

CHROM. 13,858

RESPONSE ENHANCEMENT BY METAL DOPING OF A SILICON-SELECTIVE FLAME IONIZATION DETECTOR FOR GAS CHROMATOGRAPHY

M. A. OSMAN and H. H. HILL, Jr.*

Department of Chemistry, Washington State University, Pullman, WA 99164 (U.S.A.)

(Received February 26th, 1981)

SUMMARY

A detector selective for silicon-containing compounds eluting from a gas chromatograph was constructed by modifying a commercial flame ionization detector. This detector exhibited a sensitivity for silicon-containing compounds in the nanogram range and a selectivity for these compounds over normal hydrocarbons of approximately 2500. Both the sensitivity and the selectivity of this detector were increased by doping with a variety of metal compounds. When optimum amounts of vapors from organometallics were bled into the detector's hydrogen atmosphere, the minimum detectable amount of the detector to a silicon-containing standard was found to decrease to 50 pg. The sensitivity varied with the quantity of organometallic vapor introduced into the detector, and, at high doping concentrations, silicon-containing compounds were detected as decreases in background current. The potential for the utilization of internal doping sources (such as metal wires, ribbons, or pressed pellets placed on or around the tip of the detector's flame jet) was also investigated.

INTRODUCTION

Accurate determination of oxygenated organic compounds from biological and environmental samples containing a mixture of complex organic molecules often challenges state-of-the-art analytical procedures. Specific analytical procedures are commonly based on chromatographic separation plus a selective detection method. Yet, unlike organic species containing nitrogen, phosphorus, halogens or sulfur, compounds containing oxygen cannot be detected selectively with existing gas chromatographic (GC) methods. Also, the polar and reactive nature of these molecules encourages premature loss during analysis. The lack of specific trace-analytical procedures can lead to errors from interference by irrelevant components in the mixture.

In our laboratory, we have adopted the approach of tagging certain oxygenated compounds, such as acids, alcohols and phenols, with silicon by standard silylation procedures and then selectively detecting these compounds after GC with a hydrogen-atmosphere flame ionization detector (HAFID) that is selective for silicon¹. This procedure addresses both the problem of quantitative analytical manipulation of these polar compounds and that of selective detection. Studies reported in

this paper concern the further investigation, characterization and development of this silicon-selective detector.

While other methods of selective silicon detection exist for GC, they are generally expensive and not readily available for interfacing with a gas chromatograph²⁻⁶. A silicon-selective HAFID, however, can be rapidly constructed from a commercially available flame ionization detector (FID) without modification of the existing GC interface. This conversion is accomplished by simply interchanging the oxygen and hydrogen inlets so that an oxygen-fed flame burns in a hydrogen atmosphere. Detector housing geometries require slight modifications to form a narrow cylindrical tube with a collector electrode positioned about 10 cm from the flame. Under these conditions, silicon-containing compounds combust to form ions that are more efficiently transferred through the 10-cm gap to the collecting electrode than those formed from hydrocarbon compounds, providing selective detection of silicon-containing compounds even in the presence of non-silicon-containing compounds.

Earlier, it had been observed that, if ferrocene was added to the hydrogen atmosphere, an enhancement in the response to silicon-containing compounds was obtained⁷. For larger quantities of ferrocene, the response to silicon reversed and became negative, while normal hydrocarbons retained a positive response. The amounts of doping agent used in these first investigations were not specified, except to say that low doping levels enhanced response in a positive direction and higher doping levels produced a negative response. Experiments reported here are designed to define more precisely conditions under which these response phenomena are observed.

Doping the hydrogen atmosphere by the introduction of small quantities of vapors originating from an external source complicates operation of the detector and, for routine use, is undesirable. Introducing doping reagents within the detector may be a preferred configuration for the silicon-selective HAFID. Such *in situ* doping methods for GC detectors are not new. In the early stages of the now extremely successful nitrogen-phosphorus detector (NPD), doping was achieved by the use of an alkali-coated wire inserted into the flame or pressed pellets of alkali salts upon which the analytical flame burned. In this study, similar approaches to doping are investigated for the silicon-selective detector.

EXPERIMENTAL

Instrumentation and detector design

A standard FID on a Hewlett-Packard (HP) 5710A gas chromatograph was converted into a HAFID as shown in Fig. 1. Fig. 2 illustrates the four principal parts of this modified detector. Part A is simply the base of the FID housing of the HP instrument, with the exception that the entrances for hydrogen and oxygen are reversed from their normal operation. Hydrogen was introduced into the detector through an orifice 20 mm above the jet tip, and oxygen entered the detector cavity through the flame. Part B is the standard stainless-steel jet tip that accompanied the instrument; it consisted of a 0.5 mm I.D. tube extending from the column exit through a heated zone in the detector housing (part A). The tip of this jet, where the flame burned, was drilled out to an I.D. of 1.5 mm for a depth of 5 mm to reduce the frequency of solvent "flame out"—a phenomenon that can occur when large amounts

HAFID (Si)

