Silicon Selective Non-Doped Hydrogen Atmosphere Flame Ionization Detector for Gas Chromatography

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A commercial flame ionization detector was converted to a gas chromatographic detector selective for silicon-containing compounds by simply interchanging the oxygen and hydrogen inlets so that the flame burned in a hydrogen atmosphere. The optimal configuration of various detector geometries was found to be a narrow cylindrical tube with the collector electrode positioned more than 10 cm from the flame. This configuration eliminated peak tailing which is prevalent in other designs. Helium was shown to be the carrier gas of choice since nitrogen reduced the sensitivity of the detector to silicon-containing compounds, but not to hydrocarbon compounds. The calibration curve for tetraethylsilane proved to be linear for about three orders of magnitude with a minimum detectable amount of 4 ng and a selectivity over decane of 2600. This corresponds to a silicon to carbon selectivity better than 1 × 10^4. The advantage of a silicon selective detector is demonstrated by comparing a chromatographic tracing of a mixture of n-alkanes and silylated n-alcohols to that of the same mixture obtained with a standard flame ionization detector. Three-microgram peaks of the silylated alcohols could easily be detected with the silicon selective detector while 3 µg of each alkane gave no response.

Silylation followed by gas chromatographic separation and detection is a routine analytical procedure (1) used for the determination of polar and reactive compounds such as amino acids (2), sugars (3), steroids (4), alcohols (3), etc. The silyl derivative, usually produced by substituting a trimethylsilyl, –Si(CH₃)₃ group for an active hydrogen, is generally less polar and more volatile than the parent compound, reducing its retention time in a gas chromatograph and minimizing column adsorption that can cause poor chromatographic resolution and quantification.

The most commonly used detection method for silyl derivatives is flame ionization, which relies only on the response characteristics of carbon atoms present in the silyl derivatives. Therefore there is no response discrimination between silicon-containing compounds and other carbon-containing compounds in the sample. Moreover, the FID frequently shows anomalous responses for organosilicon compounds. Availability of a GC detector selective for silicon would extend the scope of silylation methods by facilitating the analysis of complex mixtures. With a silicon selective detector, silylation would not only serve to deactivate and stabilize compounds of interest, but would also tag these compounds with silicon atoms to provide a more sensitive and selective analytical response.

Several attempts to selectively detect silyl derivatives have been reported in the literature. Fritz et al. (5, 6) doped an FID with methane to produce an unusually high background ionization and detected the elution of silicon-containing compounds as a decrease in this ionization. Morrow et al. (7) have interfaced a gas chromatograph to an atomic emission/absorption spectrometer and monitored the 2516-Å silicon line. Microwave emission detectors (MED) have also been used to produce the selective 2516-Å emission. Bostick and Talmi (6) used a reduced pressure (3–5 Torr) argon discharger while Quimby, Udén, and Barnes (9) employed an atmospheric pressure helium plasma to selectively measure nanogram quantities of organosilanes. Another, more indirect, approach to the selective detection of silyl derivatives is to introduce a chlorine atom into the structure of the silylating reagent so that the derivative can be detected with an electron capture detector (ECD) (10). None of these techniques are ideal for silicon detection: Fritz’s FID is not linear and the complication of methane doping is undesirable; emission methods require the use of expensive and cumbersome spectrophotometric equipment; and the ECD is not truly silicon-selective since it responds to all electron-capturing species in the sample.

In 1976, Hill and Aue (11) reported that when silane is added to an atmosphere of hydrogen in which an oxygen-fed flame burns, organometallic compounds efficiently ionize in the flame, providing a sensitive and selective GC detection method for metal-containing compounds. In a subsequent study (12), the effect on organosilane response of doping the hydrogen atmosphere with organometallics was investigated. As expected, they found that the metal doped flame system enhanced silicon ionization, but it did not produce a linear calibration curve. However, a non-doped hydrogen atmosphere flame system was found to exhibit a linear response curve while still providing good selectivity for silicon-containing compounds. The severe peak tailing reported in their work for silicon-containing compounds was attributed to chromatographic conditions rather than detector design.

