had relied on the transfer of energy from the recombination of ion pairs, this would not have been the case.)

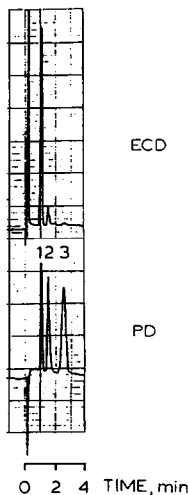


Fig. 9. Simultaneous chart recordings of electron-capture and photometric detector modes of 4 ng each of (1) 4-fluorobenzaldehyde; (2) 3-methylbenzaldehyde; (3) 4-ethylbenzaldehyde.

It is not immediately obvious in which areas of analysis the sensor will find application. Samples that come to mind are primarily those where interest centers on (luminescing) aromatic oxygenates, e.g. products of weathering or incomplete combustion, or certain types of flavors and essences (*cf.* 3). The simultaneous ECD trace could provide confirmation in this case (if it happens to be in the correct concentration range), or it could alert the analyst to the presence of compounds with high electron affinity (e.g. polychlorinated contaminants) somewhere else in the chromatogram. However, new types of detection devices rarely obey such predictions—more often they find or forge their own niche in the analytical arsenal.

#### ACKNOWLEDGEMENT

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#### REFERENCES

- 1 M. Dressler, *Selective Gas Chromatographic Detectors (J. Chromatogr. Library, Vol. 36)*, Elsevier, Amsterdam, 1986.
- 2 Y. Z. Tang and W. A. Aue, *Anal. Chem.*, 60 (1988) 1481.
- 3 Y. Z. Tang and W. A. Aue, *J. Chromatogr.*, 409 (1987) 243.
- 4 Y. Z. Tang and W. A. Aue, *Mikrochim. Acta*, 1987-II (1987) 21.
- 5 Y. Z. Tang and W. A. Aue, *Mikrochim. Acta*, 1987-II (1987) 29.
- 6 A. J. L. Collinson, J. R. Bennett and D. W. Hill, *Br. J. Appl. Phys.*, 16 (1965) 631.
- 7 M. C. Sauer and W. A. Mulac, *J. Chem. Phys.*, 56 (1972) 4995.
- 8 Y. Z. Tang, *Ph.D. Thesis*, Dalhousie University, Halifax, 1987.