PERFORMANCE OF A SILICON-DOPED HYDROGEN ATMOSPHERE FLAME IONIZATION DETECTOR FOR GAS CHROMATOGRAPHY

HERBERT H. HILL, Jr.* and WALTER A. AUE

5637 Life Sciences Centre, Dalhousie University Halifax, N.S. (Canada)

SUMMARY

The response of an earlier described detector [J. Chromatogr., 74 (1972) 319] for certain organometallics has been shown to depend on the presence of volatile silicon compounds in its hydrogen atmosphere. Trace levels of silane were therefore introduced continuously and the response for selected test compounds measured. The detector responded well to compounds of Al, Fe, Sn, Cr and Pb; showing approximately three decades of linear range and the capability for temperature programming. The best responding compound, aluminum hexafluoroacetylacetonate, could be detected in as small an amount as 6×10^{-13} g. Since the minimum detectable amount of a typical hydrocarbon standard, tetradecane, is only 4×10^{-7} g, and oxygen or nitrogen containing compounds have so far responded similarly, it is possible to use this detector for determining certain trace metalorganics contained in complex organic matrices.

INTRODUCTION

In 1972 we published a short paper entitled "A hydrogen-rich flame ionization detector sensitive to metals"[1]. It described the surprising responses of a lab-made flame ionization detector (FID) to certain metalorganics. Besides using a H_2/O_2 flame burning in a hydrogen atmosphere, and a negatively polarized collector electrode situated high above the flame, we attributed the very sensitive and selective performance of this new detector to "the happenstance of its construction".

This remark was prompted in part by the behaviour of hydrogen-rich flame detectors of different construction. For instance, the commercially available Brody–Chaney unit[2] showed much lower responses in its conductivity mode. Most of the time that followed the initial experiments was therefore taken up by the search for the elusive happenstance proper.

Flow conditions, geometric factors, and other detector parameters such as temperature and voltage were quickly optimized[3], but response still varied somewhat over longer periods of time. Such variations are not unusual for various types of detectors, and they are often attributed to detector contamination.

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* Present address: Chemistry Department, University of Waterloo, Waterloo, Ont., Canada.

Cleaning a detector thus has a good chance of restoring performance; however, in our case cleaning made matters worse: Response deteriorated and was further depressed by the use of a low-bleed column packing based on Carbowax 20M[4]. In contrast, re-use of some old, discarded detector parts appeared to restore, at least to some degree, the desired qualities. It seemed likely, therefore, that the detector was dependent on some unknown contaminant for optimum performance.

Our first guess (tin) was wrong; our second guess (silicon) was right. The important happenstance in the construction of our first detector was apparently the use of silicone rubber gaskets, kept at higher temperature in contact with the hydrogen atmosphere.

The effect could be easily proven. Bleed from a polysiloxane column, or a chunk of silicon rubber thrown into the detector, or the addition of volatile silicon compounds such as silane or tetramethylsilane (TMS) to the hydrogen stream all improved response. Low bleed from a non-silicone column, scrubbing of the detector, or injection of fluorine-containing compounds in large amounts, all decreased it.

The following experiments were set up to demonstrate and capitalize on this effect, and to conduct a survey of inexpensive and commercially available organometallics. Some experiments were also designed to provide clues, however vague, of the *modus operandi* of the detector.

EXPERIMENTAL

Addition of tetramethylsilane

A T-fitting was swaged into a 1/8-in. nitrogen line and screwed into the 1/4-in. opening of a 0.5-l stainless-steel sampling tank, such that the 1/8-in. tubing protruded about two-third into the cylinder and forced the nitrogen down close to the liquid level of TMS. Nitrogen plus TMS vapor then flowed upward and entered the 1600 ml/min hydrogen stream supplying the detector. The valving allowed the TMS tank to be shut off completely; this was necessary to obtain a true value for zero nitrogen flow (*i.e.*, no TMS added).

The tank, charged with a suitable amount of TMS, was cooled in an acetone–dry ice bath and the nitrogen flow varied. When the detector had stabilized with the chosen flow-rate, test compounds were injected into the gas chromatograph (Fig. 1).

Tests of optimization under TMS-doped conditions

Tetramethylsilane from the dry ice bath was introduced to the hydrogen supply by a 10 ml/min flow of nitrogen as described above. Under these conditions, the two important parameters of electrode height and voltage on the collector electrode were checked (Figs. 2 and 3). The former was adjusted by inserting or removing "spacers", *i.e.* sections of the detector wall that separate the collector electrode assembly from the detector base (Fig. 5).