This paper provides a more extensive characterization of the non-doped silicon selective detector system. Conversion of a commercial flame ionization detector to an improved version of the silicon selective system is described. Variables affecting the performance of the system such as detector geometry, gas flow, etc. are discussed in detail.

**EXPERIMENTAL**

**Instrumentation.** HAFID. A standard flame ionization detector on a Hewlett-Packard 5710A gas chromatograph was converted to a hydrogen atmosphere detector. Hydrogen was introduced into the detector atmosphere through an orifice 20 mm above the jet tip. Oxygen entered the detector cavity through the flame after traveling down the outside of the jet. The jet consisted of a 0.5-mm i.d. tube which extended from the column exit through a heated zone into the detector housing. The tip of the jet, where the flame burned, was drilled out to an internal diameter of 1.5 mm for a depth of 5 mm to reduce the frequency of “solvent flame out”—a phenomenon which occurs, when large amounts of a combustible compound enter the flame zone and temporarily starve the flame of oxygen. The negative terminal of a 9-V Eveready battery model 2490 provided potential to the
In all, three detector designs were investigated, each evolving from the former with variations in electrode position, internal diameter, and hydrogen introduction.

**First Design.** This design, shown in Figure 1, was patterned after a hydrogen atmosphere detector used for the determination of antiknock agents in gasolines (13). The FID collector electrode assembly was replaced by a stainless steel cap containing an electrode (the male pin of a BNC chassis connector), gas exits (1.5-mm i.d. drill holes), and an ignitor (a simple glow plug). The distance of the collecting electrode from the flame could be varied by inserting threaded cylindrical spacers of the appropriate length between the cap and the detector mount. The internal diameter of 11 mm in the lower region of the detector (the detector "well"), where the flame burned, was defined by the configuration of the FID, but the spacer and cap portion of the detector had a 19-mm i.d.

**Second Design.** As shown in Figure 2, the internal diameter of the spacer and collector electrode region of this design was reduced to 11 mm, creating a cylindrical detector cavity. This modification required four new detector parts: a detector "cap", a "spacer", a "connector sleeve", and a "fastening nut". The "cap" contained a collector electrode which was centered above the flame and an ignitor which was positioned on the side of the cap along with several exhaust vents. The "spacer" served to separate the cap with its collecting electrode from the lower portion of the detector. "Spacers" of varying lengths could be interchanged to alter the distance of the electrode from the flame. The "connector sleeve" and "fastening nut" were required to join the electrode assembly (cap and spacer) to the detector well.

**Third Design.** Figure 3 pictures a design which decreased the internal volume of the detector channel between the flame and the collector electrode and changed the flow pattern of hydrogen by adapting a stainless steel tube (8-mm i.d.) to extend into the detector well, terminating below the jet tip and just above the base of the detector. Hydrogen traveled down the outside of this tube to mix with the oxygen, GC carrier gas, and eluting compounds at the exit of the jet. All gases were then exhausted through the narrow chimney.

**Ignition.** 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 a minute of this purging, current was passed through the glow plug ignitor by a 3-V Hobby battery model 2900 and the 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. All valves and regulators, except those which controlled 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.

![Figure 1. First design of silicon detector](image)

![Figure 2. Second design of silicon detector](image)

![Figure 3. Third design of silicon detector](image)
FID. The flame ionization detector used in these studies was detector A of the dual FID unit, H.P. model 1882A, on a H.P. 5830A gas chromatograph with an H.P. 18850A terminal. Gas flows were 30 mL/min for hydrogen and 240 mL/min for air as recommended by the manufacturer.

