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## A HYDROGEN-RICH FLAME IONIZATION DETECTOR SENSITIVE TO METALS\*

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## SUMMARY

A regular flame ionization detector was operated hydrogen-rich by reversing the gas flows such that air and oxygen were fed into the column effluent and the flame burned in a hydrogen atmosphere. In this detector, several metal compounds showed strong response while the signal for carbon was repressed. Ferrocene, tetraethyllead, and tetraethyltin could be detected at the 10, 30, and 20-pg level, respectively, with selectivities over decane of four to five orders of magnitude.

## INTRODUCTION

As the separating capabilities of gas chromatographic (GC) columns have steadily been improved and have brought the complex biological and environmental samples within reach of the analyst, the search for more sensitive detectors began to shift direction to include selectivity as well. The importance of selectivity in GC detectors should not be underestimated: One can reasonably argue that much of the current public concern about the environment has originated from, been precipitated by, or made possible through, the response characteristics of the electron capture detector toward organic halides.

Other mechanisms than the associative or dissociative reaction of GC effluents with thermal electrons have been used to devise selective detectors.

Among the better understood are the chemiluminescence of HPO and S<sub>2</sub> in hydrogen-rich flames; the Beilstein test and a few similar reactions; the coulometric or conductometric behavior of products from oxidative or reductive pyrolysis; and fragmentation patterns in a mass spectrometer.

There are other detectors which are quite useful yet poorly understood—as for instance the one utilizing an alkali-doped hydrogen flame. Another selective detector which monitors flame conductivity while the carriers of electric charge are open to speculation, is introduced in this paper.

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This detector originated from an investigation of photometric responses obtainable from the diminutive flames characteristic of flame ionization detectors (FID's) in GC<sup>1</sup>. We noted that a hydrogen-rich FID—basically a regular FID with reversed inlets for hydrogen and air/oxygen run at suitable flow-rates—gave strong signals for certain organometallics while the response to carbon compounds was repressed.

Chosen as test substances were tetraethyllead, ferrocene, and tetraethyltin because of our earlier studies on these compounds; di-*n*-butyldisulfide and trimethylphosphate because of the BRODY-CHANEY detector<sup>2</sup> which is available with an additional ionization channel; and decane as a representative of carbon compounds. With these we attempted a definition of electric response parameters in the hydrogen-rich flame. The detector arrangement was the same as used in a number of previous studies<sup>1,3</sup> for both electric and optical signals.

## EXPERIMENTAL

### *Detector configuration*

This detector had been laboratory-made, resembling an inexpensive, first-generation hydrogen FID. Silicone rubber sheets provided gas-tight seals and a model airplane glow plug the means to ignite the flame. The air and oxygen were mixed with the column effluent at the base of the detector before entering a 1/8-in. O.D. stainless-steel tube, while the hydrogen entered the detector housing around the base of this jet tip. The platinum electrode, which was insulated from the detector block by a PTFE insert, formed a 5-mm I.D. single loop, positioned approximately 20 mm above the jet tip. It connected to either the negative or the positive pole of a 240-V Barber-Coleman battery box, which in turn fed the signal plus some noise to a matched-tube Barber-Coleman electrometer and on to a strip chart recorder.

### *The "shielded" flame*

In an attempt to simulate, to some degree, the shielded, hydrogen-rich flame of the BRODY-CHANEY detector<sup>2</sup>, several holes were drilled into the bottom of a 1/4-in. stainless-steel Swagelock nut and this perforated cup was held on the detector jet tip by a piece of shrunk PTFE tubing. Under these circumstances, most of the flame was hidden from view through the side window.

### *Chromatographic conditions*

Tetraethyltin, tetraethyllead, ferrocene, trimethylphosphate, and di-*n*-butyldisulfide were chromatographed (initially) at 135° on a 2 m × 4 mm I.D. Pyrex U-tube column packed with 3% OV-101 on Chromosorb W, HP, 80-100 mesh. The air, hydrogen and nitrogen flow-rates were held constant throughout the experiment at 70, 830, and 50 ml/min, respectively. The oxygen supply was varied, using the electrodes with either a positive or negative potential of 240 V.

