

Negative Response Mode of a Silicon-Selective Hydrogen-Atmosphere Flame Ionization Detector for Gas Chromatography

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When a silicon-selective hydrogen-atmosphere flame ionization detector is doped with vapors from metal-containing compounds in excess of that required for positive responses of silicon-containing compounds, an ionization quenching phenomenon occurs which produces negative chromatographic peaks that are easily identified and quantified. With optimized doping conditions of about 35 ppm ferrocene vapor in the hydrogen atmosphere, the detector exhibited a minimum detectable limit of 200 pg/s when the collecting electrode was positioned 110 mm above the flame. Silicon sensitivity can be increased by a factor of 6 by sacrificing detector selectivity and lowering the collector electrode to a position 30 mm above the flame. When responses of a variety of chemicals were investigated, alcohols, hydrocarbons, ethers, fluorocarbons, and nitrogen-containing compounds were found to produce positive responses while chlorine-, bromine-, sulfur-, phosphorus-, and iron-containing compounds produced potentially interfering negative responses. A silylated mixture of alcohols and hydrocarbons was chromatographed with FID and HAFID detection to demonstrate potential applications of this detector.

Silylation has served for years as a reliable step in many analytical procedures to increase volatility of polar compounds for gas chromatographic separation. The most common method which has been employed for the detection of silyl derivatives after gas chromatography (GC) is the flame ionization detector (FID). Because the FID responds primarily to carbon atoms, silyl derivatives are detected along with other nonderivatized organic material eluting from the gas chromatograph. Thus for trace analysis of silyl derivatives in complex mixtures, this universal detector creates complicated chromatograms which are often difficult to evaluate.

Selective detection of only those compounds containing silicon atoms would, in many cases, simplify chromatograms and aid the analyst in the identification and quantification of these derivatives. Although a number of silicon-selective detectors for GC have been proposed (1-5), the hydrogen-atmosphere flame ionization detector (HAFID) appears most promising for developing an inexpensive, routine method for the determination of silyl derivatives.

This detection method was first proposed by Hill and Aue in 1977 when they demonstrated that ions produced in a hydrogen atmosphere flame from silicon-containing organics could be formed and collected more efficiently than those from compounds containing only atoms of carbon and hydrogen (6). They also demonstrated that the addition of small quantities of ferrocene vapor to the detector's atmosphere enhances silicon responses and that the ferrocene concentration could be increased to a point where responses of sil-

icon-containing compounds reversed direction and appeared as negative peaks while responses of hydrocarbons remained as diminutive positive peaks.

This paper is the third in a subsequent series of investigations of this silicon selective detector designed to characterize the three modes of operation: (1) the nondoped mode, (2) the metal-doped positive peak mode, and (3) the metal-doped negative peak mode.

In the first paper of this series (7), in which the nondoped mode of detection was investigated, it was determined that in contrast to other flame ionization detectors the detector volume and flow pattern of combusted gases were significant considerations in maintaining the integrity of the chromatographic separation. This work, with a more efficient detector geometry, established a detection limit for silicon-containing compounds in the low nanogram region and a silicon selectivity of about 10^3 against hydrocarbons.

In a recent publication (the second in this series) (8), metal doping requirements of the hydrogen atmosphere were quantified and potentially interfering species were identified from a survey of a variety of heteroatom test compounds. Organometallic compounds and phosphorus-containing compounds are species which also exhibit enhanced responses in this detector. When optimized for positive silicon peaks, the detection limit decreased to the subnanogram range and silicon to carbon selectivity increased to greater than 10^4 .

The purpose of this paper is to report results of investigations into the operation of the detector when the hydrogen atmosphere is doped with sufficient quantities of organometallic vapors to produce negative responses for silicon-containing compounds.