**Chromatographic Conditions. HAFID Studies.** The GC column used throughout this work was a 6 ft × 2 mm i.d. borosilicate column packed with Ultra-bond 20 M (RFR Corp., One Main Street, Hope, R.I. [28381]. Nitrogen was used as the carrier gas at a flow of 20 mL/min when the jet tip had a 0.5-mm diameter and 40 mL/min when the jet tip was bored out to 1.5 mm. When helium was used as the carrier gas, flow was 43 mL/min. Injection port and detector temperatures were both maintained at 250 °C. The oven temperature was held at 65 °C during studies with tetraethyilsilane and decane. Changes in electrode height were investigated with a mixture of silylated alcohols and n-alkanes; the oven was programmed to remain at 50 °C for 2 min, then increase at a rate of 16 °C/min to a final temperature of 170 °C and hold for 2 min.

**FID Studies.** A 6 ft × 2 mm i.d. borosilicate column packed with Ultra-bond 20 M, 80/100 mesh which was similar to the column used in the HAFID studies was employed for the FID. Conditions of operation were the same as those in HAFID except that the mixture of silylated alcohols and n-alkanes was analyzed.

**Reagents.** The primary test compounds, chosen for their similar retention times, were tetraethyilsilane (Pfalz & Bauer, Inc., 375 Fairfield Avenue, Stanford, Conn. 06902) and decane (Altech Associates, 202 Campus Drive, Arlington Heights, Ill. 60004).

Each was diluted in glass distilled hexane (Burdick & Jackson Lab., Inc., 1953 S. Harvey Street, Muskegan, Mich. 49442) to produce desired concentrations. Other reagents and test compounds included dodocane, tetradeccane, and hexadecane (Altech Associates, 202 Campus Drive, Arlington Heights, Ill. 60004): 1-hexanol, 1-octanol, and 1-decanol (Chem Service, Inc., P.O. Box 194, West Chester, Pa. 19380) and Tri-Sil-Z (Pierce Chemical Co., P.O. Box 117, Rockford, Ill. 61105).

**Experimental Procedures. Optimization Studies.** Repetitive injections of ng of tetraethyilsilane and from 10 to 90 µg of decane were used to evaluate the response of each detector design as selected parameters were varied. A summary of the various parameters studied is given in Table I.

For design I, when the jet tip had a 0.5-mm i.d., oxygen was varied from 73 to 160 mL/min while hydrogen was held constant at 4 L/min, voltage on the collector was maintained at -90 V, the electrode height was 53 mm above the jet tip. Holding the oxygen flow constant at 73, 93, and 100 mL/min with 100 mL/min of nitrogen carrier gas and conditions the same as above, three runs were made in which hydrogen was varied from 4 to 11 L/min. Finally the electrode height was varied from 53 to 105 mm under constant gas flows of 150 mL/min for oxygen and 4 L/min for hydrogen. The effect of varying electrode height was investigated at electrode potentials of -90 and -235 V. No make-up nitrogen was added to the oxygen flow during the above experiments.

The effect of nitrogen was investigated for design I after the jet tip had been drilled out to a 1.5-mm diameter. The response for the test compounds was recorded when nitrogen was mixed with oxygen from 20% to 60%, while the total make-up nitrogen plus oxygen flow was maintained at 190 mL/min. for each of four electrode heights: 53, 73, 93, and 113 mm. This nitrogen/oxygen study was repeated with 29% nitrogen to 64% nitrogen in total flow reduced to 140 mL/min. Throughout these studies hydrogen was 1.6 L/min and the electrode potential was -90 V.

With the second design, oxygen flow, electrode height, and nitrogen flow were investigated. Oxygen was varied from 90 to 300 mL/min with hydrogen at 1.6 L/min, make-up nitrogen = 0 mL/min, electrode potential = -90 V and electrode height varied from 53 to 105 mm. The electrode height at 53 mm above the jet tip with hydrogen = 1.6 L/min, oxygen = 240 mL/min, make-up nitrogen = 0 mL/min, and electrode potential = -90 V. N₂ purge was varied from 0 to 40 mL/min while other parameters were held constant: electrode height = 53 mm, hydrogen = 1.6 L/min, and oxygen = 240 mL/min.