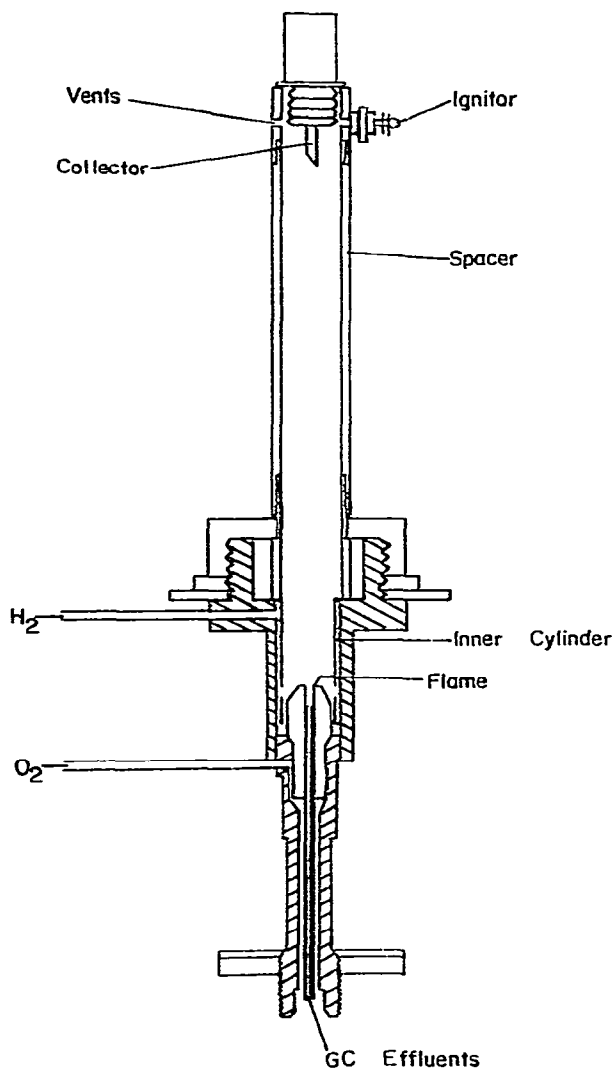


Fig. 1. Silicon-selective FID.

of a combustible compound enter the flame zone, temporarily starving the flame of oxygen.

Part C in Fig. 2 is the inner cylinder of the detector, which was machined to direct the hydrogen flow to the base of the detector by adapting a stainless-steel tube (8 mm I.D.) to extend into the detector well and terminate below the jet tip. Hydrogen traveled down the outside of this tube and mixed with jet gases at the tip.

HAFID (si)

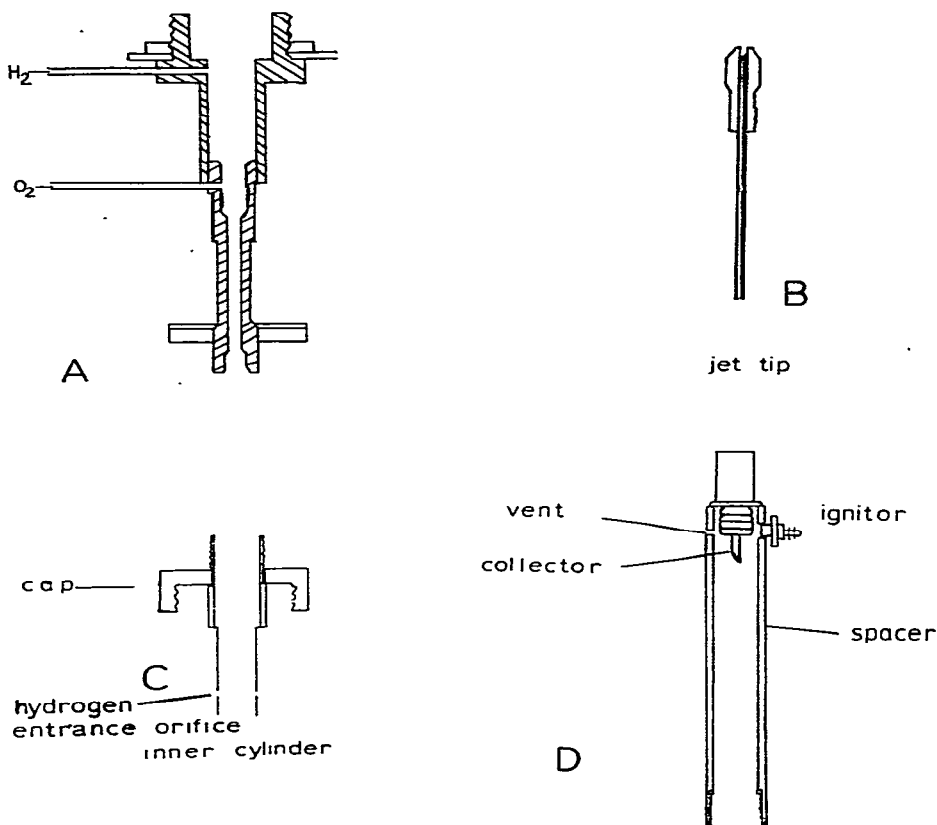


Fig. 2. Components of the silicon-selective detector.

Part D of Fig. 2 is a narrow chimney consisting of several variable spacers, with male- and female-threaded fittings, through which all gases left the detector. Spacers could be stacked together in multiple combinations to select a desired separation distance between the flame and the collecting electrode, which was mounted in the cap of this chimney assembly. The negative terminal of a 90-V Eveready battery Model No. 490 provided voltage to the collector electrode, while the positive terminal was connected to the amplifier input on the chromatograph. After amplification, the signal was recorded with a Sargent-Welch SKR strip-chart recorder.

Operating procedure

The GC column used throughout this work was a 6 ft. \times 2 mm I.D. borosilicate column packed with Superpak 20M (Analabs, New Haven, CT, U.S.A.).

Helium was used as carrier gas at a flow-rate of 40 ml/min. The injection port was maintained at 200°C, the detector at 250°C, and the oven temperature at 60°C. All valves and regulators, except those controlling the hydrogen flow, were calibrated by the soap-film technique. Hydrogen flow was determined by the displacement of water in a 1-l volumetric flask.