Addition of silane

A SiH₄ tank was cautiously connected to the hydrogen supply line via 1/8-in. copper tubing and a valve. The tubing had been squeezed such that it allowed the introduction of μl/min levels of SiH₄. This flow could be conveniently varied between 0 and 25 μl/min by adjusting the silane pressure. When the detector had stabilized with a particular setting, test compounds were injected (Fig. 4).

Final performance tests

Calibration curves were established for a variety of organometallics, using the optimized hydrogen atmosphere flame ionization detector (HAFID) shown in Fig. 5. The collector electrode, situated 50 mm above the quartz jet tip, was at —90 V potential. The gas flow-rates were as follows: hydrogen, 1600 ml/min plus 7 μl/min SiH$_4$; oxygen, 125 ml/min; nitrogen, 100 ml/min; nitrogen (through GC column), 40 ml/min. Care was taken to vent the large, unburned amounts of hydrogen via a specially constructed duct through the roof to the atmosphere.

The GC column was a 1-m, U-shaped borosilicate glass tube packed with 6% OV-17 on 60–80 mesh Chromosorb W. The injection port and detector temperatures were held at 225° and 235°, respectively, for compounds eluting under 200°; for compounds eluting above 200° they were set at 255° and 260°, respectively. Column temperatures for isothermal chromatography are given in Table I, which lists the compounds used for establishing calibration curves (Figs. 6–8), minimum detectable amounts, and selectivity as measured against tetradecane.

RESULTS AND DISCUSSION

Fig. 1 shows the increase in response of three selected organometallics with an increase in TMS vapor entering the detector. These measurements had to be started with a scrupulously clean detector, otherwise the magnitude of this effect (over two decades for ferrocene) would have been diminished. Measurements were taken in a random fashion indicated by numbers above the arrows. Note that the response of tetradecane is influenced very little by TMS and that, here as in all other experiments, the baseline current is larger than the (additional) peak height current.
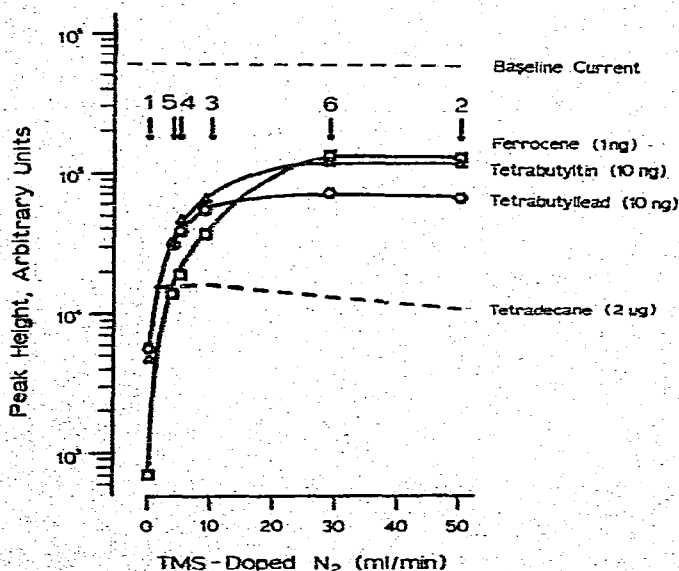

Fig. 1. Response of model compounds with various concentrations of tetramethylsilane in the hydrogen atmosphere. The numbers above the arrows represent the order in which the data points were obtained.

Using TMS-doping, electrode height and voltage profiles were checked. The correlation of electrode height with response duplicated earlier results[3]. From this correlation, shown in Fig. 2, a convenient electrode height of 50 mm was adopted for all further experiments.
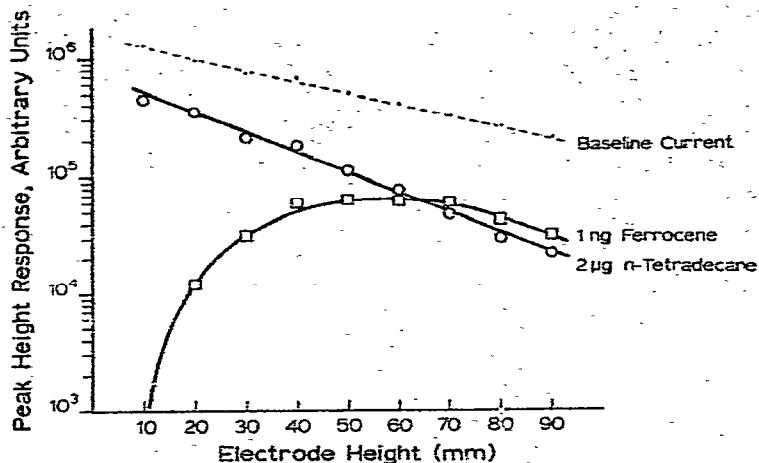