In design III, electrodes were used to investigate the electrode height, oxygen flow, hydrogen flow, nitrogen purge, and the carrier gas were investigated. The electrode potential was maintained at -90 V throughout these studies. In the initial studies, oxygen flows from 70 to 220 mL/min at an arbitrarily chosen low hydrogen flow of 360 mL/min were investigated. Other settings were: electrode height = 53 mm, nitrogen purge = 0 mL/min, and nitrogen carrier gas = 40 mL/min. Next with oxygen set at 120 mL/min, hydrogen was varied from 300 mL/min to 1.6 L/min. Then hydrogen was set at 1.6 L/min and oxygen varied from 120 to 270 mL/min. Finally in this series, oxygen was set at 150 mL/min and hydrogen varied from 300 mL/min to 2 L/min. The electrode was then raised to 103 mm above the jet tip and at settings of 1.6 L/min for hydrogen, 120 mL/min for oxygen, and 40 mL/min for nitrogen carrier gas, the nitrogen purge was varied from 0 to 30 mL/min.

A similar study was conducted with hydrogen at 1.6 L/min, oxygen at 130 mL/min, and nitrogen purge varied from 0 to 35 mL/min, but with helium as the carrier gas at 43 mL/min instead of nitrogen. With no nitrogen purge, and an electrode height of 103 mm, oxygen was varied from 70 to 260 mL/min at a hydrogen flow of 1.6 L/min and from 55 to 110 mL/min at a hydrogen flow of 360 mL/min. Finally, with nitrogen, hydrogen and oxygen flows of 0, 1600, and 120 mL/min, respectively, the electrode height was investigated from 53 to 103 mm above the jet tip.

**Calibration Curves.** The response of design three for tetraethyilsilane and decane was evaluated as a function of amount injected. Operating conditions for this study were as follows: Oxygen flow = 130 mL/min, hydrogen flow = 1600 mL/min, helium carrier flow = 43 mL/min, electrode height = 103 mm, and oven temperature = 65 °C.

**Silylation Studies.** A mixture of decane, dodecane, tetradeccane, 1-hexanol, 1-octanol, and 1-decanol was treated with Tri-Sil-Z, and this mixture was used to evaluate the response of the detector systems to these similar Ultra-bond 20 M columns with FID and HAFID (third design) detection.

**Calculations.** Detector response (R) for the test compounds was evaluated as the number of amperes produced at the peak maximum and was calculated from the straight-forward relationship shown below

\[ R = (PH/FS)(ATTN) \]

where PH is the height of the chromatographic peak, FS is the distance of a full scale response on the recorder, ATTN is the attenuation setting, and 5 × 10¹⁰ AFS is the maximum sensitivity of the amplifier. Selectivities are reported as the ratio of the peak height response per weight injected for tetraethyilsilane to decane.

The minimum detectable amount (MDA) is defined as the weight of test compound required to provide a peak height response equal to the peak to peak noise level.

\[ MDA = (N/RW) \]

where N is the peak to peak noise in A, R is the lowest response obtained for a test compound, and W is the weight of test compound injected.

**RESULTS AND DISCUSSION**

Table I provides a chronological listing of each parameter study performed on the various detector designs. Investigations were designed to evaluate each detector design with regard to their response at multiple parameter settings for a test compound containing silicon (tetraethyilsilane) and a test compound with only carbon and hydrogen (decane). The first column of the table assigns a number to the study, the next five columns give specific conditions for electrode height, hydrogen flow, oxygen flow, nitrogen purge flow, and carrier gas flow. The first two columns, respectively, report the results for the best tetraethyilsilane response and the best selectivity value with the variable setting at which this response or selectivity occurred. For example, in the first study, the electrode height, hydrogen flow rate, nitrogen purge flow rate, and the nitrogen carrier gas flow rate were held constant at 55 mm, 4 L/min, 0 mL/min, and 20 mL/min, respectively, while oxygen was varied from 73 to 160 mL/min. The largest peak obtained for repetitive injections of 100 ng of tetraethyilsilane was 17 A at the peak maximum and required an oxygen flow of 105 mL/min, while the largest selectivity obtained was 50 and required an oxygen flow of 73 mL/min.
Note that the best response and the best selectivity do not necessarily occur under identical conditions.