Although a large amount of hydrogen was used with this detector (often 1.6 l/min), flame ignition was safe, reproducible and even quiet if the proper procedure was followed. Oxygen was introduced through the jet tip at a rate of 100 ml/min. After 1 min of this purging, current was passed through the glow plug ignitor by a 3-V Hobby battery (Model 900), and hydrogen was allowed to enter the detector at 300 ml/min. A low, muffled sound indicated proper flame ignition, while a loud pop usually meant that flows were not adjusted well or that residual hydrogen had not been sufficiently swept from the detector. When the flame was ignited, the tip of the stainless-steel jet glowed red-orange and water vapor condensed readily on cold objects held in the exiting gases. After flame ignition, gas flows were adjusted to the desired rates with appropriate needle valves or pressure regulators.

External doping source

A survey of detector responses to a variety of test compounds was conducted for a number of doping concentrations of pentacarbonyliron in the hydrogen atmosphere; Fig. 3 shows a flow diagram of the apparatus used for pentacarbonyliron doping. Nitrogen is connected to the diffusion tube through a rotameter. The flow-rate was controlled at 10 ml/min of nitrogen, and the tank pressure was 60 p.s.i. at the top of the trap. The diffusion tube consisted of a 0.25-in. stainless-steel tube connected to a 0.25-in. stainless-steel tee-piece. The diffusion tube was connected by an on-off valve and an 0.125-in. tee-piece to the main hydrogen line. The tube was maintained at a constant temperature in an isothermal bath.

Three types of isothermal baths were used. One was made by adding liquid nitrogen to a Dewar vessel containing *n*-pentane until a slush was formed⁸; the

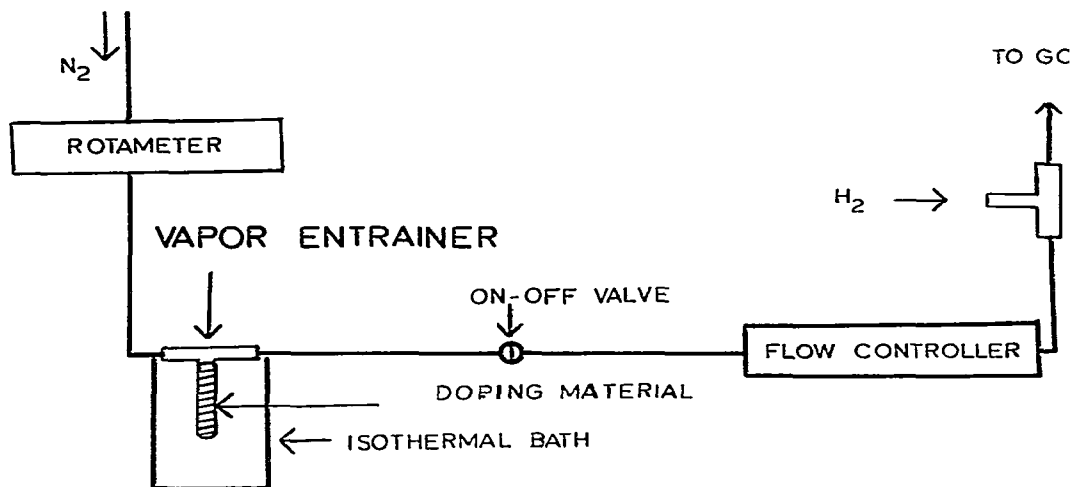


Fig. 3. Flow diagram for pentacarbonyliron doping (nitrogen tank pressure was 60 p.s.i.).

isothermal temperature of this slush bath was -131°C . The second was made by the addition of small lumps of dry ice to a selected solvent, acetonitrile or ethylene glycol, until a slight excess of dry ice remained⁹. The temperature of the acetonitrile-dry ice bath was a constant -42°C and that of the ethylene glycol-dry ice bath was a constant -15°C . The third type consisted of a single component such as pure liquid nitrogen (-195°C), ice (0°C) or water at room temperature (22°C).

Twenty-two compounds representing a wide variety of chemical structures were tested. Three primary test compounds, chosen for similarity in chromatographic retention times, were tetraethylsilane (Pfaltz & Bauer, Stanford, CT, U.S.A.), tetravinylsilane (Alfa Products, Danvers, MA, U.S.A.) and decane (Sigma, St. Louis, MO, U.S.A.). Each was diluted with glass-distilled hexane (Burdick & Jackson Labs., Muskegon, MI, U.S.A.) to produce the desired concentrations. Other reagents and test compounds used were ferrocene (Aldrich, Milwaukee, WI, U.S.A.), tri-*n*-butyl phosphate, triethyl phosphate, tetrabutyltin, tetrabutyllead, 2-methylbenzothiazole, bromobenzene, 1-bromododecane, aniline, 2-ethylhexylamine, nitrobenzene, fluorobenzene, chlorobenzene, dodecanol, *n*-hexyl ether, camphene, nitromethane, tetradecane and *n*-butyl ether (Chem Service, West Chester, PA, U.S.A.). Each compound was diluted with hexane to $100\ \mu\text{g}/\mu\text{l}$ except the silicon-containing compounds, which were diluted to $100\ \text{ng}/\mu\text{l}$, and the organometallics and phosphorus-containing compounds were prepared in concentrations between $1\ \mu\text{g}/\mu\text{l}$ and $10\ \mu\text{g}/\mu\text{l}$. Responses were converted into an ionization ratio (ϵ), the number of ions responding per number of molecules of test compound injected. These ratios were calculated from the relation $\epsilon = R/MF$, where R is the response in coulombs, M is the number of moles of test compound injected and F is the Faraday constant. Results are reported in Table I as $-\log \epsilon$ or, by analogy with *p*-functions, as p_{ϵ} . Pentacarbonyliron was purchased from Alfa Products.

