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PARAMETER STUDY OF A HYDROGEN ATMOSPHERE FLAME IONIZATION DETECTOR

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SUMMARY

A hydrogen atmosphere flame ionization detector was constructed and operated with a direct injection technique in order to investigate detector parameters that have not previously been characterized. The optimum concentration of silane added to the hydrogen atmosphere was found to be dependent on the height of the collector electrode. At higher electrode heights, the required concentration of silane decreased. In this study, a collector height of 70 mm and a silane mixing ratio of 4 ppm were chosen as the best conditions. Also, optimal response was found when the nitrogen/oxygen ratio was *ca.* 1 and when the hydrogen flow was 3 l/min.

Several observed phenomena provided indirect evidence of the detector's mechanism. The interdependence of silane doping and electrode height supports a charge transfer process within the flame as the source of enhanced metal response. Negative peaks, observed when the off-center electrode is close to the flame, are explained as the formation of ions, via charge transfer reactions, that have reduced ionic mobilities and are more inefficiently collected by the electrode than parent ions.

INTRODUCTION

Several years ago a flame phenomenon was reported in which organometallic compounds were seen to produce an ionization response three to five orders of magnitude greater than that observed for other organic compounds¹. This flame was developed into a sensitive and selective gas chromatographic (GC) detector in which compounds such as aluminum hexafluoroacetylacetonate, ferrocene, tetraethyllead and tetraethyltin were selectively detected at picogram and sub-picogram levels²⁻⁴.

Although response was a result of enhanced ionization in a flame similar to a standard flame ionization detector (FID), operating conditions are substantially different. The flame of a hydrogen atmosphere flame ionization detector (HAFID) is fed with oxygen-enriched air and burns in a hydrogen atmosphere, doped with a small amount of silane. Ions are collected with a negatively polarized electrode located 5-7 cm above the flame.

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Possible mechanisms have been discussed elsewhere⁴. Here, it need only be clear that burning a flame in a hydrogen atmosphere doped with silane and then collecting ions several centimeters from this flame are novel conditions for efficient ion detection. Previous studies have concentrated on these more notable parameters at the expense of careful documentation of the effects that gas flows have on response.

In the past, operating conditions for the detector's gas flows were selected for reasons other than the best analytical response. When this enhanced ionization phenomenon was first observed, flow-rates were optimized for a photometric detector to which the ionization response served as an auxiliary detection mode. They were 50 ml/min of nitrogen GC carrier gas, 70 ml/min of air, 96 ml/min of oxygen and 830 ml/min of hydrogen^{1,2}. Flow conditions were modified in a second detector, designed specifically as an HAFID. They were 40 ml/min of nitrogen GC carrier gas, 160 ml/min of air, 85 ml/min of oxygen and 950 ml/min of hydrogen. Their selection was based on the best combination for ignition of the flame rather than on the best response³. Later, in order to eliminate excessive baseline oscillations that occurred in certain detector geometries, these flows were adjusted to 40 ml/min of nitrogen carrier gas, 100 ml/min of nitrogen purge gas, 125 ml/min of oxygen and 1600 ml/min of hydrogen^{3,4}.

Throughout development several qualitative statements about flow parameters have been made. It was often noted that an increase in oxygen increased the response of metal compounds while it decreased the response of hydrocarbon standards¹⁻⁴ and that minor changes in hydrogen flow had little effect on response except at low flows where hydrocarbon response increased³. Nitrogen was considered only to affect the oxygen concentration. Unfortunately, much of the earlier gas flow studies were completed before the necessity of silane doping was discovered⁴, and silane concentrations were not closely controlled during these investigations.

Application of the HAFID to organotin compounds appears particularly promising because of the ease with which these compounds can be analyzed by gas chromatography and because the increasing use of organotins as antifungal agents has produced a need for their quantitation at low concentration levels. In this study, a detector was designed to investigate operating conditions of the HAFID related specifically to organotin detection with careful control of the level of silane present in the hydrogen atmosphere.