First Design. Studies 1-6 were undertaken when the detector well was identical to that in the Hewlett-Packard FID unit, but the cap containing the collecting electrode was modified to the design shown in Figure 1. Only hydrogen flows greater than 4 L/min were investigated because at lower flows the flame was difficult to keep lit. Sensitivity was good in this design. However, selectivity was lower than desired, unusually high hydrogen flows were required, and the flame often was extinguished when 0.5 μL of solvent eluted from the column. To eliminate these problems, the detector was modified by drilling out the tip of the jet to a 1.5-mm diameter. This design was used in detector design and operating conditions. The column headed "best response" reveals a quasi-inverse relationship between electrode height and hydrogen, nitrogen, and oxygen flow rates. However, selectivity was lower than desired, unusually high hydrogen flows were required, and the flame was difficult to keep lit. Sensitivity was good in this design.

Second Design. Studies 15-17 were conducted using this design. While this modification appeared to improve selectivity so that the response compared favorably to that of the Hill-Aue model described in Ref. 12, responses were often not reproducible—varying as much as an order of magnitude from day to day and even from injection to injection. The origin of this irreproducibility remains unclear but one contributing factor may have been the turbulence of the detector gas flows. The relatively fast hydrogen flow was introduced perpendicular to the chamber through a small oriﬁce in the side of the detector well (see Figures 1 and 2).

Third Design. To eliminate this turbulent flow pattern, a 8-mm i.d. tube was welded to the collector assembly and extended concentrically into the detector well, terminating just below the exit of the jet tip (Figure 3). This design changed the manner in which hydrogen was introduced into the detector well and the collector assembly 10 mm (Figure 2).