Fig. 2. Response and baseline current measured at different heights above the detector jet tip. Collector electrode at —240 V.

The voltage profiles for selected organometallics, tetradecane, and the baseline current, are shown in Fig. 3. The negatively polarized collector electrode, as has been shown before, represents the far better choice: Organometallics respond stronger, hydrocarbons weaker, and the baseline current is lower. A potential of —240 V had been used so far; on account of this graph it was reduced to —90 V for all subsequent experiments. Note that negative responses (inverted peaks below baseline) can be obtained at zero or low positive potential. Such peaks can occur under a variety of circumstances, depending on voltage, a possible bias voltage, concentration of analyte or dopant and, of course, the nature of the organometallic compound itself.

Doping the hydrogen atmosphere of the detector with TMS represented a first approach to the problem, however, there were drawbacks: The TMS level entering the detector could only be estimated and, together with silicon, carbon was being introduced continuously into the flame. The gas silane offered a suitable alternative. Its flow could be easier calibrated, it contained no carbon, and was interesting to test because silane(s) had been suspected anyway to be the active species in the hydrogen atmosphere above the flame. SiH_4 had to be treated with caution, however, since it will spontaneously ignite on contact with air.

Fig. 4 shows the pronounced correlation of response with the addition of SiH_4 to the hydrogen supply of the detector. The graph is self-explanatory, and on its account, a stream of 7 µl SiH_4/min (corresponding to a concentration of 4.3 ng SiH_4/ml in the detector) was added to the hydrogen supply in subsequent experiments.

These involved a survey of a wider variety of organometallics plus other compounds with hetero-atoms. Table I lists the compounds, the column temperatures, the
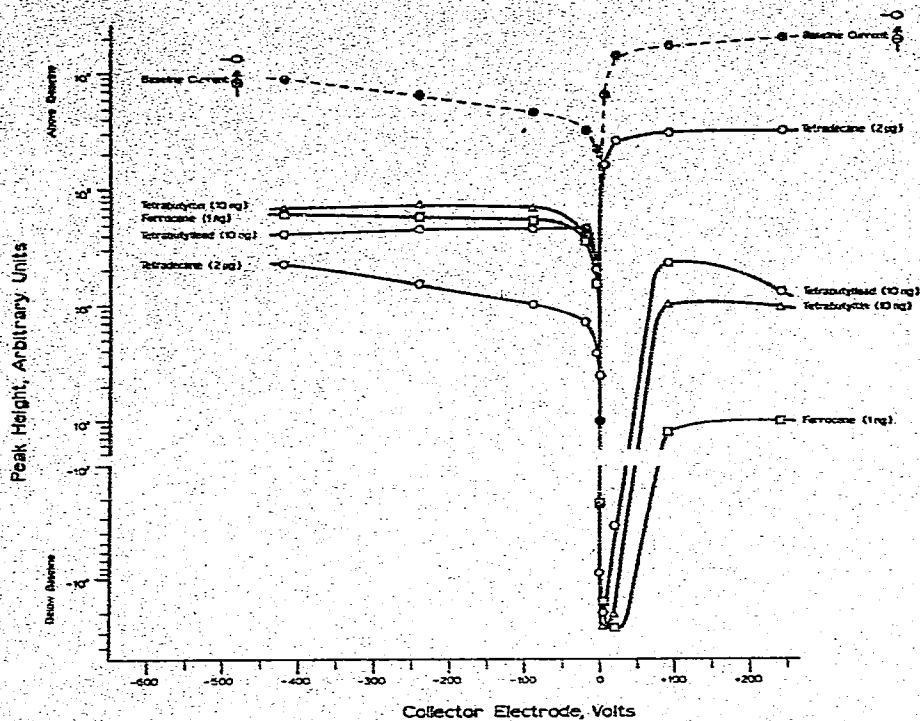
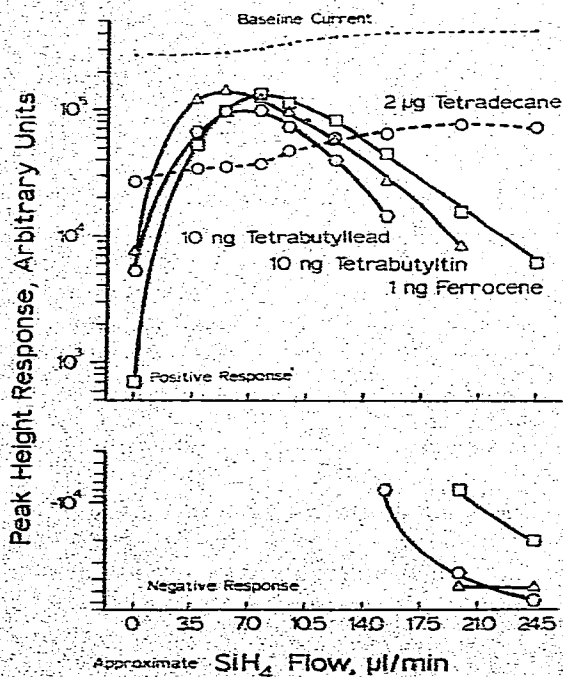Fig. 3. Baseline current and response of various model compounds at different collector electrode potentials.