Conditions for establishing calibration curves and minimum detectable amounts included minus 240 V on the electrode, 96 ml/min oxygen, and a column temperature of 160° for the iron and sulfur compounds; all other conditions being equal to those listed above.

## RESULTS AND DISCUSSION

The response characteristics of the hydrogen-rich flame render it a good candidate for the trace analysis of organometallics—even though the used detector configuration was well off from what one would consider ideal in an electronic and mechanical context, not to speak of safety considerations. The large internal volume of the detector required a hydrogen flow-rate of 830 ml/min for both easy ignition and flame stability during the passage of the solvent peak. The effect of hydrogen flow variation, from 730 to 930 ml/min, proved negligible as could be expected from the fact that the detector was filled with hydrogen. The peak size could be influenced, however, by varying the oxygen flow-rate or the direction of the electric field applied from the collecting electrode. (Figs. 1–7 show these effects, denoting electrode polarity by data point symbols.)

Response profiles with respect to oxygen flow varied considerably among the test compounds, a definite analytical advantage when selectivity is desired. Most important, perhaps, was the fact that the carbon response decreased markedly with an increase in oxygen supply, in definite contrast to the other test compounds. This meant that the selectivity of the organometallics *vs.* carbon could be maximized by adjusting the oxygen flow-rate.

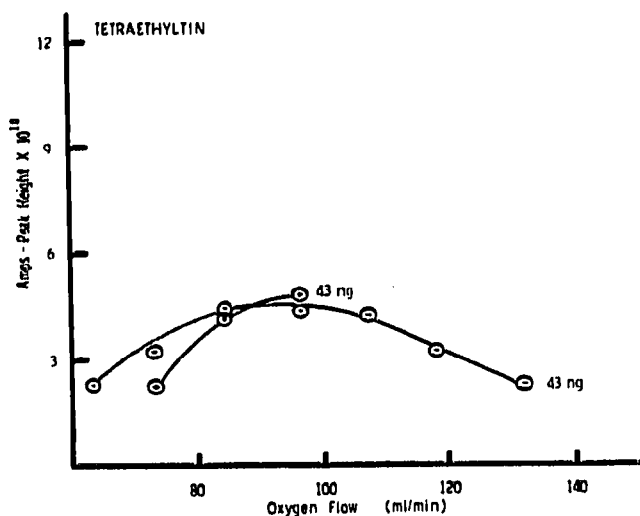


Fig. 1

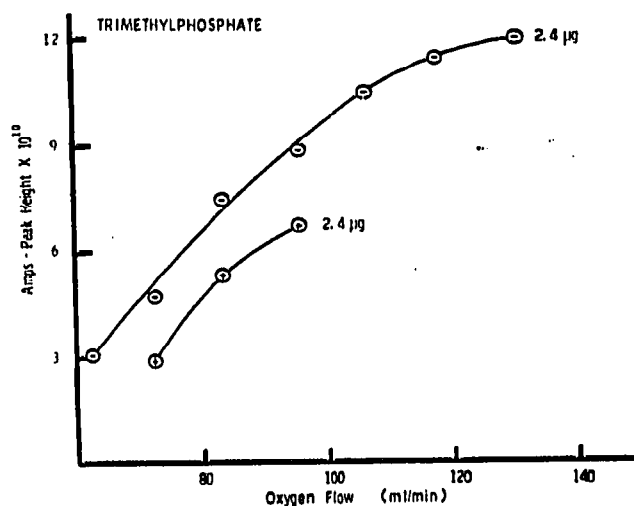


Fig. 2

The choice between positive and negative potential was easy. The responses of tin, phosphorus, and sulfur were not altered significantly by the switch in polarity (Figs. 1–3); however, iron and lead increased by factors of 16 and 4 and decane decreased by a factor of 25 (Figs. 4–6), when the potential was switched from positive to negative. These results were obtained while supplying oxygen at 96 ml/min, a flow-rate considered optimal for our particular detector configuration.