EXPERIMENTAL

Detector design

The detector, shown in Fig. 1, consists of a base, a jet, a sleeve and a cap. The base was machined from a block of stainless steel 316 which provided passages for hydrogen, oxygen and air nitrogen. Baffles where hydrogen entered the detector served to diffuse streaming effects of high flow-rates. Nitrogen and oxygen were introduced through a stainless-steel jet (20 mm × 1/8 in. O.D. × 1 mm I.D.) that was swaged to the detector's base so that an oxygen-nitrogen fed flame burned at its exit in a hydrogen atmosphere. This atmosphere was contained by a stainless steel 316 sleeve (26 mm I.D.). A number of sleeves varying in length were threaded at each end so that one end of a sleeve could be securely screwed into the detector's base and the other fitted with a cap containing a collecting electrode, glow plug ignitor and numerous exhaust vents. A male fitting BNC chassis connector served as the collecting

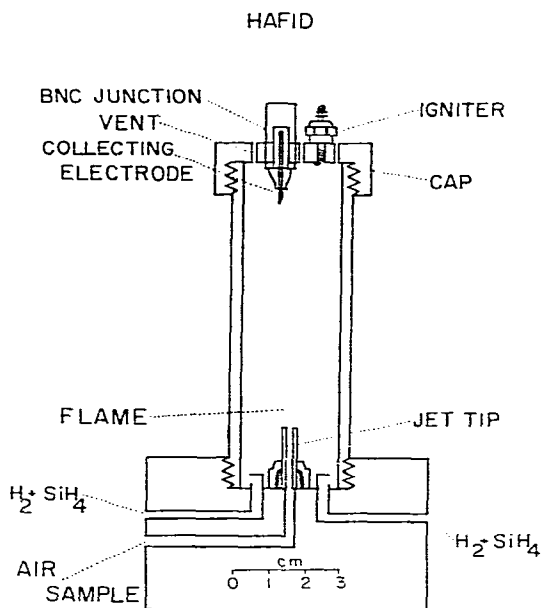


Fig. 1. Schematic of a hydrogen flame ionization detector.

electrode and was polarized with -90 V from a Model No. 490 Eveready battery which was floated between the electrode and a Keithly 427 Micro-Micro Ammeter. A Sargent-Welch SKR strip chart recorder traced the signal.

Flame ignition

Although large amounts of hydrogen are used in this detector, flame ignition is safe, reproducible and even quiet if the proper procedure is followed. With the hydrogen adjusted to *ca.* 1500 ml/min and turned off by a simple on/off valve, the oxygen and air were introduced through the jet tip at rates of 135 ml/min and 150 ml/min, respectively. After purging, the glow plug igniter was turned on followed by hydrogen introduction. A low, muffled sound indicated ignition while a loud pop usually meant flows were not adjusted properly or residual hydrogen from previous runs had not been sufficiently swept from the detector. When the flame has been properly ignited, the tip of the stainless-steel jet glows red-orange and water vapor condenses readily on cold objects held in the exiting gases.

Silane doping

In the past, doping the hydrogen atmosphere with silicon compounds has been accomplished from bleed of a polysiloxane column, silicon rubber in the heated detector, vapors of tetramethylsilane, or gaseous silane[†]. Silane appears to be the best of these doping agents but is difficult to accurately control at the low flows required (*ca.* 7 μ l/min) when pure silane is mixed with hydrogen. For these studies a tank of hydrogen was purchased, premixed with silane at the 100 ppm level ($\pm 10\%$), from AIRCO, Rare and Specialty Gases (Santa Clara, Calif., U.S.A.). It was a simple procedure to further dilute this mixture by combining gas streams to produce a hy-

drogen atmosphere in which the silane mixing ratio could be controlled down to 1 ppm.