Fig. 4. Baseline current and response of various model compounds at different concentrations of SiH_4 in the hydrogen atmosphere.

TABLE I

RESPONSES OF MODEL COMPOUNDS

A minus sign preceding a selectivity value indicates a negative response (inverted peak).

Compound	Column temperature (°C)	Selectivity	MDA (g)
Aluminum(III)			
hexafluoroacetylacetonate, Al(hfa)$_3$	50	3.2×10^5	6.0×10^{-13}
Ferrocene	145	1.9×10^5	2.1×10^{-12}
Tetravinyltin	110	2.6×10^4	1.0×10^{-11}
Tetrapropyltin	140	1.9×10^4	7.8×10^{-12}
Tetraethyltin	90	1.6×10^4	2.1×10^{-11}
Chromium(III)			
hexafluoroacetylacetonate, Cr(hfa)$_3$	60	1.6×10^4	1.5×10^{-11}
Chromium hexacarbonyl, Cr(CO)$_6$	30	1.5×10^4	2.3×10^{-11}
Chromium(III)	170	1.1×10^4	1.7×10^{-11}
trifluoroacetylacetonate, Cr(tfa)$_3$			
Tetraethyllead	100	1.1×10^4	5.1×10^{-11}
Tetrabutyllead	190	6.0×10^3	7.5×10^{-11}
Triphenylantimony	250	1.2×10^3	1.3×10^{-10}
Tungsten hexacarbonyl	50	8.6×10^2	5.3×10^{-10}
Molybdenum hexacarbonyl	30	5.0×10^2	3.5×10^{-9}
Tetrabutylgermane	140	3.5×10^2	5.5×10^{-10}
Tri-n-butyl phosphate	190	-3.2×10^2	1.1×10^{-9}
Chlorobenzene	70	-3.2×10^2	1.4×10^{-9}
Bromobenzene	80	-3.2×10^2	1.4×10^{-9}
Triphenylarsine	250	-3.2×10^2	2.3×10^{-9}
Triphenylbismuth	250	1.3×10^2	6.3×10^{-9}
Piaselenole	165	-9.2×10^1	5.7×10^{-9}
Iron(III)			
trifluoroacetylacetonate	175	8.0×10^1	4.1×10^{-9}
Di-n-butyl disulfide	140	-2.0×10^1	2.3×10^{-8}
Fluorobenzene	30	7.1×10^0	6.7×10^{-8}
Nitrobenzene	110	3.1×10^1	1.8×10^{-7}
Diethylmercury	70	2.9×10^{0a}	1.3×10^{-7}
Tetraethylsilane	50	1.9×10^0	4.1×10^{-7}
Tetradecane	140	1.0×10^0	3.7×10^{-7}

minimum detectable amounts (signal-to-noise ratio, 2:1) and the selectivities against tetradecane (taken as the ratio of injected amounts of tetradecane and the organometallic that produce the same peak area of 1×10^{-11} C). This choice of units for sensitivity and selectivity is the most direct way of describing the experimental results, and was therefore preferred to, say, using g/sec for minimum detectable amount, or basing selectivity on weight or moles of the metal itself. Had such calculation been employed, minimum detectable amounts would obviously have turned out lower and selectivity values higher.