Not only selectivity, but also sensitivity appeared to be favored by the negative mode. As seen in Fig. 7, the baseline current at the preferred oxygen flow-rate was two and a half times larger in the positive mode. It increased, furthermore, about three times as fast with respect to oxygen flow. Thermal electron emission from the glowing

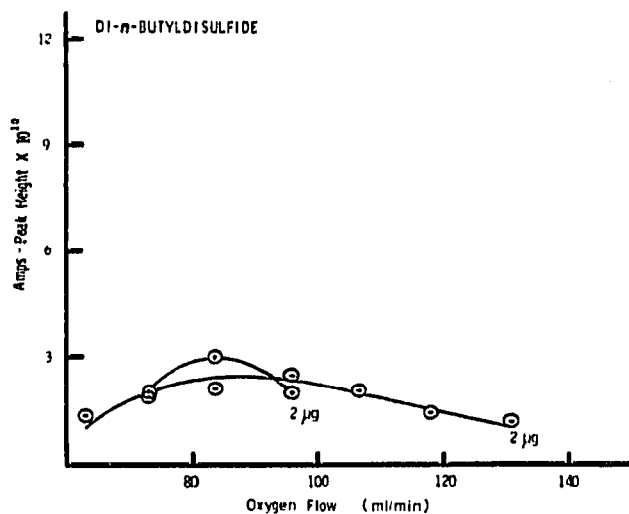


Fig. 3

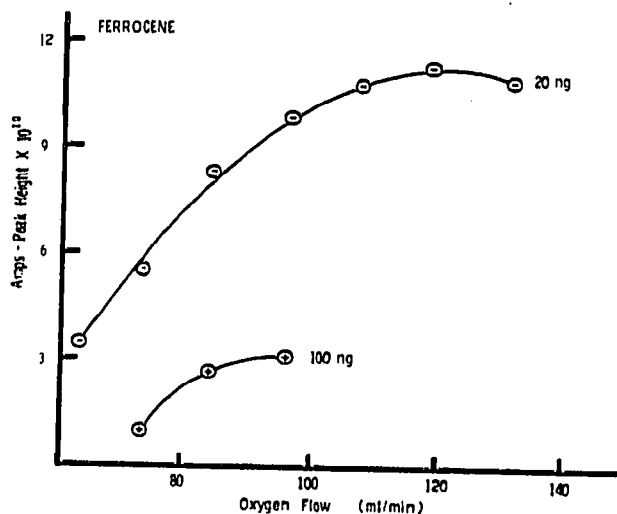


Fig. 4

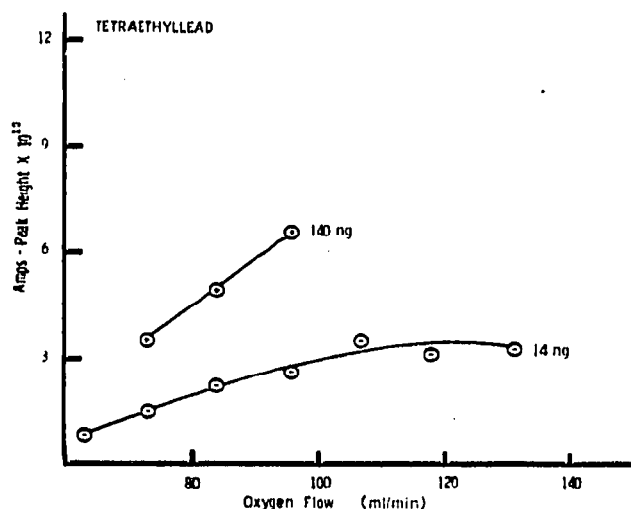


Fig. 5

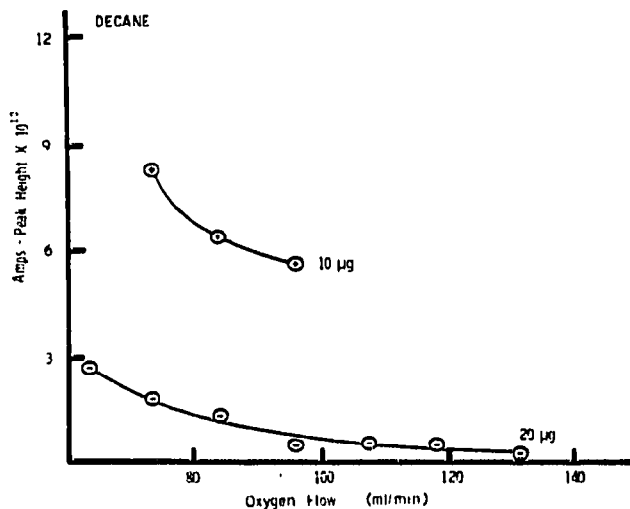


Fig. 6

jet tip may possibly have been responsible for the high background when the potential of the collector electrode was positive but the matter was not further investigated.

Calibration curves were established and, as Fig. 8 shows, indicated good working ranges for the compounds tested. The selectivity ratios, depending upon where they

TABLE I