EXPERIMENTAL SECTION

Detectors: An FID on a Hewlett-Packard 5710A gas chromatograph was converted to an HAFID, as shown in Figure 1. The detector consists of four parts: a cap, an exhaust chimney, a connection sleeve, and a fastening nut. The cap contains a collector electrode which is centered above the flame, an ignitor which is positioned on the side of the cap, and several exhaust vents. The chimney sections separate the cap from the lower portion of the detector by a distance which can be varied using interchangeable spacers. The connection sleeve and fastening nut are required to join the electrode assembly (cap and spacer) to the detector well. Hydrogen was introduced at the base of the flame and ferrocene vapors were introduced into the detector either through the hydrogen inlet or via an $1/8$ in. o.d. stainless steel tube which was connected to a spacer and extended along the wall into the detector well.

The flame ionization detector used in these studies was detector B of the dual FID unit, H. P. Model 5710A gas chromatograph. Gas flows for this detector were maintained at 30 mL/min for hydrogen and 240 mL/min for air, as recommended by the manufacturer.

Doping Apparatus. Ferrocene was mixed with Chromosorb W (80-100 mesh) and filled into a $12 \times 1/4$ in. o.d. copper tube. This tube was then inserted into a nitrogen line so that gases passing through the ferrocene/Chromosorb bed were doped with equilibrium quantities of ferrocene vapor. The exit line from this

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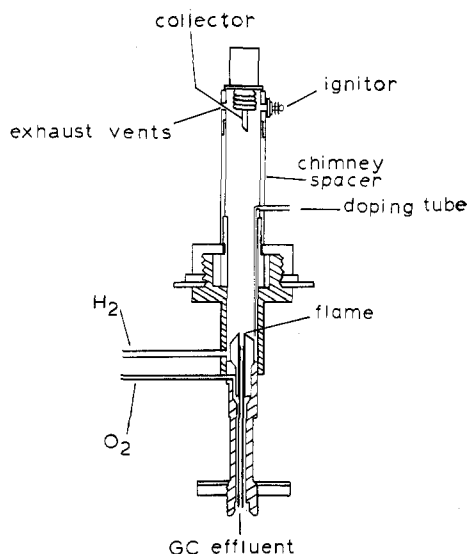


Figure 1. Hydrogen atmosphere flame ionization detector for silicon.

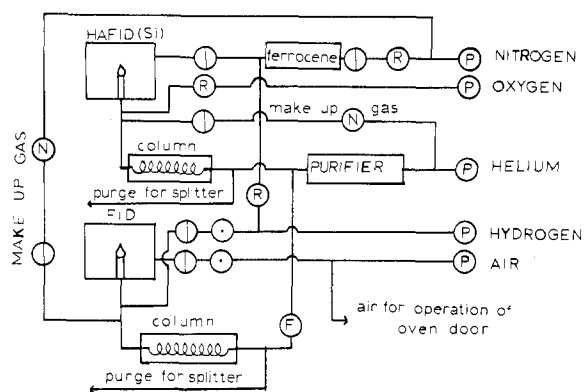


Figure 2. Gas flow diagram: (R) rotameter regulator, (O) on-off valve, (C) critical orifice, (N) needle valve, and (F) flow controller.

ferrocene vapor entrainer was connected either to the hydrogen line or to a line which introduced the metal vapor directly into the detector's atmosphere. Concentrations of ferrocene were calculated from vapor pressure data and the assumption of equilibrium. The nitrogen flow rate passing through the vapor entrainer was varied from 0 to 340 mL/min changing the doping concentrations in the hydrogen atmosphere from 0 to 40 ppm ferrocene.

Chromatographic Conditions. The GC column used throughout this work was a 10 m \times 0.2 mm i.d. methylsilicone coated fused silica capillary column (Hewlett-Packard, Avondale, PA). Flow rates were as follows: helium carrier gas at 1.2 mL/min, makeup gas (helium) at 40 mL/min, oxygen at 130 mL/min, and hydrogen at 1.6 L/min. Figure 2 shows a detailed flow pattern for all gases used. Injection port and detector temperatures were both kept at 250 °C. Split ratio was 1:30. The oven temperature was held at 80 °C during studies with tetraethylsilane and tetraethylsilane. For a mixture of silylated alcohols and *n*-alkanes, the oven was programmed to remain at 80 °C for 2 min and then to increase at a rate of 16 °C/min to final temperature 200 °C.