<table>
<thead>
<tr>
<th>Electrode Height, mm</th>
<th>Hydrogen, L/min</th>
<th>Oxygen, mL/min</th>
<th>N₂ Purge, mL/min</th>
<th>Carrier Gas, mL/min</th>
<th>Best Response, pA</th>
<th>Best Selectivity, pA</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 53</td>
<td>4.0</td>
<td>(73-160)</td>
<td>0</td>
<td>20(N₂)</td>
<td>17 at 105</td>
<td>50 at 73</td>
</tr>
<tr>
<td>(2) 53</td>
<td>(4-11)</td>
<td>100</td>
<td>0</td>
<td>20(N₂)</td>
<td>20.5 at 11</td>
<td>100 at 10</td>
</tr>
<tr>
<td>(3) 53</td>
<td>(4-11)</td>
<td>73</td>
<td>0</td>
<td>20(N₂)</td>
<td>25 at 9.5</td>
<td>200 at 10</td>
</tr>
<tr>
<td>(4) 53</td>
<td>(4-11)</td>
<td>41</td>
<td>0</td>
<td>20(N₂)</td>
<td>18 at 11</td>
<td>140 at 4</td>
</tr>
<tr>
<td>(5) (53-105)</td>
<td>4</td>
<td>150</td>
<td>0</td>
<td>20(N₂)</td>
<td>3.6 at 70</td>
<td>80 at 105</td>
</tr>
<tr>
<td>(6) (53-105)</td>
<td>4</td>
<td>150</td>
<td>0</td>
<td>20(N₂)</td>
<td>3.5 at 70</td>
<td>50 at 70</td>
</tr>
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<td>(7) 53b</td>
<td>1.6</td>
<td>(86-150)</td>
<td>(0-64)</td>
<td>40(N₂)</td>
<td>10 at 79% O₂</td>
<td>160 at 79% O₂</td>
</tr>
<tr>
<td>(8) 53</td>
<td>1.6</td>
<td>(90-150)</td>
<td>(0-60)</td>
<td>40(N₂)</td>
<td>8.2 at 79% O₂</td>
<td>100 at 79% O₂</td>
</tr>
<tr>
<td>(9) 53</td>
<td>1.6</td>
<td>(90-150)</td>
<td>(0-60)</td>
<td>40(N₂)</td>
<td>5.8 at 75% O₂</td>
<td>90 at 69% O₂</td>
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<td>(10) 113</td>
<td>1.6</td>
<td>(100-150)</td>
<td>(0-45)</td>
<td>40(N₂)</td>
<td>5.8 at 79% O₂</td>
<td>120 at 79% O₂</td>
</tr>
<tr>
<td>(11) 53</td>
<td>1.6</td>
<td>(70-100)</td>
<td>(0-30)</td>
<td>40(N₂)</td>
<td>15.0 at 64% O₂</td>
<td>200 at 64% O₂</td>
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<td>(12) 73</td>
<td>1.6</td>
<td>(70-100)</td>
<td>(0-30)</td>
<td>40(N₂)</td>
<td>15.6 at 71% O₂</td>
<td>330 at 64% O₂</td>
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<td>(13) 93</td>
<td>1.6</td>
<td>(80-100)</td>
<td>(0-20)</td>
<td>40(N₂)</td>
<td>6.1 at 64% O₂</td>
<td>450 at 64% O₂</td>
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<td>(14) 113</td>
<td>1.6</td>
<td>(70-100)</td>
<td>(0-30)</td>
<td>40(N₂)</td>
<td>5.0 at 64% O₂</td>
<td>520 at 64% O₂</td>
</tr>
<tr>
<td>(15) 103</td>
<td>1.6</td>
<td>(90-300)</td>
<td>0</td>
<td>40(N₂)</td>
<td>27 at 300</td>
<td>1700 at 240</td>
</tr>
<tr>
<td>(16) (53-103)</td>
<td>1.6</td>
<td>240</td>
<td>0</td>
<td>40(N₂)</td>
<td>8 at 53</td>
<td>1000 at 53</td>
</tr>
<tr>
<td>(17) 53</td>
<td>1.6</td>
<td>240</td>
<td>(0-40)</td>
<td>40(N₂)</td>
<td>9.3 at 40</td>
<td>1000 at 0</td>
</tr>
<tr>
<td>(18) 53</td>
<td>0.36</td>
<td>(70-220)</td>
<td>0</td>
<td>40(N₂)</td>
<td>5.8 at 120</td>
<td>400 at 120</td>
</tr>
<tr>
<td>(19) 53</td>
<td>(0.5-1.6)</td>
<td>120</td>
<td>0</td>
<td>40(N₂)</td>
<td>10.6 at 0.8</td>
<td>500 at 0.6</td>
</tr>
<tr>
<td>(20) 53</td>
<td>1.6</td>
<td>(120-270)</td>
<td>0</td>
<td>40(N₂)</td>
<td>43 at 180</td>
<td>1100 at 150</td>
</tr>
<tr>
<td>(21) 53</td>
<td>(0.3-2)</td>
<td>150</td>
<td>0</td>
<td>40(N₂)</td>
<td>27 at 19</td>
<td>800 at 19</td>
</tr>
<tr>
<td>(22) 103</td>
<td>1.6</td>
<td>120</td>
<td>(0-30)</td>
<td>40(N₂)</td>
<td>1.28 at 0</td>
<td>2400 at 0</td>
</tr>
<tr>
<td>(23) 103</td>
<td>1.6</td>
<td>130</td>
<td>(0-35)</td>
<td>43(He)</td>
<td>6.8 at 0</td>
<td>2600 at 0</td>
</tr>
<tr>
<td>(24) 103</td>
<td>1.6</td>
<td>(70-260)</td>
<td>0</td>
<td>43(He)</td>
<td>7.2 at 260</td>
<td>2600 at 140</td>
</tr>
<tr>
<td>(25) 103</td>
<td>0.36</td>
<td>(55-110)</td>
<td>0</td>
<td>43(He)</td>
<td>3.6 at 70</td>
<td>1000 at 70</td>
</tr>
<tr>
<td>(26) (53-103)</td>
<td>1.6</td>
<td>130</td>
<td>0</td>
<td>43(He)</td>
<td>8.8 at 53</td>
<td>2600 at 103</td>
</tr>
</tbody>
</table>