Sample introduction

Tetramethyltin was contained as a vapor under nitrogen in a stainless-steel tank whose exit was connected to one port of a six-port zero-volume valve (Valco Instrument Co., Houston, Texas, U.S.A.). With the tank pressurized at 5 atm the sample was passed through a 0.88-cm³ sample loop that could be flushed into the detector with a turn of the valve.

The standard was prepared by injecting 2.5 μ l of tetramethyltin into a pre-washed, prebaked and evacuated 0.5-l sample tank. The tank was then pressurized to 5 atm with nitrogen. After thoroughly mixing the tank's contents, the pressure was reduced to 1 atm and then repressurized to 5 atm with pure nitrogen, producing a standard concentration of 0.26 μ g/ml of tetramethyltin. Each 0.88-cm³ injection resulted in a 0.23- μ g injection into the flame. This value was confirmed by injecting a sample into a gas chromatograph and comparing its response with standards. Injections of 0.23 μ g of tetramethyltin were chosen because this quantity produces a response that just saturates the optimized detector while permitting studies of non-optimum regions as well.

Reproducibility of this sampling system was established by comparing peak height responses of injections made from tank pressures varying from 5 atm to 1 atm. The tank was then emptied, flushed several times with nitrogen and refilled with a fresh sample. An injection from this new sample was compared to previous ones. All responses agreed within 5%.

Experiments

Oxygen/nitrogen ratio. The optimum ratio of oxygen flow to air flow through the jet tip was established by holding the total flow of carrier gas nitrogen (20 ml/min), air and oxygen constant at 305 ml/min while varying the nitrogen from 7% to 81%. The silane was maintained at a constant mixing ratio of 9 ppm in a 1500 ml/min hydrogen flow. Ions were collected with a -90 V, electrode, 50 mm above the jet tip.

Silane doping vs. electrode height. Investigation of optimum silane doping conditions as a function of collecting electrode height was accomplished by varying the silane from 1 ppm to 11 ppm for electrode heights of 10, 30, 50, 70, 90 and 110 mm. Throughout this study gas flow-rates were held constant at 120 ml/min of oxygen, 165 ml/min of air and 1500 ml/min of hydrogen.

Hydrogen flow. With a silane concentration of 4 ppm and an electrode height of 70 mm, the hydrogen gas flow was varied from 1 to 4 l/min. For each hydrogen flow investigated, silane was adjusted so that its mixing ratio remained at 4 ppm. The oxygen and air flows were maintained at 120 ml/min and 165 ml/min, respectively.

RESULTS AND DISCUSSION

Nitrogen

Although in earlier studies nitrogen has been added to the oxygen stream, its effect on response has never been documented. Fig. 2 illustrates the effect when the total oxygen plus nitrogen flow is held constant at 305 ml/min and nitrogen is

progressively introduced into the oxygen stream by increasing the air/oxygen ratio. When no air was added to oxygen, 20 ml/min of carrier gas was the only source of nitrogen in the flame, resulting in *ca.* 7% nitrogen. When air was the only source of oxygen, 285 ml/min of air plus 20 ml/min of nitrogen carrier gave a maximum nitrogen content of 81%. From Fig. 2 it is clear that when either oxygen or air is used alone, response is diminished. Air must be enriched with oxygen to produce the maximum response. Optimal oxygen and nitrogen values were found to be 50% and 50%, respectively, corresponding to flows of 20 ml/min for nitrogen carrier gas, 165 ml/min for air and 120 ml/min for oxygen.