Reagents. Primary test compounds were tetraethylsilane (Pfaltz and Bauer, Inc., Stanford, CT) and tetraethylsilane (Alfa Products, Danvers MA). Each was diluted in glass distilled hexane (Burdick and Jackson Lab., Inc., Muskegon, MI) to the desired concentration. Other reagents and test compounds used were ferrocene (Aldrich Chemical Co., Inc., Milwaukee, WI), 1-octanol, 3,3,5-trimethylcyclohexanol, decanol, dodecanol, methanol, acetone, *n*-butyl ether, pyridine, fluorobenzene, chlorobenzene, bromobenzene, 2-methylbenzothiazole, and triethyl phosphate (Chem. Service Inc., West Chester, PA), and decane, dodecane, and tetradecane (Sigma Chemical Co., Rockford, IL).

Experimental Procedures. The response from repetitive injections of 320 ng of tetraethylsilane was monitored as a function

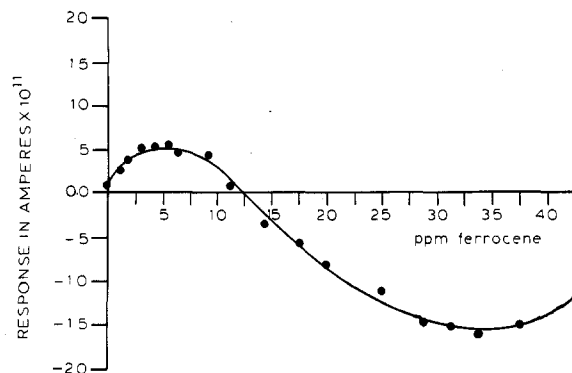


Figure 3. Ferrocene doping study (ferrocene premixed with hydrogen).

of concentration of ferrocene vapor in the atmosphere. During these studies nitrogen saturated with ferrocene was premixed with hydrogen and entered the detector below the jet tip.

Doping experiments were also conducted where the ferrocene vapor was introduced into the atmosphere at 5, 10, and 15 mm above the flame through the $\frac{1}{8}$ in. stainless steel tube shown in Figure 1. Two separate investigations of silicon response as a function of collector electrode height were performed. Because of the design of the detector housing, it was difficult to obtain measurements with the collector electrode below 50 mm. For distances of 20–60 mm the jet tip was fitted with a quartz tube which extended the jet tip so that the flame burned above the detector well. For electrode heights from 50 to 110 mm the quartz jet was removed and the normal Hewlett-Packard jet, which is positioned at the bottom of the detector well as is shown in Figure 1, was employed.

One set of electrode height studies was performed with a ferrocene doping concentration of 5 ppm and another set at 30 ppm. Tetraethylsilane was used as the test compound.

With the electrode height fixed at 110 mm, the positive (5 ppm ferrocene) and negative (30 ppm ferrocene) modes of the HAFID were compared to FID responses for a mixture of 1-octanol, 3,3,5-trimethylcyclohexanol, 1-decanol, dodecanol, decane, dodecane, and tetradecane which was treated with the silylating reagent Tri-Sil-Z. Each component in the mixture had a concentration of 10 μ g/ μ L.

The dynamic response range for the detector was investigated for an electrode height of 110 mm and a ferrocene doping concentration of 30 ppm. In this study, a series of injections of test compounds tetraethylsilane and tetraethylsilane was used. Also, responses of a variety of test compounds were determined under these conditions by direct injections of each compound.