Calibration graphs shown in Fig. 6 for tetraethylsilane, tetravinylsilane and decane were established at an electrode height of 110 mm to determine the dynamic linear range of the detector. In this study, the temperature of the diffusion tube was maintained at -15°C with an ethylene glycol-dry ice bath; all other parameters remained the same as noted above.

Internal doping source

Apparatus for initial investigations of self-contained doping methods were simple constructions where a metal wire or ribbon was wrapped around a quartz tube mounted on the original jet tip as shown in Fig. 4, or a pressed pellet of metal salt was fitted to the tip of the quartz tube, as shown in Fig. 5. Ribbons and wires that were investigated included those of aluminium, copper, molybdenum, brass, chromium, magnesium and iron. Copper sulfate, magnesium sulfate and ferric sulfate were investigated in pellet form.

Responses in these doping modes were evaluated by repetitive injections of 100 ng of tetraethylsilane and 1 mg of decane. The following testing procedure was employed. First, the flame was allowed to equilibrate for 5 min after ignition, then test compounds were injected in rapid succession every 5 min for 1 h. The flame was then extinguished for 15 min and re-ignited, and the injection procedure was continued for an additional 40 min.

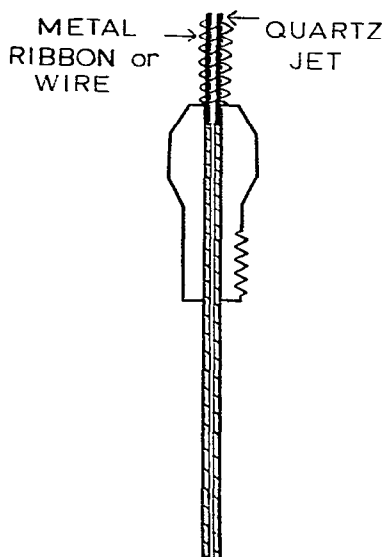


Fig. 4. Quartz jet tip with metal wires.

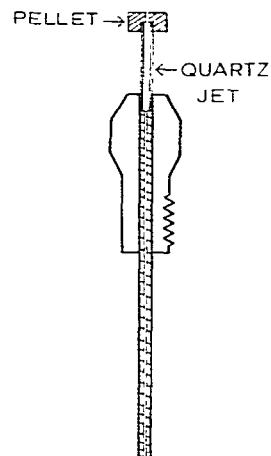


Fig. 5. Quartz jet tip with pressed pellet.

RESULTS AND DISCUSSION

Doping with external source

The objective in this first set of experiments was to characterize responses in the metal-doped and non-doped HAFID of 22 test compounds representing metal-, phosphorus-, sulfur-, halogen-, nitrogen- and oxygen-containing organic compounds, along with normal hydrocarbons. Table I provides a listing of the negative log of response efficiencies (p_e) of each test compound as a function of the quantity of pentacarbonyliron added to the hydrogen atmosphere. Compounds are listed in order of decreasing sensitivity in the non-doped condition.

The most obvious observation that can be made from Table I is that compounds listed at the top have p_e values around 6.00, while those at the bottom have p_e values around 9.00. Compounds with p_e values around 6.00 will be called the "responding" compounds and include ferrocene, tetravinylsilane, tetraethylsilane, tri-*n*-butyl phosphate and triethyl phosphate. Compounds that fall within the category of "non-responding", (p_e values around 9.00) include aniline, 2-ethylhexylamine, nitrobenzene, fluorobenzene, chlorobenzene, dodecanol, decane, *n*-hexyl ether, camphene, nitromethane, tetradecane, and *n*-butyl ether. These general observations corroborate previous reports that the detector is some three orders of magnitude more sensitive to the best responding compounds than to other organic compounds. Compounds falling between these response limits are referred to as "quasi-responding" compounds; they include tetrabutyltin, tetrabutyllead, 2-methylbenzothiazole, bromobenzene and 1-bromododecane.

Under the conditions of this investigation, where doping concentrations and gas flow-rates were at best crudely controlled, it was difficult to return to previous

TABLE I
PENTACARBONYLIRON DOPING STUDIES

Responses expressed as p_2 values (see text).

Compound (amount injected)	Non-doped	Liquid nitrogen (-195°C)	<i>n</i> -Pentane-liquid nitrogen (-131°C)	Acetonitrile-CO ₂ (-42°C)	Ethylene glycol-CO ₂ (-15°C)	Ice (0°C)	Water (22°C)
Ferrocene (1 µg)	5.98	6.0	5.93	5.95	5.98	6.01	5.84*
Tri- <i>n</i> -butyl phosphate (1 µg)	6.62	6.17	5.97	5.84*	5.87	5.85	5.86
Tetravinylsilane (100 µg)	6.79	6.38	6.28	6.28	5.97	5.97	5.95*
Tetraethylsilane (100 µg)	6.79	6.42	6.37	6.3	6.08	5.95	5.94*
Triethyl phosphate (1 µg)	6.87	6.43	6.35	6.23	6.19	6.06*	6.09
Tetrabutyltin (10 µg)	6.86	6.72	6.69*	6.73	6.79	6.73	6.82
Tetrabutyl-lead (10 µg)	7.59	7.16	7.12	7.07	7.03	6.98*	7.00
1-Bromo dodecane (100 µg)	8.07	8.00	7.88*	7.97	8.03	8.16	8.24
2-Methylbenzothiazole (100 µg)	8.13	7.85	7.8	7.06*	7.41	7.34	7.47
Bromobenzene (100 µg)	8.25	8.11	7.9*	8.25	8.15	8.17	8.19
2-Ethylhexylamine (100 µg)	8.61	8.74	8.57	8.35*	8.63	8.66	8.71
Aniline (100 µg)	8.86	8.73	8.67	8.71	8.67	8.50*	8.73
Nitrobenzene (100 µg)	9.07	8.53	8.55	8.46*	8.5	8.48	8.61
Dodecanol (100 µg)	9.13	8.78	8.56*	8.83	8.83	8.78	8.78
Fluorobenzene (100 µg)	9.24	9.06	8.62	8.7	8.64	8.67	8.45*
<i>n</i> -Hexyl ether (100 µg)	9.25	8.95	8.62*	8.73	8.95	8.83	8.89
Chlorobenzene (100 µg)	9.35	8.61	8.33*	8.49	8.75	8.91	8.84
Decane (100 µg)	9.37	9.00	9.15	8.77	8.94	8.64*	8.77
Camphane (100 µg)	9.57	9.02	9.17	8.87*	9.17	9.02	8.96
Tetradecane (100 µg)	9.4	8.86	8.56	8.70	8.80	8.50*	8.86
<i>n</i> -Butyl ether (100 µg)	9.77	9.77	9.59	9.59	9.59	9.59	9.41*
Nitromethane (100 µg)	9.89	9.59	9.19*	9.59	9.5	9.5	9.59