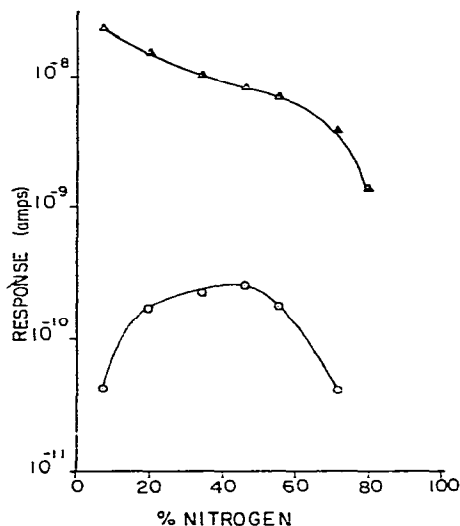


Fig. 2. Peak height response of tetramethyltin as a function of % nitrogen in oxygen with the total flow held constant at 305 ml/min. Hydrogen doped with 4 ppm SiH_4 was held constant at 1500 ml/min. Electrode = -90 V at a height of 70 mm. Flow-rate of N_2 carrier = 20 ml/min. Δ , Flame background; \circ , tetramethyltin response.

Silane doping vs. electrode height

The importance of high electrode heights and silane doping of the hydrogen atmosphere to the HAFID has been previously reported but an interdependent relationship between these two parameters as shown in Fig. 3 is truly surprising. The response in ampere for each injection of tetramethyltin was measured at the peak maximum and plotted as a function of ppm silane in hydrogen. Each curve represents a different collecting electrode height. The response curve for the collecting electrode height of 50 mm compares favorably with that from ref. 4 in which the peak height response dependence of 10 ng of tetrabutyltin with varying silane mixing ratios was demonstrated at an electrode height of 50 mm. From Fig. 3 the optimum silane mixing ratio is seen to be 9 ppm compared to the value reported earlier of 5 ppm. When holding this silane level at 9 ppm it is clear from Fig. 3 that varying the electrode height would show 50 mm to be the optimum choice. Yet, it is also clear from the graph that a more sensitive response can be obtained for tetramethyltin with an electrode height of 70 mm if the doping concentration of silane is lowered to 5 ppm.

In fact, each electrode height studied has a different optimal silane doping

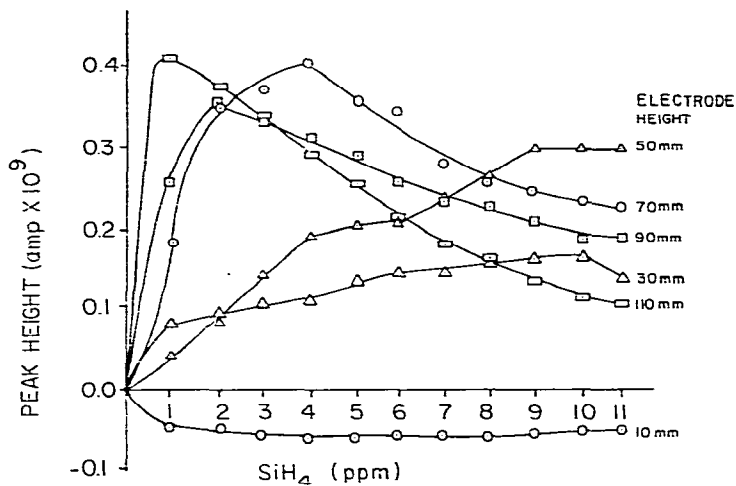


Fig. 3. Curves of silane doping vs. electrode height. Gas flow-rates in ml/min: hydrogen, 1500; oxygen, 120; air, 165; nitrogen carrier, 20.

level. Fig. 4 plots the amount of silane required for the maximum response at each electrode height. Higher electrodes require less silane in the atmosphere for best response but, in each case, when no silane is present, the response is immeasurable.

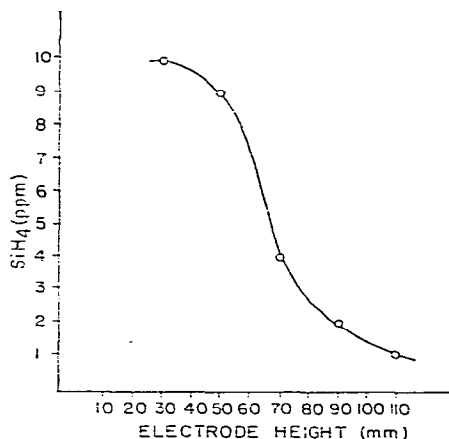


Fig. 4. Optimum silane mixing ratios for each electrode height in Fig. 3.