RESULTS AND DISCUSSION

The effect that doping the hydrogen atmosphere with ferrocene had on silicon response is illustrated in Figure 3. Starting with conditions similar to those optimal for the nondoped silicon selective detector reported in ref 7, and increasing the concentration of ferrocene vapor in the hydrogen atmosphere up to 45 ppm, the peak height response of tetraethylsilane first increased to a maximum at 5 ppm and then decreased at higher concentrations until it inverted from a positive to a negative peak around 12 ppm. This negative peak continued to increase in intensity to a maximum at about 35 ppm where its response was about 3 times larger than that obtained for an optimal positive response. This study illustrates two modes of operation of the silicon selective detector—an enhanced positive mode and an even more sensitive negative mode. Operation of the silicon selective detector in the negative mode has the added advantage of easy recognition of silicon containing compounds in the presence of a variety of other hydrocarbon compounds.

Figure 3 was obtained when ferrocene vapors were mixed with hydrogen prior to entering the detector housing. Figure 4 represents a series of similar experiments where the ferrocene vapor was introduced into the detector above the flame and separately from the hydrogen gas, which was introduced at

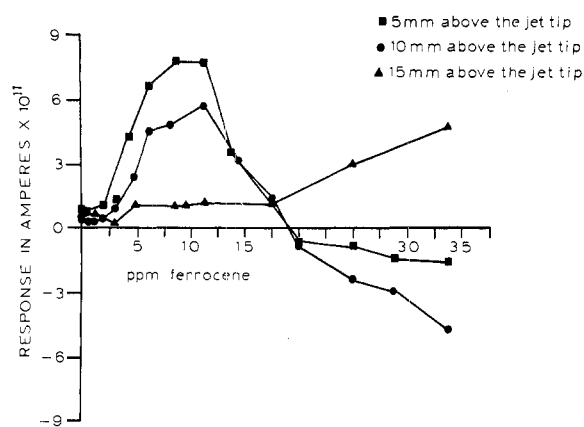


Figure 4. Ferrocene doping study (ferrocene introduced through spacer).

the base of the detector as before. While similarities between the study of Figure 3 and those of Figure 4 are strong, striking differences occur. For example, in the positive mode, response of tetraethylsilane diminishes as the orifice of the doping tube is moved further away from the flame. Also, the doping concentration required for responses similar to those obtained in Figure 3 is shifted to higher values. Both observations indicate that primary interactions between the doping agent and silicon compounds occur in or near the flame and not in the 10-cm region between the flame and the electrode.

Interpretation of results is somewhat more difficult for the 30 ppm doping condition. Negative responses were obtained only when ferrocene was introduced into the detector at 5 and 10 mm above the jet tip. When the doping agent was introduced 15 mm above the jet tip, response was positive. Moreover, negative responses were much smaller than those obtained in Figure 3. These results indicate that the doping agent is rapidly swept out of the detector, requiring higher doping quantities to achieve concentrations near the flame similar to those obtained when the doping agent was introduced beneath the flame. This effect can most readily be recognized by evaluating responses obtained when the doping metal is introduced 15 mm above the jet tip. Even when the doping agent is introduced into the detector at the 15 ppm level, response for tetraethylsilane is not increased over that normally obtained for the nondoped detector. Only at the highest doping level does an increase in response become evident, presumably due to back-diffusion of the doping agent into the reaction region.

In general, negative response in a flame detector is obtained as a decrease in background current. As the ferrocene concentration was increased from 1 to 40 ppm, the background current of this flame was found to increase from a few picoamperes to a little over a nanoampere. Maximal negative response for this detector occurred when it was doped with 35 ppm of metal vapor and the electrode was positioned 30 mm from the flame. For greatest selectivity, the detector was commonly operated with an electrode height of 110 mm. Moving the collector to this higher position reduced its sensitivity by a factor of 6, but response remained about 2–3 times greater than that achieved in the positive response mode. In the positive mode, changes in electrode height between 30 and 110 mm had little effect on response.