* Most sensitive response obtained.

settings and obtain previous results. When such experiments were performed, responses within a factor of 2 of a previous response could be expected. Since electronic integration was not employed to obtain area counts, errors in the measurements of small peaks resulted in relatively large fluctuations when calculating response efficiencies. Further, since response efficiencies for many compounds were small, large quantities of a compound often had to be injected in order to obtain a measurable response. Often as much as 100 μg were injected into the GC column, which resulted in asymmetric elution profiles due to overloading of the column. The degree to which asymmetry affected the hand-calculated area measurements varied with the injection technique and the operating conditions. A combination of such error-introducing operations caused the data obtained for the less sensitive compounds to become more scattered and less dependable than those collected for the test compounds of high sensitivity. Nevertheless, trends in responses of test compounds could be detected as the concentration of pentacarbonyliron was increased in the hydrogen atmosphere.

As expected, test compounds containing silicon exhibited an increase in response with introduction of pentacarbonyliron. Unexpected, however, was the fact that all responses of test compounds were enhanced when pentacarbonyliron was added to the hydrogen atmosphere. Even decane, a compound without heteroatoms or functional groups, exhibited an increase in response when pentacarbonyliron was present. Decane response more than doubled between non-doped and doped conditions. As the concentration of pentacarbonyliron was increased, the response of decane did not follow a clearly identifiable trend. With increasing concentration, responses for decane were 2.3, 1.7, 4.0, 2.7, 5.3, and 4.0 times higher than that obtained under non-doping conditions. Other test compounds with similar chemical compositions showed similar increases in response for the doped system over the non-doped system.

Such results have important implications both for the elucidation of the mechanism of this detector and for development of this detector as an analytical tool. They indicate that the doping process is not the primary source of selectivity in the detector, but rather serves simply to enhance (most probably through charge-transfer reactions with primary ions) the collection efficiency of the detector. From a practical viewpoint, these results mean that only detector sensitivity (not detector selectivity) will be most efficiently increased by the use of doping agents. Although oxygen, nitrogen, and halogenated compounds were also found to have reduced responses in the detector, phosphorus-containing compounds were identified as potentially interfering species. Responses to these compounds were found to be as sensitive as those to silicon compounds. Moreover, phosphorus compounds are more likely to be present in such matrixes as environmental or biological samples where silylation procedures are used to tag compounds of interest for detection with this silicon-selective flame method.

Fig. 6, a calibration graph for tetraethylsilane, tetravinylsilane and decane, shows a linear response of more than three decades for the silicon-containing compounds from 500 pg to 1 μg injected. Decane, however, had a narrow linear range, which affected selectivity calculations. When lower amounts of decane were injected, the selectivity was almost 10,000, and, at higher levels, it was much more than 10,000.

Selectivity of the silicon-containing compounds over the carbon-containing

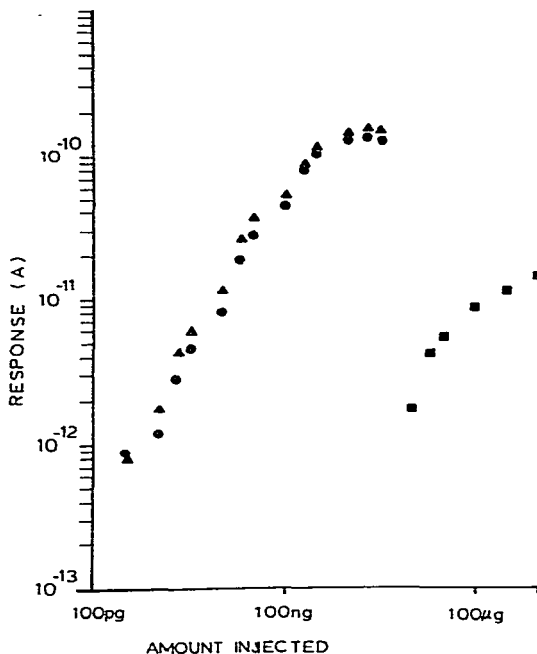


Fig. 6. Calibration graph for tetraethylsilane (▲), tetravinylsilane (●) and decane (■). Conditions: electrode height, 110 mm; hydrogen, 1.6 l/min; oxygen, 130 ml/min; helium, 40 ml/min; 10 ppm of penta-carbonyliron doping.

compounds is about four decades according to the calibration graph shown in Fig. 6, but Table I showed a selectivity of about three decades for the same compounds. In the former case, the selectivity was calculated by comparing the responses in amperes, which depend only on the peak height. Since the hydrocarbon peak was in the non-linear range, the results favour the silicon-containing compounds. In Table I, the calculations were based on peak areas. A comparison of the response to 100 μg of decane with that to 100 ng of tetravinylsilane based on peak areas calculated in terms of coulombs (data taken from Fig. 6) gave a selectivity of about three decades, the same as in Table I.