Speculation about the mechanism of the HAFID response has suggested that a charge transfer process within the flame or in the afterglow region is responsible for the enhanced ionization of organometallic compounds⁴. These data support that postulate. It suggests that SiH₄ is not involved in the initial ionization process since the production of ions by reaction of neutral molecules or fragments with SiH₄ in the flame region would be independent of the height of the electrode. However, the inverse relationship of these two parameters may indicate that SiH₄ is involved with an ion-molecule reaction. When the electrode is closer to the flame and the electric field is greater, ions spend less time in the reaction zone. If SiH₄ is the molecular

portion of an important ion-molecule reaction, then it would seem reasonable that an increase in SiH_4 would be required to insure optimal interaction when the residence time of the ion is decreased.

For application, it is important to realize that sensitivity may be enhanced at higher electrode heights by reducing the amount of SiH_4 in the atmosphere. Furthermore, hydrocarbon response, background ionization and noise decrease with increasing electrode height, making it desirable to operate at the highest electrode height at which the sensitivity required for analysis can be obtained.

Negative peaks

Contrary to results reported earlier where all electrode heights produced positive peaks⁴, the response of this detector at an electrode height of 10 mm produced negative peaks (a decrease in ionization) at all silane concentrations studied. An explanation of this phenomenon can be based on the specific design of this detector. The collecting electrode of the detector described in ref. 4 was a platinum loop centered above the jet tip while the collector of this work was a pin electrode positioned at some angle θ from the jet tip (see Fig. 5). At electrode heights of 30 mm or more, θ is small and has little effect on the response since as the linear velocity decreases above the flame, ions are more easily attracted to the electrode's negative field. At 10 mm, however, the angle between the jet tip and the collector is sufficiently large to permit the competition between mass flow and ion flow.

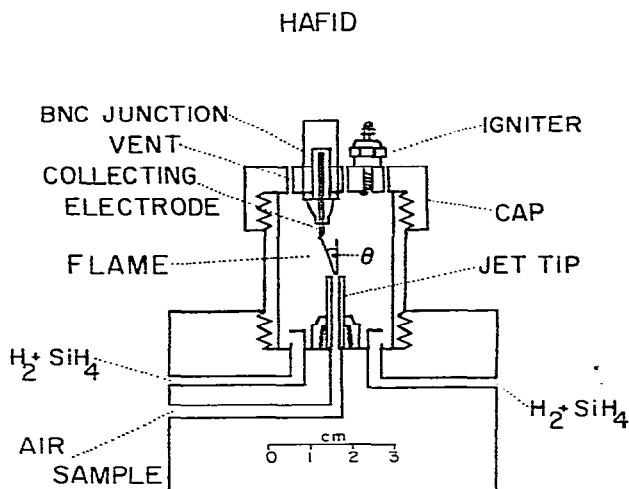


Fig. 5. Schematic of HAFID with electrode height of 10 mm. θ is the angle of ion drift for collection at a "pin" electrode.

The mass flow velocity of an ion or molecule emerging from the flame can be approximated to be 650 cm/sec from the flow-rate (305 ml/min) and the diameter of the jet tip (1 mm). The ion drift velocity as a result of the electric field intensity can be approximated from a rearrangement of the "reduced mobility" (K_0) equation⁵

$$V_d = K_0 E \left(\frac{760}{P} \right) \left(\frac{T}{273} \right)$$

where K_0 is a constant for a given ion species called the "reduced mobility", P is the gas pressure in Torr, T is the gas temperature in degrees Kelvin, E is the electric field intensity and V_d is the ionic drift velocity. Assuming a constant pressure of 700 Torr within the detector, a temperature of 700 °C above the flame, an electric field of 90 V/cm and a K_0 value of 2 cm²/sec · V (typical⁶ values range from 1 to 3 cm²/sec · V), the ion drift velocity can be calculated to be *ca.* 700 cm/sec. Although these calculations are crude since conditions such as electric field intensity and gas temperature are not homogeneous within the HAFID, they point out that ions formed in the flame may have two competing modes of transportation, a coulombic attraction to the electrode where the ion will be reduced to produce a measurable current and a mass flow of the ion past the electrode to the detector's cap.

