

A SILICON DETECTOR FOR GAS CHROMATOGRAPHY*

HERBERT H. HILL, Jr.

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

and

WALTER A. AUE

Department of Chemistry, Dalhousie University, Halifax, N.S. (Canada)

(Received April 25th, 1977)

SUMMARY

Silicon compounds can be detected by a hydrogen-atmosphere flame ionisation detector with moderate sensitivity (nanogram range) and selectivity (two to three orders of magnitude vs. hydrocarbons). The detector can be operated with or without ferrocene vapor present in its hydrogen atmosphere: The former mode is more sensitive, the latter more practical.

INTRODUCTION

Volatile compounds of silicon are frequently encountered in chemistry, both academic and industrial. For many of them, gas chromatography (GC) is the preferred method of analysis. Conversely, the particular demands of GC have stimulated considerable activity in silicon chemistry.

Foremost among these activities are the silylation reactions which have in recent years been used in a multitude of cases to prepare more volatile and less polar derivatives of alcohols, acids, etc., for GC analysis. On occasion, these silylations have also served to introduce halogen into the analyte molecule for increased response in the electron capture detector, although the more common detector for silicon compounds is, no doubt, the flame ionization detector (FID).

The FID responds, of course, to the carbon portion of the molecule, but the matter is more complicated than that: the response of organosilicon compounds can be negative; *i.e.*, inverted peaks may be observed. The inversion depends on the presence of carbon in the flame and a critical silicon mass flow-rate¹.

It is obvious that a GC detector selective for silicon would be an advantage to many types of analysis. No such detector is commercially available and, to our knowledge, only one system designed for selective determination of silicon has been described². It uses the 2516-Å line of silicon and is based on either atomic emission in an oxygen-acetylene flame or atomic absorption in a nitrous oxide-acetylene flame.

* Presented at the 58th CIC Conference, Toronto, Ont., Canada, May 1975.

In some recent studies on the detection of organometallics containing Fe, Al, Sn, Pb, Cr, and other elements, we noted an unexpected phenomenon: the response of a detector named hydrogen-atmosphere flame ionization detector (HAFID) was influenced by the presence of silane³. In fact, silane (or other silicon compounds) had to be introduced continuously to keep the detector at its optimum performance level, a level characterized by sensitivities in the lower picogram range and selectivities (against C, H, N, O compounds) of five orders of magnitude.

Compared to an undoped detector, the addition of silicon-containing compounds brought about an improvement in performance, *i.e.* the response towards organometallics, of two to three orders of magnitude. It appeared likely, therefore, that the changes in the response of organometallics caused by the introduction of organosilanes could be used to determine the latter rather than the former. Furthermore, it was interesting to investigate whether the HAFID would also respond to silicon-containing species in the absence of other organometallics.

A study along these lines is contained in this paper. Its subject is treated in a strictly exploratory manner, designed to indicate the feasibility and potential of the chosen approach rather than to optimize the technique for a particular analytical usage or to elucidate the flame mechanism(s) responsible for the observed effects.

EXPERIMENTAL

The general construction of the HAFID was described earlier (*e.g.* ref. 3). The particular model used is shown in Fig. 1; it was situated under appropriate exhaust facilities to vent safely the large amounts of unburned hydrogen as well as any other toxic gases. Unless stated otherwise, the detector flow-rates (ml/min) were hydrogen 1600, oxygen 150, nitrogen 25, nitrogen (column) 40; and the collector electrode, polarized at -90 or -240 V, was situated 50 mm above the quartz jet tip.

For experiments involving the addition of ferrocene, the organometallic was coated onto, and mixed with, Chromosorb W (80–100 mesh). This material was filled into a $12 \times 1/4$ in. O.D. copper tube mounted in by-pass configuration on the hydrogen supply line. A variable and easily measured flow of hydrogen could thus be passed through the finely dispersed ferrocene at ambient temperature, and an estimation of the ferrocene introduction rate could be obtained from vapor pressure data and the assumption of equilibrium. The total hydrogen flow-rate entering the detector remained approximately constant at 1600 ml/min.

The electrode height was varied by using appropriate "spacers". The only other parameter investigated was the oxygen flow-rate.

Several silicon-containing compounds were injected onto a 5 ft. \times 4 mm I.D. U-tube borosilicate glass column packed with Chromosorb W modified by a non-extractable layer of Carbowax 20 M (ref. 4), except where noted. No efforts were made to optimize chromatographic conditions.