    The measurements were made on the detector shown in Fig. 5, a slightly modified version of earlier models[3]. Calibration curves are shown in Figs. 6–8. The first of these, Fig. 6, also demonstrates effects of operating somewhat off optimum —in this case a drop of one-fifth in oxygen flow— denoted by dashed lines: organometallic response decreases and hydrocarbon response increases dramatically, depressing selectivity by more than an order of magnitude.

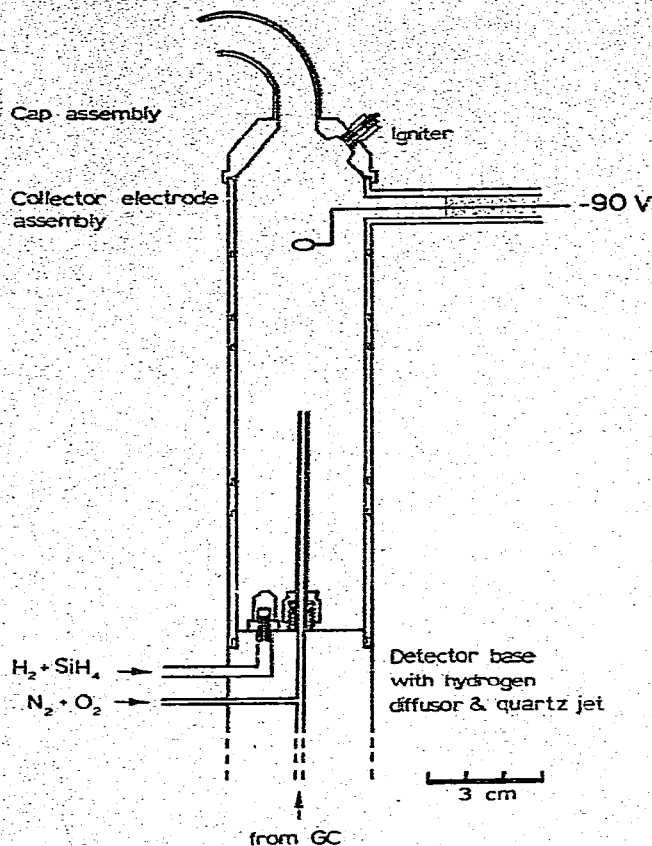   The calibration curves are rather self-explanatory, but a few points bear

Fig. 5. Cross-section of silane-doped HAFID. Flows-rates: hydrogen, 1600 ml/min $+ 7 \mu l/min$ SiH$_4$; oxygen, 125 ml/min; nitrogen, 100 ml/min; nitrogen from GC column, 40 ml/min.
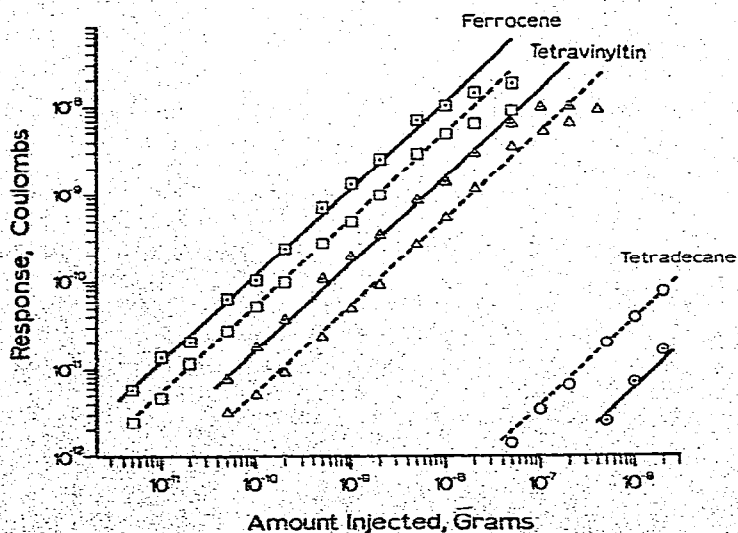

