Selective Determination of Hetero-Organics by a Dual-Channel Detector Based on Flame Conductivity and Emission

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A simple dual-channel detector was constructed from a regular FID and a spectrometer. The response of this system was studied with compounds of iron, lead, and tin, as well as phosphorus and sulfur, under air-rich and hydrogen-rich conditions. Both emission and ionization responses can be used to determine the metals in the nanogram and picogram ranges, respectively; while the response to carbon is repressed by several orders of magnitude.

Despite its obvious wealth of sensitive and selective detectors, gas chromatography is still in need of some improvement in the area of organometallics. The determination of metals as chelates, the detection of volatile environmental contaminants, and the monitoring of agricultural and industrial chemicals would all benefit from detection systems specific for certain hetero-elements.

This paper describes studies on a simple dual-channel GC detector based on the ionization and emission processes occurring in a hydrogen flame. The small flames of the air-rich FID and the hydrogen-rich Brody-Chaney detector *(1)* have been remarkably successful in their respective areas; yet, one may justifiably argue that neither should be particularly applicable to the detection of typical metals.

The air-rich flame can be made selective to phosphorus (and, to a lesser degree, nitrogen, chlorine, bromine, and iodine) by the addition of alkali—but responses to typical metals are not particularly noteworthy in this *ionization* mode *(2)*. The hydrogen-rich flame is very sensitive to phosphorus and sulfur *(1)*, also to boron *(3)*, in the *photometric* mode—but this mode depends on molecular emission *bands* which are prevalent in (or especially above) "cool" flames (POH, S_2, BO).

The spectral determination of metals has—in contrast to the conditions prevalent in the Brody-Chaney detector —always relied on the hot (high-energy) flames for atomic emission. The large amount of energy is required because samples are introduced as aqueous solutions and, furthermore, one needs to obtain a sizable, strongly excited free atom fraction. The introduction of metals as gases would lower the energy requirement, of course *(4)*, but one could still view the puny GC flames as inadequate excitation sources.

Consequently, larger flames *(e.g. 5)* have been used for the determination of metalorganics in gas chromatographic effluents. Yet, the minute flame characteristic of the FID has certain conveniences—low cost, small safety haz-

ard, easy control, good noise characteristics, and easy construction on top of a gas chromatograph—not to mention its excellent response to carbon which makes it the most widely used detector in trace analysis. These traits prompted us to attempt, even with the odds against success, to use it as an optical excitation source.

We decided to test both its electrical and optical responses, in both air-rich and hydrogen-rich configurations.

EXPERIMENTAL

The detector was a lab-built unit, resembling a first-generation FID as shown in Figure 1. It was held on top of a column-conditioning oven by screws and kept gas-tight by silicone rubber gaskets. Its shell was cast aluminum, with a bore for the PTFE-insulated collector electrode and a quartz window to observe the flame with a Jarrell-Ash half-meter grating spectrometer. This basic arrangement had been used, with minor modifications, in several prior investigations *(6, 7)*. Not shown in the figure is a glow plug (as is frequently used in model air planes) to ignite the flame in the hydrogen-rich mode.

The flows of hydrogen and oxygen/air were reversible such that either could be mixed with the GC effluents, while the other entered the detector around the base of the jet tip.

The ionization channel involved a 5-mm i.d. single loop platinum collector electrode, connected to either the negative or positive pole of a 240-V Barber-Colman battery box which, in turn, fed the signal plus some noise to a matched-tube Barber-Colman electrometer. The optical channel consisted of a half-meter Jarrell-Ash grating spectrometer, an inexpensive IP28 photomultiplier tube, a Keithley 240-A power supply and a Keithley 417 highspeed picoammeter. Two single channel strip chart recorders were used to monitor the amplified signals.

Isothermal gas chromatography was performed on 3% OV-101 or 10% OV-17 on Chromosorb W, H.P. 80/100 mesh, in a 2-m × 3-mm i.d. borosilicate glass U-tube column. Nitrogen served as the carrier gas at 50 ml/min.

Standard gas flows to the detector in ml/min were, in the airrich mode: 90 hydrogen and 335 air; in the hydrogen-rich mode: 830 hydrogen, 96 oxygen, and 70 air. (Caution should be exercised in regard to the relatively large amounts of hydrogen leaving the detector.)

In exploratory experiments, the spectrometer was used with 250-μ slits for preliminary spectral scanning, introducing a nitrogen stream saturated with the test compound into the flame. In later response studies, the slits were removed and the lightpath was restricted only by the two slit assemblies, yielding an effective slit width of approximately 3 mm. The wavelengths to be used for the various metal emissions were chosen either from the major lines obtained in the preliminary spectral scan or from the results of testing, with repeated injections, the strongest emission lines reported in the literature.