RESULTS AND DISCUSSION

Ferrocene present in the hydrogen atmosphere

The presence of ferrocene in the hydrogen atmosphere of the detector definitely affects the response of organosilanes coming from the chromatographic column and

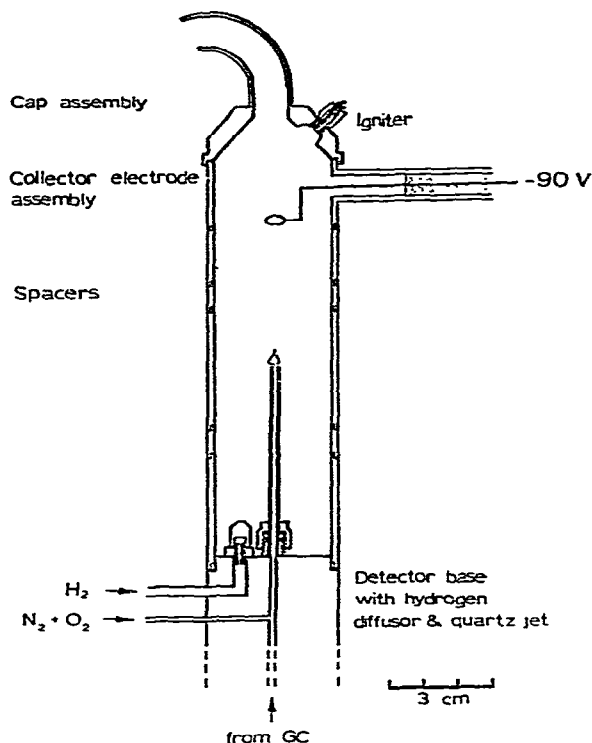


Fig. 1. Hydrogen-atmosphere FID as used for silicon compounds.

burning in the flame (Fig. 2). At low concentrations of ferrocene, positive peaks (increases in detector current) are obtained as expected. At high concentrations of ferrocene, however, the peaks are negative (inverted).

The HAFID has a very large baseline current, and peak inversion is not an uncommon phenomenon. It shares the latter, albeit only formally, with such detectors as the alkali flame, the electron capture, or the flame photometric detector. Here as there, a precise correlation of detector processes with peak inversion can be difficult to establish. The response of the HAFID reflects, most likely, a rather complex system of reactions that is difficult to investigate. A general, speculative picture of these reactions has been developed⁵; however, no experimental data are at present available that would unequivocally establish the detector mechanism(s).

Fig. 3 shows two chromatograms obtained with different ferrocene levels but under otherwise identical conditions; tetramethylsilane is the compound chosen to demonstrate peak inversion.

Fig. 4 presents the variation of organosilane response with oxygen flow, the results being close to expectations based on earlier studies of organometallics⁶: increased oxygen flow increased response of the silanes and decreased response of hydrocarbons.

Determination of organosilanes in the presence of ferrocene is fairly sensitive (down to nanogram amounts of injected compounds) and selective (up to four orders

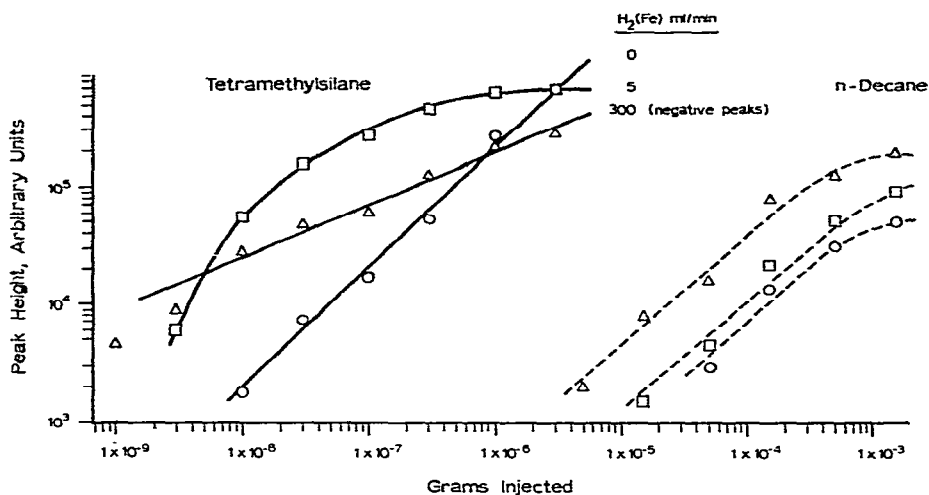


Fig. 2. Calibration curves for tetramethylsilane (TMS) and decane with different amounts of ferrocene present in the detector atmosphere. Fraction of hydrogen saturated with ferrocene at room temperature: Δ = 300 ml/min; \square = 5 ml/min; \circ = 0 ml/min (blank). Response of TMS for 300 ml/min: negative (inverted peak); for 5 and 0 ml/min: positive. Response of decane: all positive. General conditions: column 5 ft. \times 4 mm I.D. borosilicate U-tube packed with Chromosorb W AW (80–100 mesh) modified by *ca.* 0.2% Carbowax 20M. Electrode height, 50 mm; potential -240 V. Temperatures, detector 240° , injection port 220° , column 70° . Flow-rates (ml/min): H_2 , 1600 (total), N_2 (detector), 25; N_2 (column), 40; O_2 , 150.