Negative peaks that occur when tetramethyltin is burned in the flame can be explained by the formation of ions, via charge transfer reactions, with reduced ionic mobilities (indicating a higher molecular weight) which are more inefficiently collected by the electrode than are the ions responsible for the background current.

Hydrogen

The effect that various hydrogen flow-rates have on response has not previously been reported except for cursory investigations⁴ where it was not clear whether changes in response resulted from the varying hydrogen flow or the varying silane concentration. Fig. 6 shows the results of changing hydrogen flows and silane flows so that the mixing ratio remains constant at each flow tested. With a silane concentration of 4 ppm and an electrode height of 70 mm the response for tetramethyltin increased with increasing hydrogen flows to a maximum of 3.0 l/min. Since these high flows limit the practical potential of this detector, future developmental work will be aimed at redesigning the detector to reduce this hazardous hydrogen flow while maintaining the increased sensitivity.

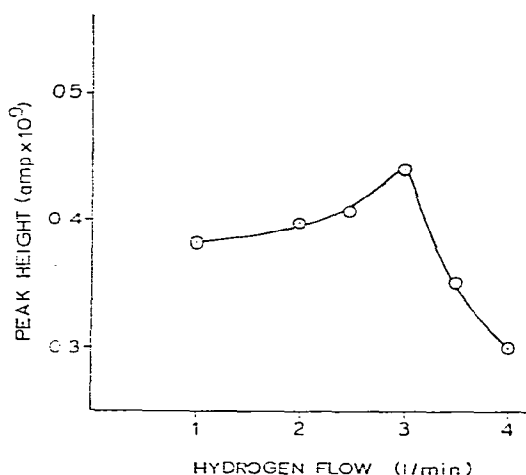


Fig. 6. Peak height response of tetramethyltin at various hydrogen flow-rates. The SiH₄ mixing ratio held constant at 4 ppm. Electrode height: 70 mm. Gas flows in ml/min: oxygen, 120; air, 165; nitrogen carrier, 20.

CONCLUSION

This study has served to document several novel parameters associated with fine tuning procedures of a metal-sensitive hydrogen atmosphere flame ionization detector. While tetramethyltin was the only compound investigated, organotin response is known to behave similarly to a variety of organometallic compounds⁴, indicating that parameters discussed here are also important for the application of this detection system to the determination of other volatile metal compounds.

The optimal values that have been established in this study are not necessarily expected to be identical for other hydrogen atmosphere flame systems which differ in detector geometry. Nevertheless, this study has identified operating parameters which are important to optimize to obtain the best sensitivity from the system. Interdependency of two parameters, silane doping and electrode height, has been demonstrated which leads to concern over the interrelationship of other detector parameters. Such a complicated optimization procedure is best left to the analyst who is developing a specific analytical procedure. Total optimization would require collected consideration of the oxygen/nitrogen flow ratio and rates, the electrode height and potential, the hydrogen flow-rate and the silane doping level.

Similar to the highly successful electron capture detector which is seldom operated at its optimum, accurate adjustment of all parameters to obtain absolute optimization of the HAFID is not required for its use as a sensitive and selective metal-sensing device. Following guidelines for operation presented in this and related papers will allow the facile conversion of a commercial flame ionization detector into a selective ionization detector that is practical for many organometallic determinations in the sub-nanogram and picogram range.

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