Fig. 6. Calibration curves of ferrocene, tetravinyltin, and tetradecane at optimum (full line) and off-optimum (dashed line). Oxygen flow-rates; ———, 125 ml/min; — — —, 100 ml/min. Nitrogen flow-
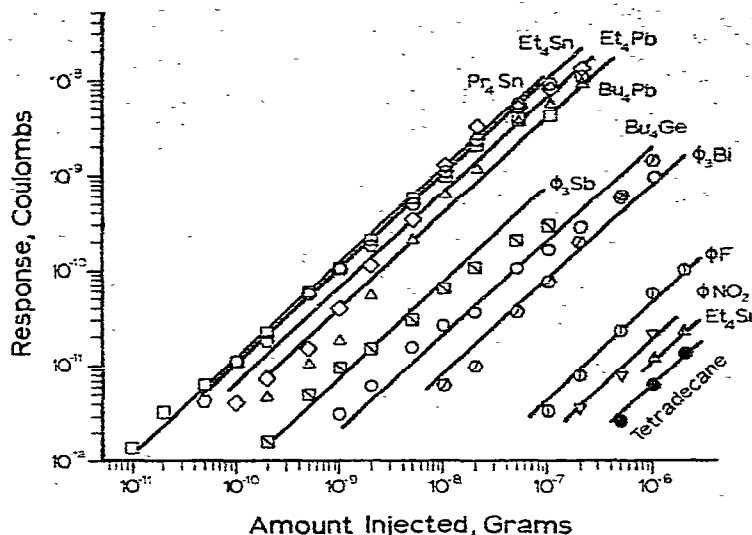
Fig. 7. Calibration curves for tetrapropyltin, tetraethyltin, tetraethyllead, tetrabutyllead, triphenyl-antimony, tetrabutylgermane, triphenylbismuth, fluorobenzene, nitrobenzene, tetraethylsilane, and tetradecane.
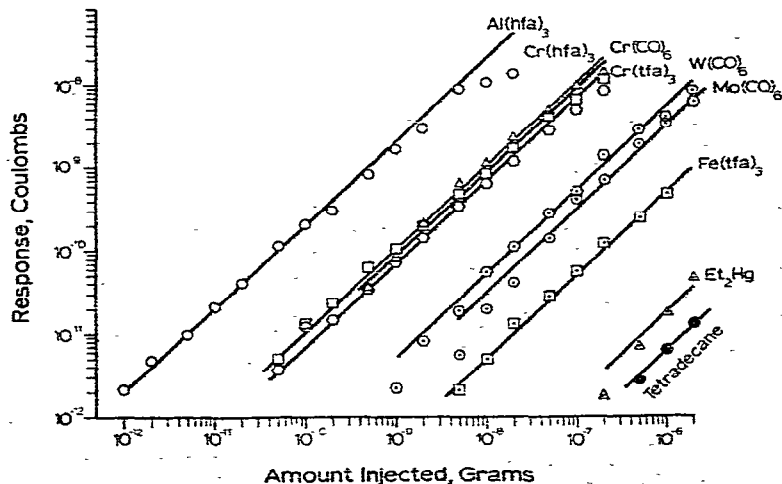

Fig. 8. Calibration curves for aluminum hexafluoroacetylacetonate, chromium hexafluoroacetyl-acetonate, chromium hexacarbonyl, chromium trifluoroacetylacetonate, tungsten hexacarbonyl, molybdenum hexacarbonyl, iron trifluoroacetylacetonate, diethylmercury, and tetradecane.

emphasizing. The slopes have all been drawn at precisely 45° angles, i.e., the angle of a linear plot. The linear range for all well-responding compounds is three decades.

The calibration curves for a variety of compounds containing As, P, Cl, Br, Se, and S are not shown. Response was quite low and thus of no apparent analytical interest, and peaks were mostly inverted. (Negative response is designated by a minus sign in the selectivity column of Table I.) Chlorobenzene, bromobenzene and tri-

butylphosphate changed from negative to positive response as their concentrations were increased.