The linear response range for the detector was determined to be a little better than 2 orders of magnitude for test compounds of tetraethylsilane and tetravinylsilane. As has been stated earlier, the sensitivity in the negative mode was 2–3 times greater than that observed in the positive doped mode. However, due to an increase in the noise level of the detector at the higher doping concentration, the minimum detectable amount for these compounds was only about 1 ng with a

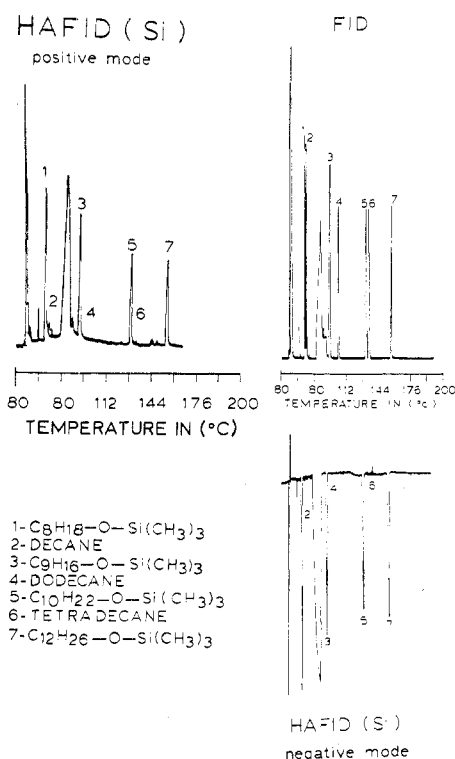


Figure 5. Chromatograms of a mixture of silylated alcohols and *n*-hydrocarbons.

minimum detection limit of about 0.2 ng/s. The minimum detection limit for silicon-containing compounds in the positive doped mode is about 10 times lower (8). The increased sensitivity of the negative mode over that of the positive mode provides a significant analytical advantage when determining silicon-containing compounds in amounts larger than 1 ng/injection (quantities which are normally used with flame ionization detectors) since absolute selectivity of the detector against hydrocarbons is increased, reducing the possibility of interference from the sample matrix.

Like most selective detectors, the negative mode HAFID does experience interferences from certain compounds. A variety of organic compounds which may be encountered during routine analysis of real samples with the HAFID were investigated. Hexane, decane, tetradecane, acetone, methanol, *n*-butyl ether, pyridine, and fluorobenzene produced relatively insensitive responses which appeared as positive peaks while tetraethylsilane, tetravinylsilane, triethyl phosphate, ferrocene, 2-methylbenzothiazole, bromobenzene, and chlorobenzene produced negative peaks. These results indicate that while most organic compounds will not interfere significantly with organosilicon response, organometallic, organophosphorus, organochlorine, and organobromine compounds respond well in the negative mode and are potential interferences.

Figure 5 compares both positive and negative modes of this detector with the response of a traditional flame ionization detector for a mixture of silylated alcohols and normal hydrocarbons. The two chromatograms in the upper region of the figure are of the HAFID(Si) in the positive mode and the FID. The FID chromatogram has three more peaks (no. 2, 4, and 6), corresponding to the *n*-hydrocarbons, than the HAFID(Si) in the positive mode. In the lower region of Figure 5, a chromatogram for HAFID(Si) in the negative mode shows the same pattern as the HAFID(Si) in the positive mode with the exception that all silicon-containing compounds responded in a negative direction. Of the three unnumbered peaks shown in these chromatograms, the first and third are residual silylating reagents which were also found in the blank. The second peak is the solvent, hexane, which produced a positive

response, even in the negative mode.

This paper has served to demonstrate conditions necessary for the successful operation of the HAFID for the selective detection of silicon-containing compounds as negative peaks. However, further characterization of this response mode is still needed. While it is clear that silicon-containing compounds exhibit a negative response (to date, all silicon compounds investigated have produced this quenching phenomenon), it is not certain what effect molecular structure has on the sensitivity of this response. Nevertheless, for specific applications this detector has proven to be a useful method for identifying silicon-containing compounds. In our laboratory the negative response has been used successfully for the determination of salicylic acid in human urine (9).