Since silicon-containing compounds exhibited a trend of increased sensitivity with increased doping, responses to these compounds, plus those of ferrocene, were evaluated at higher doping concentrations by increasing the flow of transfer gas through the entrainment tube. Fig. 7 is a histogram of the peak-height responses of these three compounds as a function of doping-agent concentration. The non-doped condition and doped conditions up to a mixing ratio of 40 ppm are data taken from Table I. Doping values of 60, 90, 130 and 200 ppm were obtained by increasing the flow of transfer gas through the entrainment tube at 22°C. When flow-rates were increased, detector noise increased to the point at which non-responding compounds such as decane or tetradecane could no longer be detected. Continued increase in the amount of doping agent decreased the response to the silicon-containing compounds more significantly than that to the ferrocene compound, and, at even higher doping

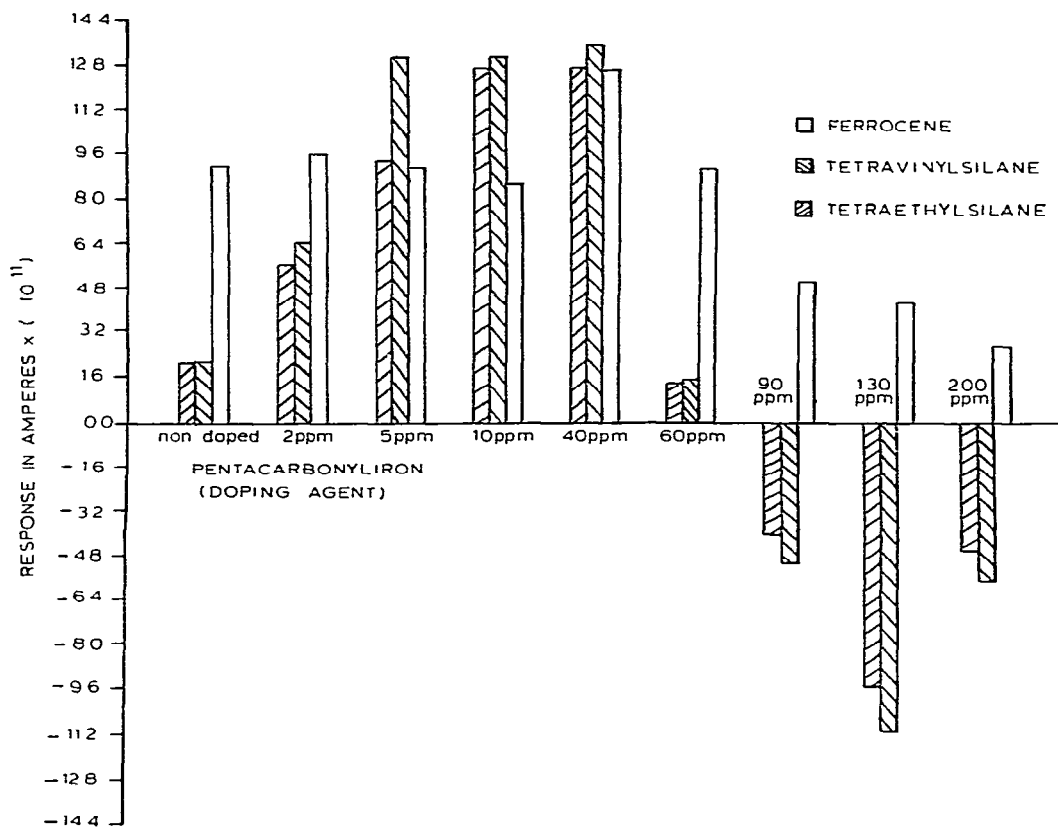


Fig. 7. Histogram of pentacarbonyliron-doping study.

concentrations, responses to silicon-containing compounds became negative, while those for ferrocene were less sensitive and remained positive.

Fig. 8 shows typical chromatograms of two silicon-containing compounds under two different modes of operation (the positive peak mode, and the negative peak mode). Note that the solvent, hexane, responded positively even when the silicon response was negative.

By switching from one mode to the other, silicon-containing compounds can be easily identified in the presence of hydrocarbons, and both qualitative as well as quantitative information can be achieved. More studies are necessary before it will be clear if silicon compounds can be distinguished from other hetero-organic species or if co-elution of non-silicon-containing compounds with silicon-containing compounds will affect response.