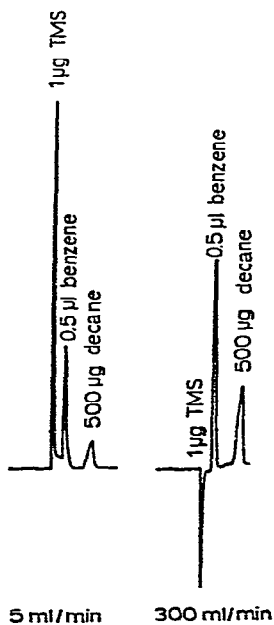


Fig. 3. Inversion of TMS peak caused by larger amounts of ferrocene in the detector atmosphere. Fraction of hydrogen saturated with ferrocene at room temperature: left, 5 ml/min; right, 300 ml/min; out of a total 1600 ml/min. Other conditions as in Fig. 2.

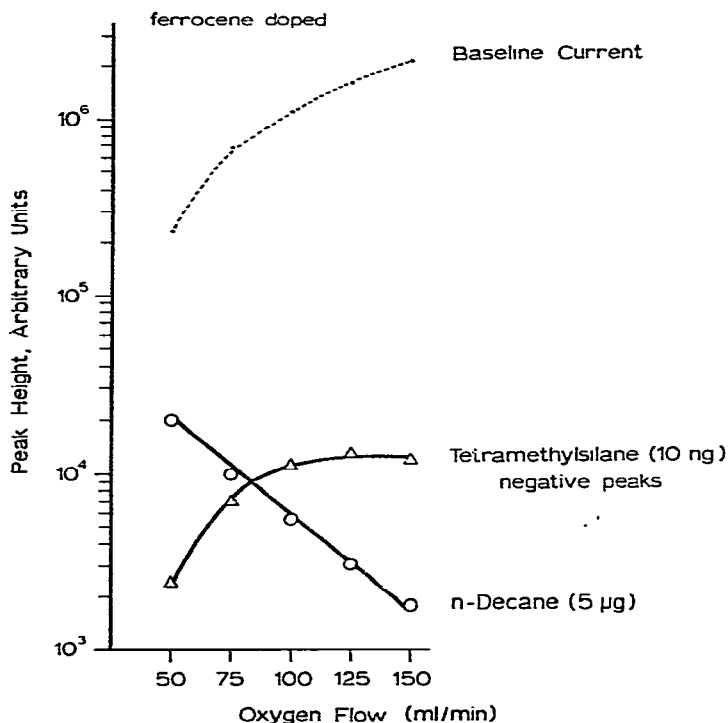


Fig. 4. Variation in response of TMS with different oxygen flows in a ferrocene-doped HAFID. Fraction of hydrogen saturated with ferrocene: 300 ml/min; out of a total 1600 ml/min. Response: TMS negative, decane positive. Other conditions as in Fig. 2.

of magnitude depending on concentrations). On the other hand, the calibration curves (Fig. 2) are non-linear and the amount of ferrocene entering the detector would obviously have to be carefully controlled. Ferrocene was the only doping agent investigated; but it is reasonable to assume that other organometallics could also bring about increased response. If small amounts of their vapors were added to the bottled hydrogen supply, analytical reliability and ease of operation may also be improved.

In its present form, though, the HAFID is less cumbersome to operate without ferrocene, and some noteworthy responses can still be obtained.

Ferrocene absent from the hydrogen atmosphere

Fig. 5 shows the expected variation of response with a change in electrode height. The baseline current and the response to hydrocarbons decrease as the electrode is moved upwards, a characteristic of the HAFID and presumably the FID as well. The response to silicon compounds stays constant up to over 60 mm in contrast to the organometallics determined earlier in a silane-doped detector³, whose response increased. This behavior was expected from a working hypothesis developed to explain the response of organometallics⁵, which speculates that SiH_3^+ (or a similar ion) has a lower rate of neutralization than other ions, e.g. H_3O^+ , under HAFID conditions and can therefore serve as the principal charge carrier. When silane compounds are