Electrode potential = -225 V. For all other studies, electrode potential = -90 V. Internal diameter of jet tip drilled out from 0.5 mm to 1.5 mm.
between sensitivity and selectivity. Throughout the course of these investigations, selectivity improved from a low of 50 in the first design to a high of 2600 in the last design while response decreased from a high of 25 pA in the first design to a low of 3.6 pA in the third design when He was used as the carrier gas. That corresponds to a 52-fold increase in selectivity and a 7-fold decrease in sensitivity.

The response value of 25 pA, given for the first design, was obtained for an electrode height of 53 mm while the response of 3.6 pA, given for the third design, was obtained at an electrode height of 103 mm. Figure 4 compares the decrease in relative response of tetraethylsilane for each detector as a function of electrode height. In design I and II, response decreases more rapidly than in design III as the electrode height is raised.

When evaluated on the basis of selectivity as in Figure 5, it is clear that design III gives the most desirable results. For design I, electrode height had only a moderate influence on selectivity, increasing its value from 73 to 500 as the electrode height increased from 53 mm to 113 mm. Design II, however, decreased in selectivity as the electrode height was raised from 53 to 73 and then remained reasonably constant at about 200 for electrode heights of 73 to 103 mm. The sharp reduction in selectivity, from 1000 to 200, between electrode heights of 53 and 73 mm was due to a loss of sensitivity for the detector to tetraethylsilane at the higher electrode heights. It may be that the introduction of H₂ at high velocities orthogonal to exiting flame gases, coupled with a smaller detector diameter, created sufficient turbulence to sweep the ions into the detector walls where they could be neutralized. With design III, where the H₂ was introduced beneath the flame jet, tetraethylsilane response decreased much less as a function of increased electrode height than in design I or II (see Figure 4). The result is increased selectivity at the higher electrode heights. When the electrode is moved from 53 to 103 mm, selectivity increases from 450 to 2600. In these studies the optimum electrode height for selectivity could not be achieved because, at electrode heights greater than 103 mm, water began to condense on the electrode shorting it to ground. More efficient heating of the detector will no doubt allow the use of greater electrode heights, possibly increasing the selectivity to values more than 2600 (Note that 2600 is equivalent to a gram-atom Si/gram-atom C selectivity of $1.1 \times 10^4$).

Figures 6 and 7 depict response characteristics of design III as a function of detector gas flow rates. In Figure 6, the
addition of nitrogen to the detector is seen to decrease the response of tetraethylsilane while having little effect on the decane response. This effect is supported by noting that silicon sensitivity is increased when 43 mL/min of helium is used as the carrier gas rather than 40 mL/min of nitrogen (see Table I, studies 22 and 23).

Study 17 in Table I is the only exception to the observation that nitrogen decreased silicon response. While from the table it would appear that response increases with nitrogen since the best response obtained was 9.3 pA at 40 mL/min nitrogen purge, nitrogen had little effect on the response under these conditions. Peak height values were 8.0, 8.7, 8.0, 8.7, and 9.3 pA for nitrogen purge flows of 0, 10, 20, 30, and 40 mL/min, respectively. Since the oxygen flow was higher in this study than in any of the other nitrogen purge studies, it would appear that an increased oxygen supply minimizes the effect of nitrogen.

Figure 7 illustrates that the relationship between reaction mechanism and oxygen flow is complex since the response of decane relative to tetraethylsilane is high for both low and high oxygen flows. Silicon response increased with increasing oxygen flow but the maximum selectivity was obtained at 140 mL/min.