Doping with internal source

The most obvious internal source of metal for doping the HAFID is from the stainless-steel jet tip, which glows bright orange in the hydrogen atmosphere when the flame is burning. Figs. 9, 10 and 11 present results of a comparison between a stainless-steel jet tip and a quartz jet tip. In Fig. 9, the response to the hydrocarbon

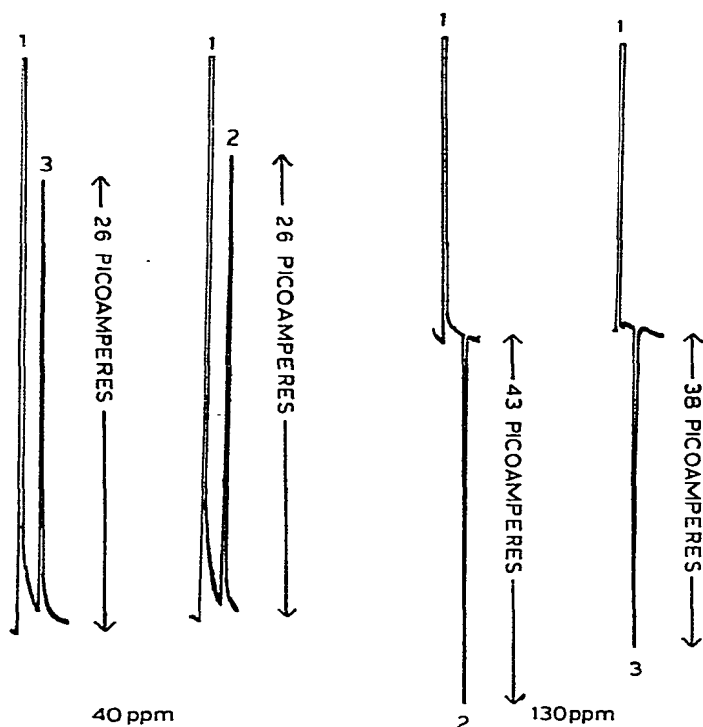


Fig. 8. Chromatograms of tetraethylsilane (100 ng; peak 2) and tetravinylsilane (100 ng; peak 3) in hexane (peak 1) for positive and negative detection modes (pentacarbonyliron doping).

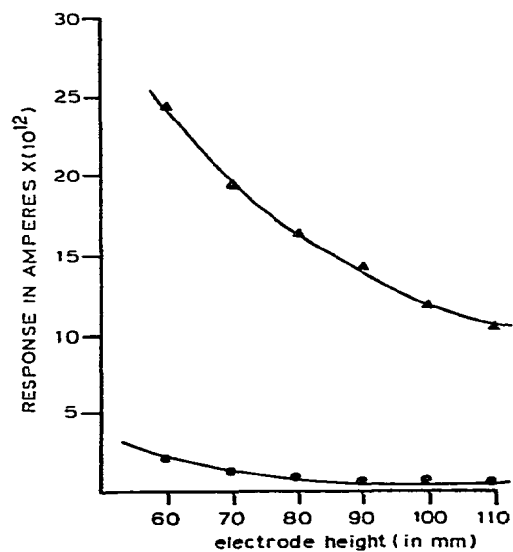


Fig. 9. Electrode height study. Obtained with stainless-steel jet tip (▲) and quartz jet tip (●) for 1-mg injections of decane.

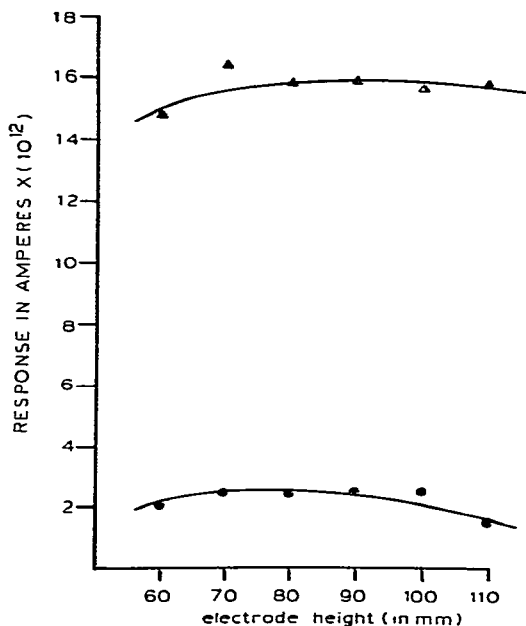


Fig. 10. Electrode height study. Obtained with stainless-steel jet tip (\blacktriangle) and quartz jet tip (\bullet) for 100-ng injections of tetraethylsilane.

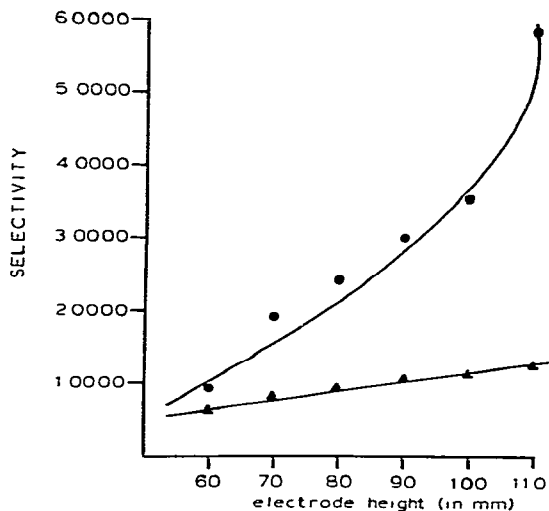


Fig. 11. Selectivity at different electrode heights using stainless-steel (\blacktriangle) and quartz (\bullet) jet tips for tetraethylsilane and decane.

standard, decane, is plotted as a function of the position of the collecting electrode above the flame for both the stainless-steel jet and the quartz jet. In this study two effects are evident. First, as the electrode height is increased, response is reduced; secondly, hydrocarbons respond more sensitively with a stainless-steel jet than with a fused-silica jet. The former effect may be credited to diffusion and mutual charge repulsion of the positive ions to the walls of the detector, while the latter effect may be a function of the temperature in the pre-combustion zone of the flame. With the stainless-steel jet, heat is conducted away from the oxygen-rich pre-combustion zone more efficiently than it is with the quartz jet. Thus, with the quartz jet, organic compounds are more completely combusted to CO_2 and H_2O before entering the flame.