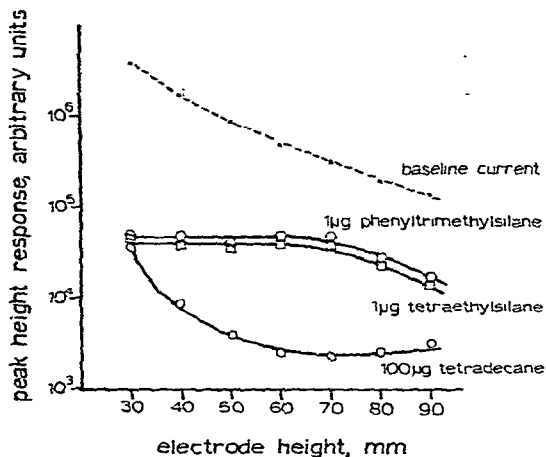


Fig. 5. Variation in response of two silicon compounds and a hydrocarbon with height of the collector electrode above the jet tip. No ferrocene doping. Electrode potential, -90 V. Temperatures: column, 60° (phenyltrimethylsilane), 30° (tetraethylsilane), 120° (tetradecane); detector, 250° ; injection port, 225° . Other conditions as in Fig. 2.

chromatographed, the SiH_3^+ (or similar) ion would presumably form in the upper parts of, or right above the flame, explaining the unusual phenomenon of an ion current which remains approximately constant over more than 60 mm above the flame. While the still speculative nature of this explanation needs to be stressed, it is obvious that a judicious choice of electrode height, together with a suitable adjustment of oxygen flow-rate, can lead to an effective suppression of the sample matrix for analytical purposes.

Fig. 6 gives calibration curves for three organosilanes, in the absence of any deliberately added doping agent. These are linear, though only over a restricted range. Minimum detectable amounts are around 10 ng and selectivities are between two and

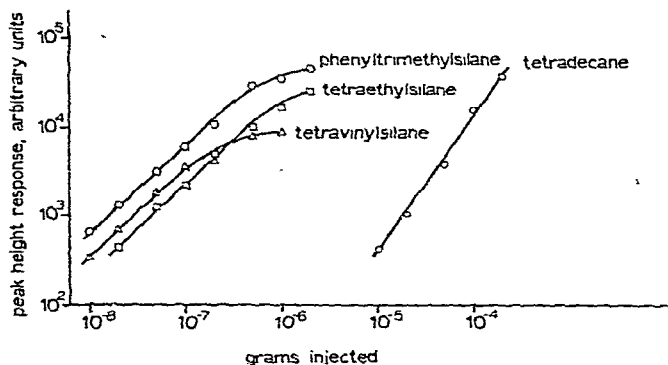


Fig. 6. Calibration curves for three silicon compounds and a hydrocarbon. No ferrocene doping. Electrode height, 50 mm; potential, -90 V. Column: 5 ft. \times 4 mm I.D. borosilicate U-tube packed with 5% Carbowax 20M on Chromosorb W AW (80-100 mesh). Column temperatures: 30° (tetraethylsilane), 60° (tetravinylsilane), 80° (phenyltrimethylsilane), 125° (tetradecane). Other conditions as in Fig. 2.

three orders of magnitude. Fig. 7 shows a chromatogram of a typical standard mixture.

This performance should make the detector of interest for several types of GC analysis. While it would not be considered suitable at present for trace analysis (*e.g.* the sub-nanogram range), typical applications could provide information on whether or not a particular GC peak represents a silane, and could facilitate the analysis of samples with interfering carbonaceous backgrounds.

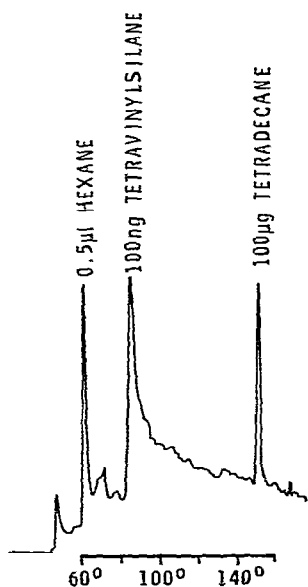


Fig. 7. Temperature-programmed chromatography of tetravinylsilane and a hydrocarbon standard. Program 60° to 150° at 40°/min. Other conditions as in Fig. 6.

There is little doubt that a more thorough study, perhaps involving varied doping agents, improved chromatographic conditions, optimized construction and operation parameters, etc., could lead to future improvements in detector performance.

ACKNOWLEDGEMENT

This study was supported by NRC grant A-9604 and AC grant EMR-7401.

REFERENCES

- 1 D. Fritz, G. Garzó, T. Székely and F. Till, *Acta Chim. Hung. Tomus*, 45 (1965) 301.
- 2 R. W. Morrow, J. A. Dean, W. D. Shults and M. R. Guerin, *J. Chromatogr. Sci.*, 7 (1969) 572.
- 3 H. H. Hill, Jr. and W. A. Aue, *J. Chromatogr.*, 122 (1976) 515.
- 4 W. A. Aue, C. R. Hastings and S. Kapila, *Anal. Chem.*, 45 (1973) 725.
- 5 H. H. Hill, *Ph. D. Thesis*, Dalhousie University, Halifax, April 1975.
- 6 W. A. Aue and H. H. Hill, Jr., *J. Chromatogr.*, 74 (1972) 319.