## MINIMUM DETECTABLE AMOUNTS OF VARIOUS TEST COMPOUNDS

Compound	MDA (g)	Selectivity to decane <sup>a</sup>
Ferrocene	$10 \times 10^{-11}$	$1.6 \times 10^5$
Tetraethyllead	$3 \times 10^{-11}$	$6.1 \times 10^3$
Tetraethyltin	$2 \times 10^{-11}$	$1.2 \times 10^4$
Trimethyl phosphate	$1 \times 10^{-9}$	$6.1 \times 10^2$
Di- <i>n</i> -butyldisulfide	$1 \times 10^{-8}$	$7.3 \times 10^1$
Decane	$8 \times 10^{-7}$	$1.0 \times 10^0$

<sup>a</sup> Calculated from Fig. 8 at the ordinate value of  $2.5 \times 10^{-11}$  A.

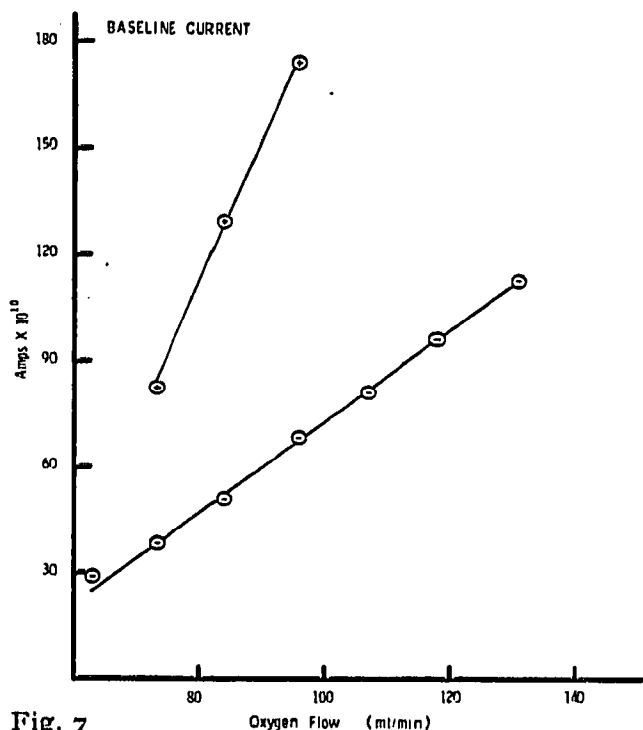


Fig. 7

were measured, lay in the range of 3 to 5 orders of magnitude for the three organometallics. Both phosphorus and sulfur compounds, however, responded also significantly stronger than the standard decane (Table I). It must be noted, though, that trimethylphosphate showed up as an unsymmetrical peak under the particular conditions and its measurements should therefore be considered approximate.