The analytical interest rests obviously with the typical metal compounds. Here it appears that it is indeed the metal that dominates response. For example, the organo-tin compounds produced very closely spaced calibration curves, tetrabutyllead behaved very similar to tetraethyllead, and the responses from the two chromium chelates clustered around that of chromium hexacarbonyl. (Apparently, the presence of fluorine in small amounts is not particularly detrimental.) The only notable exception is found in the disparate behavior of the two iron compounds; however, it may be well to remember that iron trifluoroacetylacetonate is notorious for decomposing during gas chromatography.

The danger of solute decomposition prior to detection is of course always present, both inside and outside the chromatographic system. Experimentally, it is difficult to remedy, or even to define precisely, in the pertinent range between 10^{-13} and 10^{-9} g. Some of the reported minimum detectable amounts may therefore be too high, and comparisons of response should be approached with caution.

The sensitivity of the silane-doped HAFID for the well-responding metal-organics is quite good. The response of $Al(hfa)_3$, for instance, reaches saturation in the HAFID at a level which would barely start to show up in a regular FID. A few chromatograms taken at high sensitivity are shown in Fig. 9.
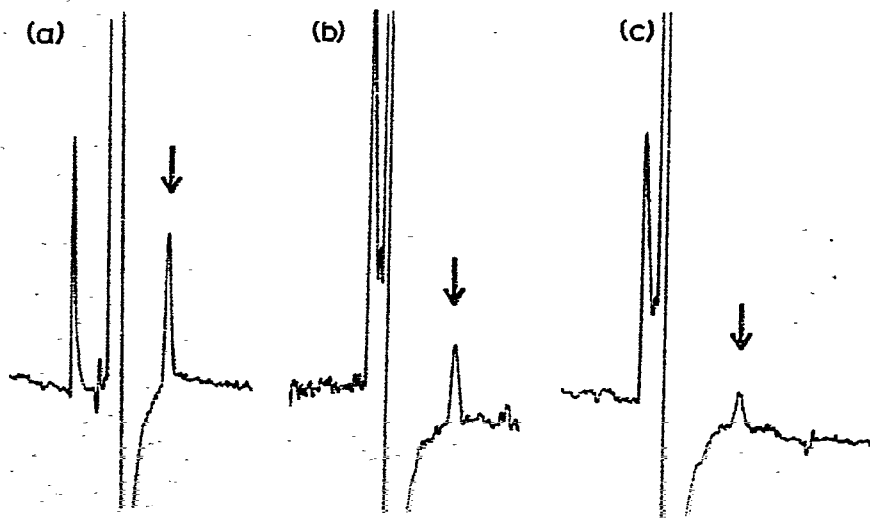

Fig. 9. Typical chromatograms of model compounds at high sensitivity (1×10^{-11} a.f.s.), at column temperatures as indicated. (a) 5 pg $Al(hfa)_3$, 50°; (b) 10 pg ferrocene, 145°; (c) 50 pg $Cr(tfa)_3$, 170°.

More important than sensitivity, however, may be selectivity. A great variety of metalorganics occur and often play important roles in our animate and inanimate environment. Some of them are volatile, and it seems reasonable to assume that we may not even be aware of their presence in many cases. The extent to which an analytical method discriminates against the organic background, is often the decisive factor in the analysis of biological or environmental samples. A demonstration of

selectivity is provided in Fig. 10. It was made possible by the fact that the HAFID is but little disturbed by changes in column bleed, nitrogen flow, etc., that come about by temperature programming. The chromatogram reproduced in Fig. 10 includes some of the better-responding organometallics, some hydrocarbon standards, and piaselenol as an example of a weakly and negatively responding compound. The injected amounts do vary (by six orders of magnitude if we include the solvent in this comparison) for proper peak display.
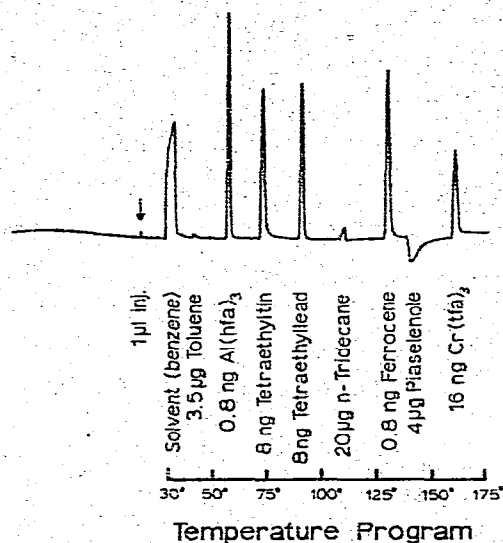

Fig. 10. Temperature-programmed chromatography of model compounds.