Emission profiles in the *air-rich* flame were monitored by a glass image conduit (Edmund Scientific) which had been twisted 90° in a Bunsen burner flame and painted black on one end, leaving only a 1-mm slit untouched. This end was inserted into the spectrometer slit assembly such that the slit appeared vertical to the spectrometer but horizontal to the flame. The image conduit could be displaced vertically at the detector end by the jaw of a vernier caliper. Emission profiles in the *hydrogen-rich* flame were measured through the quartz window with a slit formed by black

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Table I. Summary of Detector Performance, Determined with Model Gas Chromatographic Effluents in Optical vs. Electrical and Air-Rich vs. Hydrogen-Rich Modes

Compounds	Dodecane	Trimethyl-phosphate	Di-n-butyl-disulfide	Tetraethyl-lead	Tetraethyl-tin	Ferrocene
PHOTOMETRIC MODE						
Nominal wavelength, nm	405.8	526.0	394.0	405.8	485.0	373.5
Air-rich						
~MDA, grams[a]	4×10^{-6}	8×10^{-8}	3×10^{-7}	4×10^{-8}	5×10^{-9}	2×10^{-9}
~Selectivity[a,b]	1×10^{0}	5×10^{1}	1×10^{1}	1×10^{2}	8×10^{2}	2×10^{3}
~Maximum emission in flame	Middle	Middle-low	Middle	Tip	Middle-tip	Tip
Hydrogen-rich						
~MDA, grams[c]	1×10^{-5}	2×10^{-8}	2×10^{-8}	1×10^{-8}	5×10^{-9}	8×10^{-10}
~Selectivity[b,c]	1×10^{0}	5×10^{2}	(5×10^{2})[d]	1×10^{3}	2×10^{3}	1×10^{4}
Maximum emission in flame	Tip	Tip & above	Above	Tip & above	Tip & above	Tip
IONIZATION MODE—Hydrogen-rich						
~MDA, grams[e]	8×10^{-7}	1×10^{-9}	1×10^{-8}	3×10^{-11}	2×10^{-11}	1×10^{-11}
~Selectivity[b,e]	1×10^{0}	(6×10^{2})[f]	7×10^{1}	6×10^{3}	(1.2×10^{4})[d]	1.6×10^{5}
~Maximum, electrode height, mm	5	35, 5	5	25	25	25
Best potential (240 V)	(+)	(−),(+)	(+)	(−)	(−)	(−)

[a] Total flame. [b] Selectivity = [Response/weight (test compound)]/ [Response/weight (hydrocarbon standard)]. [c] Flame tip and above. [d] Depends on concentration. [e] At ~20 mm electrode height. [f] Asymmetric peaks, value questionable.
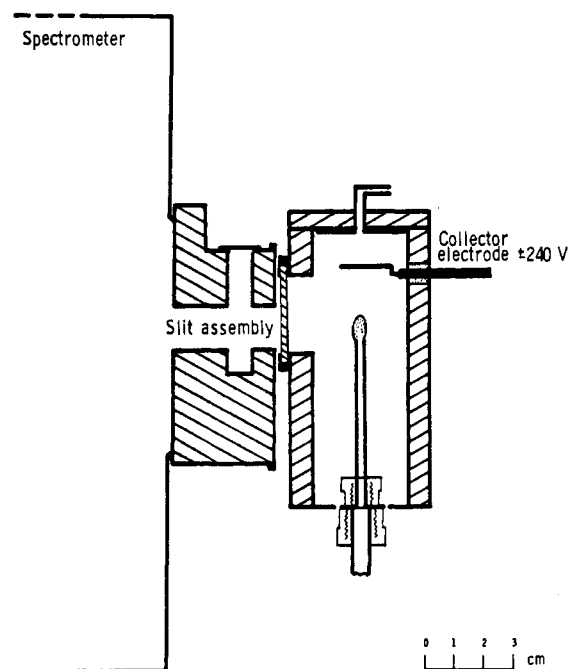
Figure 1. Cross section of detector for dual-channel operation

tape at the spectrometer inlet. The spectrometer itself rested on two large labjacks and could be raised or lowered in a level position.

Several metalorganic compounds which were commercially available and could be easily chromatographed, were used for initial testing. Most gave some selective response, but only three were chosen for a more detailed study: Ferrocene, tetraethyllead and tetraethyltin. Because of the widespread use of the Brody–Chaney detector, trimethylphosphate and di-n-butyl-disulfide were chosen for a more detailed study: Ferrocene, tetraethyllead taining molecules. Decane or dodecane served as carbon standards.