By presetting optimal doping concentrations and switching from one to another, identification of silicon-containing compounds in a complex mixture becomes a relatively easy task of noting which peaks invert. Ratios between positive and negative responses may permit the identification of silicon-containing compounds in a sample containing other negatively

responding compounds. The negative response mode offers a convenient method for detecting silicon-containing compounds in complex organic mixtures, derived from urine and other biological material, where primary interfering species are compounds of carbon, hydrogen, and oxygen.

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Isolation of Strontium-90, Yttrium-90, Promethium-147, and Cerium-144 from Wet Ashed Urine by Calcium Oxalate Coprecipitation and Sequential Solvent Extraction

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A method has been developed for separating low-level activities of the β -emitting isotopes strontium-90, yttrium-90, promethium-147, and cerium-144 from urine and aqueous solutions. They are subsequently estimated by direct counting of sources on planchets or by liquid scintillation counting. The radionuclides are separated from each other and from interfering elements by solvent extraction with HDEHP ((di-2-ethylhexyl)phosphoric acid) in *n*-heptane. It is possible to separate the elements of interest with a minimum cross contamination by selecting appropriate pHs and solvent concentrations. Percentage recoveries for the above radionuclides are as follows: ⁹⁰Sr, 100 \pm 12; ⁹⁰Y, 65 \pm 4; ¹⁴⁷Pm, 90 \pm 8; ¹⁴⁴Ce, 87 \pm 11. The limits of detection are as follows: ⁹⁰Sr, 0.6 pCi; ⁹⁰Y, 0.7 pCi; ¹⁴⁷Pm, 1.0 pCi; ¹⁴⁴Ce, 0.8 pCi (1 pCi = 37 mBq).

The Bioassay Laboratory routinely carries out gross β urinalysis at Chalk River Nuclear Laboratories (CRNL) by a calcium oxalate precipitation from a buffered urine sample (pH 3.8) and subsequent counting of the β -particle emissions. This method will detect the presence of radioactive fission products that do not emit γ -rays, but it is difficult to identify which radionuclide is present; hence a chemical separation procedure has been developed for this purpose (1). The elements Ce, Pm, Sr, and Y, if injected or inhaled, will be retained in the body for an appreciable length of time con-

centrating in the bone and the liver (2). Better estimates of the retention and the subsequent doses in an actual contamination case can be made if an analysis method to measure any or all of these radionuclides in urine is available. A survey of the literature shows that there are numerous analyses for the elements above; however, none of them has been developed as a sequential separation method, particularly from urine.

The use of (di-2-ethylhexyl)phosphoric acid (HDEHP) as a liquid cation exchanger was shown (3) to be promising because promethium, cerium, and yttrium can be easily extracted into an organically diluted HDEHP solution. The partition coefficients have been determined for the trivalent ions, Ce(III), Pm(III), and Y(III), using purified HDEHP (3) and also for Ce(IV) using purified HDEHP (4). HDEHP in toluene (7% v/v) has been used previously in a bioassay procedure (5) for promethium-147 (cerium-144 follows through), and promethium-147 has been separated from other fission products (5) using HDEHP in toluene (50% v/v). A thenoyltrifluoroacetone (TTA) extraction was used to remove accompanying cerium (6). HDEHP in *n*-heptane (0.75 mol/L) has also been used to estimate cerium-144 in biological materials, seawater, and fission product solutions, all giving quantitative recovery of radiocerium (7-9). Yttrium-90 has been separated from strontium-90 using HDEHP (0.45 and 0.6 mol/L in *n*-heptane (10) and toluene (11), respectively). HDEHP in toluene (50% v/v) has also been used to indirectly estimate strontium-90 in urine (12, 13).

Urine is a complex matrix. Any analytical separation that attempts to isolate an almost insignificant mass of material from urine must be capable of overcoming the high variability

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