In Fig. 10, tetraethylsilane, the silicon-containing standard, also showed increased response in a stainless-steel jet when compared with that in a quartz jet, but the response remained essentially constant throughout studies in which the collecting-electrode height was varied. Constancy of response at the various electrode heights may be indicative that response-ions of silicon-containing compounds are less mobile than those produced from hydrocarbons, and, rather than rapidly diffusing to the walls of the detector, remain in the space above the flame to be more efficiently collected by the electrode. The greater sensitivity of tetraethylsilane with the stainless-steel jet compared to that with the quartz jet does not indicate that metal doping from the metal jet is important, since arguments based on the temperature of the pre-combustion zone may also be made.

TABLE II
SUMMARY OF RESULTS OF METAL WIRE AND RIBBON DOPING

Quartz tube	Iron wire	Aluminum foil	Nickel wire	Chromium ribbon	Molybdenum ribbon	Brass ribbon	Platinum wire	Copper ribbon	Magnesium ribbon
Noise level (pA)	1.3	6.4	1.3	0.6	1.6	1.3	1.3	1.9	5.6
Values of p_t for tetraethylsilane (100 μ g)									
10 min	5.58	5.37	5.81	5.48	5.97	5.62	5.84	5.22	5.31
60 min	5.58	5.68	6.22	5.68	6.24	5.89	6.01	5.51	5.29
90 min*	5.5	5.5	6.26	5.79	6.2	5.89	6.06	5.49	5.53
Values of p_t for decane (100 μ g)									
30 min	9.99	—**	10.07	10.02	9.96	9.45	10.1	10.07	—**
90 min	9.96	—**	10.12	10.29	10.17	9.51	10.29	10.17	—**

* The flame was turned off after 60 min for a period of 15 min.

** No visible peak detected for 1 mg of decane injected.

Fig. 11 compares the selectivity found with the stainless-steel jet with that of the quartz jet. Note that selectivity here appears to be higher than that calculated from the data reported in Table I. This can be attributed to the higher amount (1 mg) of decane required in this study in order to obtain a measurable peak. This was particularly so at high electrode settings when the quartz jet was used. Thus, measurements were made in the non-linear response region for hydrocarbons, demonstrating that the selectivity of this detector becomes greater when large quantities of hydrocarbons are encountered.

A more decisive method to test internal metal doping is to introduce metal wires or ribbons into flames burning on quartz jets; Table II lists results of such studies. In all, nine doping metals were investigated: iron, aluminium, nickel, chromium, molybdenum, brass, platinum, copper and magnesium. For each metal, responses at 10, 60, and 90 min after flame ignition were obtained for 100 ng of tetraethylsilane, and responses after 30 and 90 min for 1 mg of decane were obtained to evaluate the short-term stability of detector response. The flame was extinguished after the first 1 h of burning time for 15 min, then re-ignited for the injection at 90 min.

In every instance, tetraethylsilane showed a substantial increase in response over that obtained with the non-doped system, while response to decane remained similar to that obtained with the pure quartz tube. Aluminium and magnesium exhibited the greatest amount of enhancement for tetraethylsilane, but, as can be seen from the table, the noise level of the detector during these studies was also higher, and no significant gain in the signal-to-noise ratio was obtained under these conditions compared with those involving less sensitive doping metals. Quantitative comparisons between different doping conditions should be made cautiously, since it was impossible to control the amount of metal that was introduced into the detector. It may simply be that aluminium and magnesium enhanced response more than the other metals because they were more efficiently introduced into the flame. With time, all responses for tetraethylsilane dropped significantly. A more suitable method for *in situ* doping is desirable if the analytical utility of such a method is to be realized.

Doping with metal salts as pressed pellets in the manner shown in Fig. 5 produced results similar to those obtained when metal wires and ribbons were used,

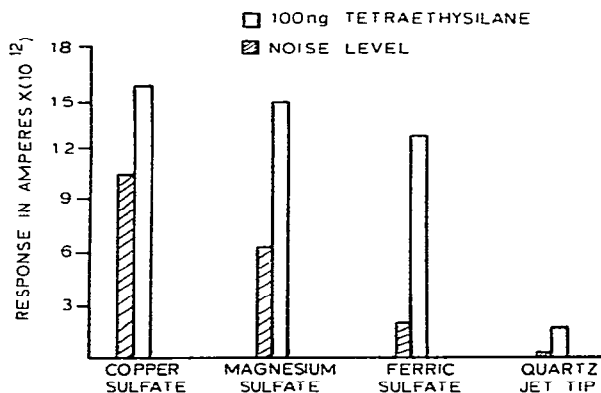


Fig. 12. Pressed-pellet study.

with enhanced sensitivity for tetraethylsilane accompanied by increased noise and instability of the detector. A histogram of responses and noise obtained for several pressed pellets of metal sulfates, along with those obtained for the non-doped quartz jet, is shown in Fig. 12.

These initial and somewhat cursory studies of internal doping systems for a silicon-selective FID have revealed possibilities for *in situ* metal doping. However, in these investigations, it was difficult to control the quantity of doping agent introduced into the flame, and the level of base-line noise was increased to a point where the gain in sensitivity did not appreciably increase the signal-to-noise ratio of the detector. Perhaps more carefully controlled internal doping systems, such as the use of metal silicate beads with uniform electrical heating, may provide a reliable method for doping.

ACKNOWLEDGEMENTS

This research was supported by grant No. GM 24970 from the Public Health Service. The authors would like to extend their appreciation to Dr. Karl Pool for his help in pressing pellets for this work.

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