This chromatogram may well prompt the question why a particular compound responds as it does, and what distinguishes one metal from the other in this regard. It is fortunate that knowledge of the response mechanism of a detector is not required for its effective analytical application, because there is no answer available to this question at present.

One of us (H.H.H.) has attempted to formulate possible mechanisms in his thesis; however, without mass spectrometric sampling of various detector regions little can be securely established. All that is possible to do at this time is to point out some relevant facts and offer some highly speculative comments.

One of the predominant features of the HAFID is its large baseline current (BLC). At the customary electrode height of 50 mm above the jet tip it is $2.2 \cdot 10^{-9}$ A, at 10 mm height it is $5.7 \cdot 10^{-9}$ A (values taken from the experiment shown in Fig. 2). The highest peak height ever recorded at 50 mm [from Al(hfa)$_3$] was $2.6 \cdot 10^{-9}$ A —less than the BLC drop between 10 and 50 mm. It would therefore be possible to assume that the (combustion products of the) organometallic may simply act in charge transfer reactions, converting the charge carriers of the BLC to species less prone to neutralize before reaching the collector electrode.

As can be seen from Fig. 2, response for ferrocene diminishes at low electrode height, i.e., the ferrocene does not form appreciable amounts of additional ions in or

close to the flame. Thus, straightforward thermal ionization can be pretty well excluded. This is corroborated by the following consideration:

The HAFID flame is capable of melting a 0.25-mm-diameter rhodium wire (m.p. 2239 °K) and its temperature is probably not far from 2373 °K (the temperature of a premixed H_2/air flame[5]). For comparison, thermal ionization in an air/propane flame of 2200 °K was estimated from the Saha equation to convert one out of every 1000 free atoms of aluminum to an ion[6]. The HAFID, however, collects one ion for every ten molecules of Al(hfa)$_3$. Clearly, thermal ionization could not alone be responsible for this large response.

Chemi-ionization of tin has been proposed to follow the following reactions[7]:

$$Sn + OH \rightarrow SnOH^+ + e$$
$$SnO + H \rightarrow SnOH^+ + e$$
$$SnOH^+ + H \rightarrow Sn^+ + H_2O$$
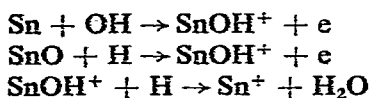
Generally, chemi-ionization of metals in H_2/O_2 flames is thought to occur by the reaction

$$A + H_3O^+ \rightarrow A^+ + H_2O + H$$

with the ionization at maximum when the ionization potential of the metal A is ca. 7.5 eV[8]. The elements responding best in the HAFID do have ionization potentials between 6 and 8 eV, but there appears little correlation between response and ionization potential otherwise.

Furthermore, any reasonable explanation of the mechanism of the HAFID will have to account for the fact that response peaks at some 5 cm above a flame only a few millimeters tall; not to speak of the fact that silane (or a similar species) has to be present to obtain maximum response.

The BLC of the HAFID is very large, but the species which carry the charges and their distribution have not been established. The FID (which has a very small BLC) has been closer scrutinized[9]. Its predominant charge carriers, besides electrons, are H_3O^+ and OH^-. When the FID responds to hydrocarbon, the predominant cation is H_3O^+, formed by charge transfer from the primary ion CHO^+ (ref. 10). Not all of the questions concerning the mechanism of the FID, however, have yet been settled either[11].

If the same species that are found in the FID are also assumed to dominate ion distribution in the HAFID, H_3O^+ (or larger clusters) should be the major BLC carrier. That may change when SiH_4 and combustion products from the metalorganic are introduced. Though done in a different context and system, it is interesting to note that Cheng and Lampe, in a study of positive ion reactions in SiH_4/H_2O, found that the most rapid reaction was hydride abstraction leading to the SiH_3^+ ion[12].

It would be interesting to see what happens to the silane and metal species above the flame; whether a chemi-ionization reaction between them produces the response; whether they are part of a chain leading to more stable ion carriers; and what that final charge-carrying species is. However, such a study is beyond our instrumental capability. It would appear, though, that similar silane-doped systems should also be of substantial interest to other areas of chemistry, well outside the analytical context.

ACKNOWLEDGEMENTS

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