For these compounds, the following data were established: Minimum detectable amounts, selectivities against a carbon standard (on a response/weight basis of injected compounds), and calibration curves at standard conditions; as well as the variation of optical response with vertical slit replacement and oxygen flow; and the variation of electrical response with the height and polarity of the collector electrode, and the oxygen flow. Care was taken to stay within the linear range of response in the course of various measurements and to calculate from such data whenever a direct comparison was prevented by detector limitations.

RESULTS

Table I contains a comprehensive summary of the conditions and results of our study. The ionization response in the air-rich mode has been omitted since it was considered similar to that of a regular FID.

Because of the exploratory nature of this study, we were satisfied to test all compounds at similar conditions and made no efforts to optimize the chromatographic or spectroscopic conditions for a particular element. The gas flow rates in the hydrogen-rich mode, for instance, were chosen mainly with the objective of keeping the flame lit during passage of a 1- or 0.5-μl solvent peak.

Both modes—air-rich and hydrogen-rich—gave good photometric responses for the three metals. In the latter mode, the selectivity against carbon could be noticeably improved by monitoring the upper part of, or the space above, the hydrogen-rich flame. This had been shown in exploratory experiments (8), using either horizontal slits or a stainless steel cup which fitted on the detector jet tip and surrounded the flame, similar to the Brody–Chaney design (1). Although the sensitivity of such an arrangement is usually lower, the discrimination against carbonaceous background may, in certain types of analysis, represent the decisive feature.

Photometric responses were somewhat better in the hydrogen-rich mode which, however, required more attention on part of the operator. The detector arrangement shown in Figure 1 represents a typical FID and was not designed with a hydrogen-rich flame in mind.

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The conductivity response of the flame in the hydrogen-rich mode presented a pleasant surprise in terms of sensitivities. Ferrocene, the compound with the highest response, could have been detected at the 3-pg level, had not chromatographic ghosting effects prevented an actual measurement at this level. The calibration curves in this mode were generally linear over two or more decades (Fe, Pb, S, and C standard compounds; while Sn was linear only on a log/log scale), then trailed off at a response level of approximately 10^{-9} ampere peak height.

At its lower end, the linear range was limited by noise as usual. Thus, the range could vary considerably with the stability of the flame and the electronics used to measure its conductivity. Likewise, the signal/noise characteristics of the photomultiplier tube in the chosen wavelength region, as well as noise incurred from the flame, formally limited the linear range in the *optical* modes. As expected, calibration curves were again linear—with the well-known exception of sulfur—in all cases measured (tin and iron in air-rich mode; tin, iron, and lead in hydrogen-rich mode). Typically the linear range spanned two to three decades.

As shown in Table I and illustrated by an example in Figure 2, the sensitivity and the selectivity against carbon were functions of electrode height and, to a lesser degree, oxygen flow. Different flame geometries were tried by varying the inner diameter of the $\frac{1}{8}$-in. o.d. stainless steel tube serving as a jet tip but, after some adjustment of flow rates, no real strong change in performance could be detected. However, the matter was not further investigated.

We attempted to reproduce the *conductivity* response of the hydrogen-rich mode with one of the commercially available models of the Brody-Chaney detector (Tracor, Inc., Austin, Texas), both with shielded and unshielded flame arrangements. The attempt was not successful. Whether or not this failure was due to the vastly different detector geometry or flow rates, or any other cause, has not been determined.

Using an electrode height of approximately 20 mm above the jet tip, the effects of polarity were investigated. A negative potential on the collector electrode proved highly advantageous. While the response of tin, phosphorus, and sulfur compounds remained essentially unaltered by a switch in polarity, the response of ferrocene and tetraethyllead increased by factors of 16 and 4, respectively, and the response for decane decreased by a factor of 25. Furthermore, the background current was lower in the negative mode and increased less with an increase in oxygen flow rate than in the positive mode. The flame chemistry responsible for these effects, however, has not been further investigated beyond this indication of analytical utility.