**Peak Tailing.** Not only did the third design produce selectivities exceeding those reported in the earlier paper, but it also eliminated an important difficulty which made the earlier detector impractical for chromatographic analysis. Peaks for silicon-containing compounds in the design of Ref. 12, and in designs I and II in this paper, were asymmetrical, exhibiting severe tailing (see Figure 7 in Ref. 12 and Figure 8 of this paper). When the tube in design III was extended into the detector well, reducing further the internal diameter of the detector and forcing the hydrogen into the reaction region beneath the flame, sharp, nontailing chromatographic peaks were observed.

In earlier work, this tailing effect was attributed to chromatography of silicon compounds, for at that time, a relatively new and unproven chromatographic phase consisting of an ultra-thin film of Carbowax 20M coated on Chromosorb W (14) was used in the GC column. Since then, this phase has become commercially available and has been shown to be a very deactivated support when handled properly (15). Our results indicate that detector geometry, not column activity, is the primary reason for tailing peaks of compounds containing silicon.

Apparently, if combustion products formed in the flame are not efficiently swept from the detector atmosphere, they diffuse back into the flame creating a lingering response. For detectors with large internal volumes as in Ref. 12, or when hydrogen is not introduced into the housing in a manner that efficiently purges the detector as in design I and II, the detector housing becomes a quasi-exponential dilution flask.
for the combustion products. The fact that hydrocarbon compounds have not been seen to exhibit this tailing phenomenon in any of the designs, indicates that their combustion products do not ionize in the flame. One would assume that the products from carbon and silicon combustion would predominantly be CO₂ and SiO₂, although the possibility of hydride formation cannot be excluded in the hot hydrogen rich region above the flame.

Based on silicon selectivity and peak shape, design III was chosen as the optimal detector configuration for the remainder of this study.

Calibration Curves. Conditions for operation were based on best selectivity rather than sensitivity. However, highest selectivity occurred at parameter settings where reasonably good sensitivity was also obtained. Operating conditions were as follows: a hydrogen flow of 1600 mL/min, an oxygen flow of 130 mL/min, a nitrogen purge flow of 0 mL/min and an electrode height of 103 mm above the jet tip. Figure 9, a calibration curve for tetraethylsilane and decane, shows a linear response for the silane standard from its minimal detectable amount of 4 ng to the low microgram region where the compound begins to saturate the detector. This is a linear range of three orders of magnitude. Note that the decane response saturates the detector at a lower current density than does the TES. This means that the selectivity of the detector improves for larger amounts of hydrocarbons injected. For example, in the low range of the calibration curves, the selectivity factor is about 1000 but, for the largest amount of decane injected, the selectivity factor increased to about 10,000.

Application. To illustrate the utility of this detector, a mixture of n-hydrocarbons and n-alcohols was prepared. The alcohols were converted to their trimethylsilyl derivatives with Tri-Sil Z and the mixture was chromatographed on two different instruments, one equipped with a standard flame ionization detector and the other with the third design of the silicon sensitive hydrogen atmosphere flame ionization detector.

Figure 10 is the FID response tracing of this mixture in which each component is detected with approximately equal sensitivity. Hydrocarbons were chosen that could be easily separated from the silylated derivative but, in a real sample, where such separation is not assured, the presence of hydrocarbons may interfere with quantitative analysis. Figure 11 is the hydrogen atmosphere silicon selective detector tracing of the same test mixture under similar chromatographic conditions. With the exception of the solvent, only compounds containing silicon are detected. In this case, overlapping hydrocarbon peaks may not interfere with quantitative results.

CONCLUSIONS

Application of this detector to the multitude of analytical silylation procedures that are in routine use could increase the reliability of these analyses by eliminating or reducing errors associated with poor chromatographic resolution or interfering nonsilicon-containing compounds. A principal disadvantage to routine and widespread adoption of the HAFID is the large quantity of hydrogen required for optimal response. Detector configurations with lower hydrogen flows are currently being investigated. Yet, ease of construction and operation of this non-doped hydrogen atmosphere flame ionization detector makes it appealing for immediate application to silicon analysis. Increasing silicon sensitivity by doping the atmosphere with volatile metal compounds appears promising for the future and will also be the subject of subsequent investigations.

LITERATURE CITED


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