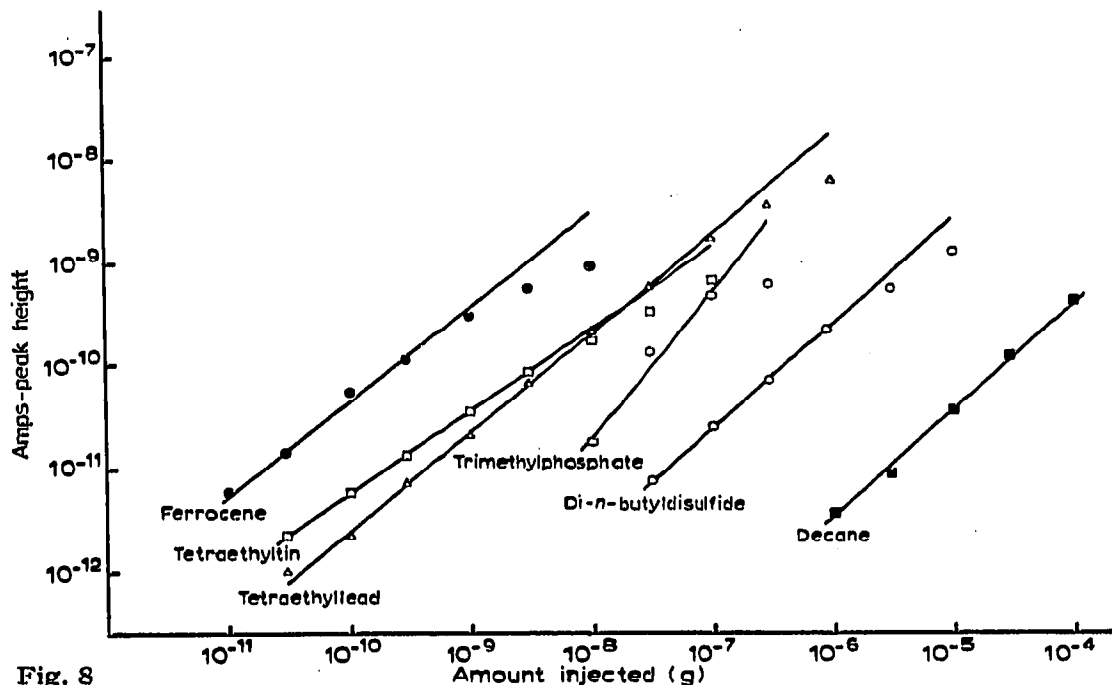


Fig. 8

Working with a shielded flame made those quite attractive results lose most of their attractiveness. The ionization efficiency of the metal compounds decreased by 2 orders of magnitude and the carbon response increased to twice its former value. We did not investigate the question whether cooling of the flame, catalytic effects, flame geometry, ion recombination, or a number of other plausible mechanisms could be responsible for this effect. (A shielded, hydrogen-rich flame is, of course, the major element of the—however differently constructed—BRODY-CHANEY detector<sup>2</sup>.) Minimum detectable amounts for the shielded flame were determined as 2.3, 3.5, and 2.3 ng of tetraethyltin, tetraethyllead, and ferrocene.

It appears entirely possible to shield the hydrogen-rich flame by means of other than a metal enclosure, for instance by light guides or slits, in order to obtain two channel operations in both photometric and ionization modes. In fact, dual channel operation of our prototype detector has caused us to discover the ionization phenomenon in the first place.

There are some indications that the surprising performance of the detector is due, at least in part, to the happenstance of its construction. We used the same, simple arrangement in a variety of studies over the past two years and, here as there, made no attempts at optimizing the basic set-up.

Work is underway, however, to clarify the role of detector elements and dimensions in obtaining desirable response characteristics. At present, the mechanisms involved in the conductivity phenomenon are unknown. As stated earlier, however, ignorance of the *modus operandi* of the detector should not detract from its analytical usefulness.

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