An increase in oxygen flow rate generally increased the response of metal compounds and decreased the response of the hydrocarbon standards (with maxima and minima apparent), although not as much as the change in electrode height. Because of the many possible conditions of measurement and the wide range of concentrations and responses involved, the sensitivity and selectivity data given in Table I should be considered as approximate. Furthermore, it was not possible in our detector arrangement to change the electrode height smoothly, *e.g.*, by a screw-type mechanism operated from the outside *(9)*; rather, the height had to be set crudely by bending the platinum wire. The construction of a vertically displaceable electrode in a confined gas environment may entail a
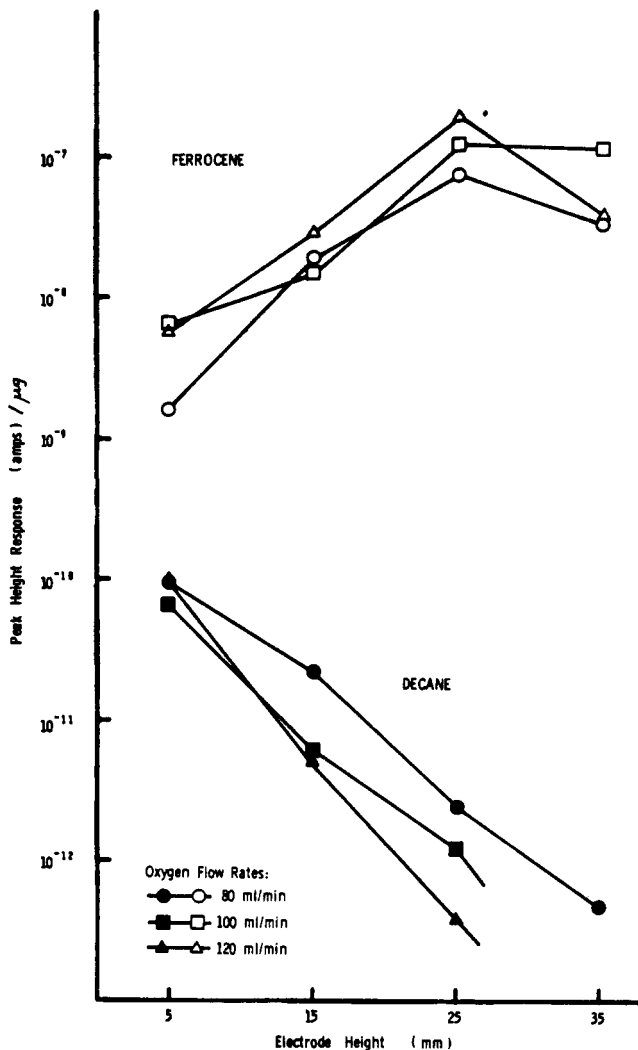
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Figure 2. Response profiles (in amperes peak height/μg) as a function of electrode height and oxygen flow; calculated from data obtained within the linear ranges of both ferrocene and decane. 10% OV-17 on Chromosorb W at 175 °C; hydrogen-rich ionization mode with flows of N_2 at 50, air at 70; and H_2 at 830 ml/min

few difficulties, but would be considered necessary for fine-tuning the detector.

DISCUSSION

As mentioned in the introductory part of this manuscript, the excitation capabilities of the minute flames used in gas chromatographic detectors were questionable in the case of metals. It came as a pleasant surprise, therefore, to find minimum detectable amounts in the lower nanogram ranges when the spectral response of three selected metal compounds was used. The low noise generated by the small flame did, no doubt, add to its success. In fact, some measurements were limited by phototube noise rather than flame noise. On the other hand, the use of open slits (which correspond to bandpath widths at half-height in the vicinity of 50 Å) contributed greatly to the high sensitivity.

Using open slits seemed permissible from the viewpoint of anticipated analytical applications, namely, the GLC determination of volatile metal compounds contained in complex extracts of environmental or biological origin (*i.e.*, in a C, H, O, N matrix). If metals need to be distinguished from each other, one obviously would have to use

different optical parameters. In this study, metal/metal selectivity has not been of concern.

Comparing the far superior response of the Brody-Chaney detector for P and S (1) with our photometric measurements, one could be tempted to assume that the use of such an optimized arrangement should greatly enhance the sensitivity for metals as well. This may be true in some cases and not in others. The comparison of molecular bands with atomic lines, the location of the emission in relation to the flame, the different bandpaths and stray light conditions in filter/photomultiplier combinations as compared to a spectrometer, and the current magnitude permissible from a highly sensitive phototube—all these considerations play a significant, perhaps decisive, role. In this exploratory study, the spectrometer was chosen primarily for its capability of wavelength and bandpath selection, with little thought given to the best possible optical arrangement. The selection of the "best" arrangement depends, furthermore, on particular analytical needs.

Such needs could be served not only by the optical emission but also by the ionization responses of the hydrogen-rich flame. The sensitivity of detection is remarkable in the three selected cases; the more so because the detector construction derives from happenstance and the electrical channel is far from what one would regard an efficient arrangement. The selectivity against carbon compounds should be adequate for most projected environmental samples.

The mechanism of response has not been determined; nor could we predict how different detector constructions would respond. Our failure to obtaim comparable responses from the Tracor detector certainly underscores this point. Other open questions include the response of metals other than iron, lead, or tin. There is some evidence for the possible usefulness of the detector for other elements (8) but the matter has, to date, not been further investigated.

This simple, dual-channel detector could find application in the analysis of trace metal compounds in an environmental, agricultural, or industrial context. It does demonstrate·the potential of small GLC flames for analytically useful light emission from metals. Furthermore, the observed ionization effects in the hydrogen-rich flame should be an interesting object of studies in flame chemistry.

ACKNOWLEDGMENT